Interphase Modeling and Data Analytical Approaches for Polymer Nanocomposites Design

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ABSTRACT

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Polymer nanocomposites are a class of advanced materials comprised of soft polymer matrix and nano-filler inclusions. While it has been found qualitatively that enhancements of material properties could be achieved by dispersing inorganic nano-particles into organic polymer matrix, the intrinsic governing principles of such composite has not been thoroughly studied and quantified. Given that the current trial-and-error exploration of such materials is very time-consuming, it pushes the envelope of drawing in-depth understandings of such materials’ behaviors and utilizing the state-of-the-art statistical learning techniques to facilitate the design of such materials. In this regard, the objective of this dissertation are two folds: 1). to develop the quantitative processing-structure-property relationship for polymer nanocomposites 2). to establish a generic data-driven framework for analyzing and designing microstructural materials systems.

To develop the quantitative processing-structure-property relationship for polymer nanocomposite, descriptors for representing the processing procedures are explored. Two energy-mediated descriptors that reveal different aspects of the processing of polymer nanocomposites are developed and a quantitative processing-structure relationship is established. The development of this quantitative relationship completes the loop of processing-structure-property quantification using descriptor-based approach.

In addition, with the access to the experimental measurements of local interphase property, a new gradient interphase representation is proposed to better quantify the effects of interphase in modeling the viscoelastic property of polymer nanocomposites. The proposed interphase
representation is implemented with Finite Element Analysis, and it improves the capability of structure-property prediction for polymer nanocomposite material system.

This dissertation also addresses the limitation of the generality of existing microstructure reconstruction approaches by presenting a transfer learning-based microstructure reconstruction approach. Utilizing a pre-trained deep convolutional network, the presented approach is shown to be applicable for a wide range of materials systems. It is also demonstrated that, the knowledge learned in the analysis of network hierarchy could be leveraged in improving the structure-property predictive using deep convolutional network.

Last but not the least, for designing microstructural materials with complex microstructure characteristics, a deep adversarial learning approach is developed to minimize the information loss in learning the latent variables that represent microstructures. The learned microstructure latent variables are integrated into a Bayesian optimization framework to improve the material properties of microstructures.

The developments in this dissertation are shown advantageous by either numerical comparisons or experimental validations, and they significantly improve the capability of modeling polymer nanocomposite via processing-structure-property deductive analysis and inductive design. In addition, the integration of deep learning and materials science in this dissertation greatly improve the generality and the accuracy of the computational analytical approaches for studying polymer nanocomposites, and it could potentially be extended to other aspects in materials science and engineering.
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# Table of Contents

Chapter 1 Problem Descriptions and Research Objectives .................................. 20

1.1 Needs for Advanced Composite Materials and Computational Materials Science & Engineering ........................................................................................................... 20

1.2 Challenges in Computational Materials Science and Engineering for Polymer Nanocomposites ........................................................................................................... 25

   1.2.1 Challenges in modeling processing-structure relationships ..................................... 25

   1.2.2 Challenges in modeling structure-property relationships ........................................... 27

   1.2.3 Challenges in microstructure characterization and reconstruction .......................... 29

1.3 Challenges in Computational Materials Design ..................................................... 30

   1.3.1 Challenges in Design Representation ........................................................................ 30

   1.3.2 Challenges in Design Evaluation ............................................................................. 32

   1.3.3 Challenges in Design Optimization .......................................................................... 33

1.4 Research Tasks ........................................................................................................ 33

1.5 Dissertation outline ............................................................................................... 35

Chapter 2 Technical Background ............................................................................. 37

2.1 Polymer extrusion and its quantification ............................................................... 37

2.2 Microstructure characterization and reconstruction .............................................. 39

   2.2.1 Microstructure characterization ............................................................................. 41

   2.2.2 Microstructure reconstruction ............................................................................ 43

2.3 Numerical modeling approaches for assessing the structure-property relationship .... 45

2.4 Deep learning ........................................................................................................ 46
2.4.1 Fundamentals of deep learning ................................................................. 48
2.4.2 Deep Convolutional Neural Networks .......................................................... 51
2.4.3 Deep generative models .............................................................................. 52
2.4.4 Applications of deep learning models in computational materials science .... 54

Chapter 3 Developing a quantitative processing-structure relationship for polymer nanocomposite ............................................................................................................. 57

3.1 Introduction ........................................................................................................ 57
3.2 Energy-mediated descriptors for representing processing conditions ................. 60
  3.2.1 Experimental settings .................................................................................. 60
  3.2.2 Interfacial Energy Descriptors .................................................................... 64
  3.2.3 Processing Descriptors ............................................................................... 65
3.3 Descriptor-based microstructure characterization ................................................. 67
  3.3.1 Image preprocessing and Niblack binarization ............................................. 67
  3.3.2 Microstructure characterization on 2D microscopic images ....................... 69
3.4 Supervised learning based key descriptor identification ..................................... 72
3.5 Data-driven quantification of processing-structure relationship ......................... 75
3.6 Summary .......................................................................................................... 82

Chapter 4 Gradient Interphase Representation for Modeling Viscoelastic Property .... 84

4.1 Introduction ........................................................................................................ 84
4.2 Gradient Interphase Representation ................................................................. 88
  4.2.1 Single-body Interphase Gradient ................................................................ 89
  4.2.2 Multi-body Compound Effect .................................................................. 91
4.3 Implementing the Proposed Interphase Representation in Finite Element Modeling .... 92
4.3.1 Finite Element Model

4.3.2 Interphase property

4.3.3 Bayesian Inference (BI) for identifying the hyper-parameters in the interphase representation

4.3 Results

4.3.1 Data mining to identify the functional forms of interphase representation

4.3.2 Determination of the shifting factors at each location in the interphase

4.3.3 Numerical studies of the interphase effects

4.4 Summary

Chapter 5 A transfer learning based approach for microstructure reconstruction and structure-property prediction

5.1 Introduction

5.2 Microstructure reconstruction via transfer learning

5.2.1 The workflow of the proposed approach

5.2.2 The detailed implementation of the proposed workflow

5.2.3 Results

5.3 Numerical pruning and understanding the network model hierarchy

5.3.1 Quantification of model complexity

5.3.2 Investigating model hierarchy via inspecting reconstructions

5.3.2 Investigating model hierarchy via receptive fields

5.4 Structure-property prediction by leveraging the knowledge of model hierarchy

5.4.1 Transfer learning-based strategy for developing structure-property predictive model

5.4.2 Dataset
5.4.2 Numerical validation .......................................................................................................... 143

5.5 Summary .......................................................................................................................... 146

Chapter 6 A Deep Adversarial Learning Methodology for Designing Microstructural
Material Systems .................................................................................................................. 148

6.1 Introduction ....................................................................................................................... 148

6.2 Microstructural Design Representation using Deep Adversarial Learning ................ 153

6.2.1 Fundamentals of Generative Adversarial Network (GAN) ........................................ 153

6.2.2 Network architecture .................................................................................................... 155

6.2.3 Loss function ................................................................................................................. 155

6.2.4 Numerical Validation of Latent Variables .................................................................... 158

6.3 Microstructure Design Evaluation .................................................................................... 163

6.4 Microstructure Design Synthesis ..................................................................................... 164

6.4.1 Exploration of Design Variable Space using Design of Experiments (DoE) .............. 165

6.4.2 Gaussian Process Metamodeling and GP-Hedge Bayesian Optimization ....................... 165

6.5 Scalability and Transferability .......................................................................................... 170

6.5.1 Scalability of the generator .......................................................................................... 170

6.5.2 Transferability of the discriminator .............................................................................. 172

6.6 Summary .......................................................................................................................... 175

Chapter 7 Contributions and Future Works ......................................................................... 178

7.1 Summary of the contributions .......................................................................................... 178

7.2 Recommendations of future works ............................................................................... 182

REFERENCE ......................................................................................................................... 187
List of Figures

Figure 1-1 The applications of polymer nanocomposites .......................................................... 21
Figure 1-2 Olson's three-link chain of hierarchical materials design ........................................ 23
Figure 1-3 Dissertation outline ..................................................................................................... 35
Figure 2-1 An illustration of the single screw extrusion ................................................................. 38
Figure 2-2 An illustration of the simplest neuron unit ................................................................ 48
Figure 2-3 An illustration of deep neural network ...................................................................... 49
Figure 2-4 An illustration of convolutional filtering ..................................................................... 51
Figure 2-5 The comparison between auto-encoder (AE) and Variational Auto-encoder (VAE) .... 53
Figure 2-6 An illustration of generative adversarial network (GAN) ............................................ 54
Figure 3-1 The comparison of global and Niblack local thresholding based binarizations (a)
Original grayscale TEM image (b) Binary image processed using global thresholding (using the same VF=0.0173 as obtained from Niblack algorithm (c). Binary image processed using Niblack algorithm ................................................................. 69
Figure 3-2 The impact of the filler-matrix compatibility descriptor (WPF/WFF) on the microstructure dispersion (Ifiller) ........................................................................................................ 76
Figure 3-3 The impact of processing energy descriptor (Eγ) on the microstructure dispersion
(Ifiller) in log scale. The polymer types and the surface modification methods that correspond to the data points could be found in Table 3-5 ...................................................................................... 77
Figure 3-4 Regression model of the influence of interfacial energetics and processing conditions on the normalized interface of the nanocomposites ......................................................... 79
Figure 3-5 Regression of both polymer matrices within one model with the help of a matrix-dependent term $f_{\text{matrix}}$. Here $f_{\text{PP}}$, $f_{\text{PS}}$ and $f_{\text{PMMA}}$ are set as 15.120, 1.0 and 0.759 respectively to account for the difference of the regression slopes in Figure 3-4.

Figure 4-1 Illustration of interphase functions. (a) Single-body interphase gradient. (b) Multi-body compound effect. The blue dashed line represents the single-body interphase gradient created by one single aggregate and the red curve shows how the compound effect makes an impact on the resultant interphase property.

Figure 4-2 An illustration of the periodic boundary assignments of interphase.

Figure 4-3 The illustration of the assumptions of the interphase viscoelastic properties (a) left – the two locations A and B in the interphase are identified; right – the corresponding viscoelastic properties (tan$\delta$ peak) for A and B. Since A is closer to the filler than B, the shifting factor $S_A$ is greater than $S_B$. (b) left – location A again experience a single-body effect from the left filler, but point P, at the same distance from the left filler as point A, is located also close to the right filler in the interacting interphase region. For point P, the distances from two filler aggregates $d_C$ and $d_D$ are identified and used to determine the resultant property using single-body and multi-body effects; right – the “virtual” property for point P is found by first inferring single-body interphase gradient by $d_C$ $(S_C)$ and $d_D$ $(S_D)$. $S_{\text{compound}}$ for point P is then determined using the multi-body compound effect function $G$ $\cdot$ in Eqn. (4.3).

Figure 4-4 The workflow of the Bayesian Inference approach for identifying the values of the hyper-parameters $\Phi$ and $\Omega$.

Figure 4-5 Regressions of the AFM experimental data. The regression of 520 nm sample is utilized for investigating the functional form of the single-body interphase gradient ($\alpha' = 5.14, \beta' = $...
0.079), while the 156nm sample ($\alpha' = 7.07, \beta' = 0.077$) would be utilized later in the study of multi-body compound effect.

Figure 4-6 Linear regression for functional form of compound effect

Figure 4-7 An illustration of the conversion between the normalized magnitude of complex modulus and shifting factor for interphase. $E_{\text{compound}}$, $f^*$ is the normalized magnitude of complex modulus at frequency estimated by multi-body compound effect and $S_{\text{intph}}$ is the corresponding shifting factor.

Figure 4-8 Microstructures used for studying the effects of interphase representation. (a) a dilute microstructure (VF=0.29%) for studying single-body interphase gradient, (b) a moderately loaded microstructure (VF=1.77%) for studying multi-body compound effect, (c) Transmission Electron Microscopy (TEM) image of Polystyrene-silica composite, and (d) the binarized image (VF=1.83%) of (c) using Niblack algorithm[177, 178].

Figure 4-9 Effects of single-body interphase gradient. (a) the comparison between the simulated viscoelastic properties by different $\alpha$, (b) the comparison between the simulated viscoelastic properties by different $\beta$, (c) the distribution of shifting factor magnitude when altering $\alpha$, and (d) the change of shifting factor distribution when altering $\beta$. The color map represents the value of the shift factor, $S$ (see Figure 3); e.g. in (c) a shift of 1 decade from the matrix properties is reflected by a color value of 1.

Figure 4-10 Effects of multi-body interphase compound effect. (a) the comparison between the simulated viscoelastic properties by different $\eta$, (b) the comparison between the simulated viscoelastic properties by different $\xi$, (c) the distribution of shifting factor magnitudes when altering $\eta$ and (d) the distribution of shifting factor magnitudes when altering $\xi$. The color
map represents the value of the shift factor, S (see Figure 3); e.g. in (c) a shift of 1 decade from the matrix properties is reflected by the color value indicated for 1.

Figure 4-11 The comparison between the FE models using uniform interphase and gradient interphase via Bayesian Inference. (a) the distribution of shifting factor magnitude for the uniform interphase FE model. The interphase property is uniformly distributed and shifted from matrix property by 2 decades, (b) the distribution of shifting factor magnitudes for the proposed gradient interphase FEA model, (c) the comparison between the matrix property and the simulated properties of the two models, and (d) the history of Bayesian Inference.

Figure 4-12 The results of numerical validation of the proposed gradient interphase representation on experimental data from [179]. (a) Microstructure image gathered from [179] (b) binary image of the microstructure. (c) the distribution of shifting factor magnitudes for the proposed gradient interphase FEA model. (d) the comparison between the matrix property, experimental measurements of the composite property and the simulated property. (e) the history of Bayesian Inference.

Figure 4-13 The distributions of the number of overlapped interphases in the two test cases of this work. (a) & (b) correspond to the microstructures in Figure 4-11 & 4-12 respectively.

Figure 5-1 The workflow of the proposed microstructure reconstruction approach.

Figure 5-2 The comparison of the original microstructures and their corresponding reconstructions using different approaches. The proposed transfer learning approach reconstructions are presented in the second row, highlighted in red. N/As represent the cases where the microstructure in that column cannot be reconstructed by the approach specified for that row.
Figure 5-3 Original microstructure of block copolymer sample and its reconstructions using the proposed deep convolutional network-based approach and decision tree based approach. 136

Figure 5-4 Original microstructures of 3-phase rubber composite and their reconstructions using the proposed deep convolutional network-based approach. (a&b) Original and reconstructed microstructures of BR(35.7 wt%)/SBR(35.7 wt%)/CB(28.6 wt%) sample. (c&d) Original and reconstructed microstructures of BR(41.7 wt%)/SBR(41.7 wt%)/CB(16.6 wt%) sample. Color map: Butadiene rubber (BR, white color), Styrene-Butadiene rubber (SBR, blue color), carbon black (CB, cyan color). 137

Figure 5-5 Microstructure reconstructions for copolymer and carbonate using different selections of neural network layers in Gram-matrix matching. (Figure index: A ~ copolymer, B ~ carbonate, 0 ~ original microstructure, 1 ~ 4 lowest pooling layers + lowest convolutional layer, 2 ~ three lowest pooling layers + lowest convolutional layer, 3 ~ two lowest pooling layers + lowest convolutional layer, 4 ~ the lowest pooling layer + lowest convolutional layer, 5 ~ lowest convolutional layer only). C. Comparison of the reconstruction errors of each pruned model for copolymer sample using correlation functions. D. Comparison of the reconstruction errors of each pruned model for carbonate sample using correlation functions. 140

Figure 5-6 Examples of the generated microstructures for developing structure-property predictive model. 145

Figure 5-7 The comparison of the mean-squared-error (MSE) and the mean-absolute-error (MAE) between the proposed approach and two control groups. 145

Figure 6-1 The flowchart of the proposed deep adversarial learning methodology. 151

Figure 6-2 The architecture of the proposed generative adversarial network. 154
Figure 6-3 The composition of loss function and information flow in the proposed architecture. .................................................................................................................................................. 158

Figure 6-4 Examples of original (training) microstructures and microstructures produced by the generator. .................................................................................................................................................. 160

Figure 6-5 Comparison of two-point correlation functions and lineal-path correlation functions of original microstructures and microstructures generated by proposed generator ............... 163

Figure 6-6 The integration of Gaussian Process metamodeling and GP-Hedge Bayesian Optimization .................................................................................................................................................. 166

Figure 6-7 The microstructure optimization history and microstructure designs indicated at a few iterations.................................................................................................................................................. 168

Figure 6-8 The comparison of the optical absorption property between 1) 30 randomly sampled microstructures from training dataset, 2) 30 microstructures generated by the trained generator, and 3) optimal design.................................................................................................................................................. 168

Figure 6-9 An illustration of microstructures of different sizes generated by the scalable generator .................................................................................................................................................. 172

Figure 6-10 The comparison of the mean-squared-errors (MSE) for training from scratch and transfer learning .................................................................................................................................................. 175

Figure 6-11 The comparison of the mean-absolute-errors (MAE) for training from scratch and transfer learning .................................................................................................................................................. 175
List of Tables

Table 3-1 Interfacial energies of the used silane-modified silica and the polymers ...................... 62
Table 3-2 Descriptors describing the interfacial energy of the various material combinations. The compatible combinations are given in light grey ................................................................. 65
Table 3-3 Descriptors studied in the microstructure characterization, divided into three physically based categories .................................................................................................................. 71
Table 3-4 Top 10 significant descriptors from Table 3 as identified by supervised learning (The subscripts following the descriptors are the number of their statistical moments) ............ 73
Table 3-5 Descriptor values of the composite samples .................................................................................................. 75
Table 4-1 Cut-off distances and their equivalent physical length for each computational example in this chapter .................................................................................................................. 116
Table 5-1 Error rate (%) of two-point correlation function for reconstructions using different approaches for various material systems (bold font indicates the method with the lowest error rate for each material system). The method presented in this work is highlighted in red. . 134
Table 5-2 Error rate (%) of lineal-path correlation function for reconstructions using different approaches for distinct material systems (bold font indicates the lowest error rate, red highlight indicates the proposed method.) .................................................................................. 135
Table 5-3 Error rate (%) of the two-point correlation function for reconstructions on three-phase rubber composite samples in Figure 5-4 using the proposed deep convolutional network-based approach .................................................................................................................. 137
Table 5-4 Receptive field for each layer used for computing loss function in the proposed approach ........................................................................................................................................... 142
Table 6-1 The dimensionality of each layers in the proposed network architecture (bs. is the abbreviation of batch size)
Chapter 1 Problem Descriptions and Research Objectives

1.1 Needs for Advanced Composite Materials and Computational Materials Science & Engineering

Advanced composite materials are a class of materials comprised of multiple constituents of traditional materials but renders superior material properties. It has been demonstrated in the last decades that, the discoveries, developments and applications of advanced composite materials could fundamentally make profound impacts on people’s daily life, national security and global environments. For instance, the application of dielectric composite materials makes it feasible to produce capacitor with higher permittivity, retaining a greater charge at a certain voltage. In addition, the development of rubber composite materials significantly increases the mechanical properties of vehicle tires and thus enhances their durability. Moreover, carbon fiber reinforced polymer composites have been widely employed in aircrafts manufacturing to increase the body strength while reducing the weights. What’s more, the wide deployments of optical composite materials in modern buildings significantly increase theutilizations of sunlight and thus save our planet by reducing the energy consumptions tremendously. Figure 1-1 elaborates several applications of composite materials in engineering applications and our daily life.
Despite these plethora of successes, it has been reported in 2011 by the White House that, the current discovery and deployment of a new class of advanced materials take a huge amount of time, typically about 10-20 years’ timeframe from the initial research to the final deployment in industry. Driven by the needs of rapid developments and deployments of advanced materials, in 2011, the White House announced the Materials Genome Initiative (MGI) [1], aiming to reduce the time and the cost from discoveries to market by a factor of two.

Traditionally, the material developments are mostly heuristic-based and the development cycle relies a huge amount of trial-and-error experiments that are time-consuming and economically expensive. In recently years, the emerge of computational materials science and engineering (CMSE) has changed the way that people discover and develop new advanced materials. In CMSE, traditional experimental trial-and-error processes are fully or partially replaced by computational tools such as Finite Element Analysis (FEA), statistical learning tools and Molecular Dynamic (MD) simulations. As a consequence, the time for assessing the property of a current material design and the total number of iterations are reduced.

Figure 1-1 The applications of polymer nanocomposites
Historically, the research field of CMSE is thought to be established based on Smith’s and Zener’s [2, 3] visions on the interactive structural hierarchy of material systems, in which both hierarchical and history-dependent complexity of material systems are considered. Later, Cohen [4] presented his “reciprocity” principle, which made the theory of computational materials science more comprehensive and systematic. In the “reciprocity” principle, Cohen argues that, in addition to the common sense that material properties are controlled by its structures, structure can be equally treated as being governed by property. What’s more, he states that if a complex structure is examined from the viewpoint of specific properties, useful relations between processing-structure-property can be established. The “reciprocity” principle reveals the underlying relationships in the hierarchical structural material systems, and it establishes the foundations of the scientific analysis and the tool developments in materials design.

In the spirit of Smith’s structural duality, Olson [5] expands Cohen’s reciprocity by demonstrating a three-link chain diagram (Figure 1-2). The structure is interpreted to “offer a resonant bond between the science and engineering of materials, in which the deductive cause-and-effect logic of science flows to the right, while the inductive goal-means relations of engineering flows to the left” [5]. In the research community of metallic alloys, the chain of Figure 1-2 has been adopted since 1985, when the Steel Research Group at Northwestern University was initially founded by National Science Foundation (NSF) to identify and prioritize the key structure-property and process-structure relations [5]. Based on the processing-structure-properties-performance (p-s-p-p) paradigm, a lot of successful developments of metallic alloys emerge. [6-9]
Beside the metallic alloy material system, polymer nanocomposites have drawn a lot of attentions from the material science research community because of its outstanding properties and its wide applications in industry [10, 11]. Polymer nanocomposites, by its name, are materials composed of polymeric matrix in which inclusions (spheres, nanotubes, etc.) of nano-scale length are incorporated. Interactions between the nanofillers and the surrounding polymers alter the mobility of the polymer chain, leading to a distinctive regime of “interphase” in the polymer. The significant difference between the properties of the interphase and the bulk matrix and the high surface-to-volume ratio of nanofillers consequently lead to the tremendous enhancement of the composite property. Because of the capability of enhancing composite property, interphase and its underlying principles controlling the exceptional behaviors becomes a topic of interest in materials science community.

During the last decades, two major factors that accelerate the developments of polymer nanocomposites are CMSE and Materials Informatics (MI). On one hand, CMSE provides a huge amount of simulation tools that replaces the traditional experimental explorations so that the process of developing new polymer nanocomposites is accelerated. On the other hand, the emerge
of a new interdisciplinary research domain, materials informatics, impulses the discovery of new polymer composite by utilizing the power of big data and the related statistical learning tools. In the last decade, the rocketing developments of computer hardware, as well as the related database techniques, has greatly drive the material science community to build databases that are highly accessible. In the past few years, efforts have been made in establishing and improving the infrastructure of materials databases, as well as exploring the data mining techniques to draw insights from existing experimental data or simulations. Examples of materials databases include but not limited to PolyInfo [12], a materials database that contains processing information of polymers in thousands of published literatures; NanoMine [13], a NoSQL based materials database focuses on accumulating data of nanocomposites and integrating related simulation or statistical analytical tools; Materials Project [14], which aims to harness the power of supercomputing and the state of the art electronic structure materials. As these materials databases are mostly open-sourced and they provide efficient tools for querying and visualizing data, it becomes easier nowadays for materials scientists to quickly access the materials that satisfy the desired properties or to locate the experimental conditions for a particular sample in a published work. Apparently, the power of the materials data will not be fully exploited without analyzing them using statistical learning tools. In the last few decades, statistical analysis and machine learning methods have been adopted in studying the materials data and the successes have been demonstrated via a plethora of works.

To date, CMSE and MI have been widely applied in completing the processing-structure-property paradigm of polymer nanocomposites and a lot of new designs of such material have also been developed. However, limitations and challenges still exist. In the upcoming section, some of these limitations and challenges are elaborated and the interests of this dissertations is presented.
1.2 Challenges in Computational Materials Science and Engineering for Polymer Nanocomposites

Based on Cohen’s reciprocity theory and Olson’s chain paradigm, the explorations and developments of new advanced materials requires solid understandings of the processing-structure-property relationships. In other words, understanding and modeling the processing-structure-property relationships is the crucial backbone in accelerating the development of new materials and the deployment to market.

The typical process of developing processing-structure-property relationship is, 1) specify the material system being studied and limit the study to material samples produced by one or several processing techniques. 2) Choose one or several material properties or behaviors of interest according the application of such material. 3) Conduct sufficient number of experiments or numerical simulations with the above circumstances prescribed. 4) Determine effective representations for each of the processing-structure-property phases such that these representative features can be used to develop processing-structure-property models 5) Develop predictive models via data analysis or numerical simulations, and validate the models using experiments.

Three major challenges are addressed in this dissertation: a) processing-structure relationship modeling (step 5) via energy-mediated representations (step 4), b) structure-property modeling via Finite Element Analysis by introducing gradient interphase representations (step 3), and c) generic microstructure reconstruction approach for a wide range of material systems (step 3).

1.2.1 Challenges in modeling processing-structure relationships

The first challenge to be addressed in this dissertation is to develop the processing-structure relationships of polymer nanocomposites. Developing such quantitative relationship is of great
importance because 1) it could potentially save us from repetitive experimental efforts and thus significantly reduce the time period of exploring the optimal processing conditions for a desired microstructure, and 2) microstructure could be estimated even without producing the experimental samples so that redundant experiments could be eliminated.

In this work, the material system of interest is the polymer nanocomposite produced by non-equilibrium processing conditions (step 1) and the processing techniques being considered is prescribed as single screw polymer extrusion (step 2). A great amount of experimental data covering a wide range of composites system (e.g. silica-PMMA, silica-PS and silica-PP with different nano-particle surface modifications) has been gathered by our collaborator at Rensselaer Polytechnic Institute (step 3). While statistical quantification approach for microstructures of such composite has been developed in our prior works [15], there is not a systematic way to quantify the processing conditions. While single screw polymer extrusion is one of the simplest processing techniques for producing polymer nanocomposites, there are many processing parameters associated with this process. For instance, to described the geometry of the extruders, parameters such as channel width, channel depth and screw diameter are necessary. In addition, controllable processing parameters (e.g. processing temperature or screw rotation speed) and properties of the constituents (e.g. the densities of the particle and the polymer or viscosity of the melt polymer) could also play a significant role in determining the final dispersion in the microstructure. While encountering such high dimensional representations, a typical way is to apply dimension reduction techniques. While such techniques such as Principal Component Analysis (PCA) could potentially reduce the dimensionality of the representation, the reduced representation loses the physical meaning. As a consequence, the learned processing-structure relationship via PCA will not be helpful in providing us physical understandings of the composite. In addition, when a desired
microstructure is demanded, it is difficult to retrieve the processing parameters from the PCA representations. Therefore, it is necessary to *develop a concise but physically meaningful representation (a.k.a. processing descriptors) to describe the processing procedure*. In our prior works, physical descriptors for structure and property of polymer nanocomposites have been developed [15-17]. The development of the processing descriptor not only solve the challenge of quantifying the processing-structure relationship for a particular processing technique, it also provides a general procedure for processing quantification that could be further extended to analyzing other processing techniques. In addition, the completion of the descriptor-based processing-structure relationship marks the completion of the entire processing-structure-property paradigm using descriptor-based approach.

1.2.2 Challenges in modeling structure-property relationships

The second challenge to be addressed in this dissertation is to develop a gradient interphase representation for numerically modeling the structure-property relationship (step 3). A first category of studies that access the material property of given microstructures are experimental approaches, and most of them emphasize on understanding the interphase behavior of polymer nanocomposites. For instance, Seiler et al. [18] applied Electric Force Microscopy (EFM) to verify the existence and to estimate the thickness of interphase in silicon nanocomposites. Ciprari et al. [19] utilized data from thermal gravimetric analysis (TGA), transmission electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) to study the structure and density of interphase for six nanocomposite systems. Besides the experimental investigations, theoretical models have also been proposed to analyze the impacts of interphase for composites and estimate the bulk property of the composite. Review articles by Hashin [20] and Christensen[21] cover most
of the mathematical models for modeling composite material behaviors, including the popular Mori-Tanaka method [22]. Fisher and Brinson [23] further extended the Mori-Tanaka method into 3D and conducted a rigorous comparison with Benveniste’s method[24].

Promoted by the developments of modern computers, Finite Element (FE) Modeling provides an inexpensive alternative to the traditional experimental approaches. A plethora of successes using FE methods to study the effects of interphase has been made. For instance, Zhu et al. [25] developed a FE model for predicting elastic property of polymer nanocomposites and the simulated property agreed with the reported experimental measurements. Another promising example is Read et al. [26], in which a FE model for predicting the viscoelastic property of polymer blends was presented. Our earlier works [27-31] also illustrated FE models to study effects of interphase on viscoelastic property of polymer nanocomposites. Despite these successes, it is noteworthy that in these works, the interphase property was simplified to be uniformly distributed in interphase region, and only the effective property was considered. In other words, the spatial distribution of interphase property and the effects of microstructural dispersions were not taken into account in these prior works.

In recent years, the development of Atomic Force Microscopy (AFM) technique makes the local mechanical property measurable. Cheng et al. [32] and Zhang et al. [33] have manufactured a special structured substrate-file-substrate composites to probe the local interphase property in polymer nanocomposites. With the available local property measurements, it becomes feasible to describe the interphase behaviors with more detailized information (e.g. interphase property gradient). Therefore, in this dissertation, a newly developed interphase representation, which features two disentangled parts that describe different aspects of interphase behavior is presented.
The presented interphase representation is then implemented into Finite Element Modeling and numerical studies are conducted to study the effects of the new interphase representations.

1.2.3 Challenges in microstructure characterization and reconstruction

The third challenge that this dissertation aims to address is microstructure reconstruction. In accessing the structure-property relationships (step 3), microstructure reconstruction is a commonly used technique to generate multiple statistical equivalent microstructures as the input of Finite Element simulations. Recently, Bostanabad et al. [34] conducted a comprehensive review of the existing microstructure characterization and reconstruction (MCR) approaches. Despite the successes made by these existing methods, almost all these approaches are originally developed upon a specific material system and their generality is very limited. In other words, while these approaches have demonstrated successes in characterizing and reconstructing microstructures of a certain material system, it is difficult to apply them on a very different material system whose microstructure characteristics are distinctively complex, while retaining the reconstruction precision. The limited generality significantly hinders the wide application of each existing approach and difficulties would occur when facing an unexplored material system. Therefore, a generic microstructure reconstruction approach that is applicable for a wide range of material system is desired to accelerate the discovery of new advanced material systems.

In era of big data, the rapid developments of advanced hardware have stimulated the revival of deep neural network. Plethora of successes in the field of Artificial Intelligence has shown deep learning’s advantages in model capacity and generality, and make it a good potential alternative to existing MCR approaches. This dissertation would address the challenge of developing a generic MCR approach using deep learning. In addition, instead of treating the deep learning model as a “black box”, some physical interpretations about the relation between deep learning model
hierarchies and microstructure dispersions are desired. Last but not least, it is worth exploring if these interpretations would be helpful in other applications in materials science such as structure-property modeling.

1.3 Challenges in Computational Materials Design

In addition to the deductive analysis in the processing-structure-property paradigm[5], the inductive analysis starting from the desired material property/performance and trying to identify the corresponding microstructure dispersions and the appropriate processing conditions is also an indispensable component in CMSE. To tackle these inductive analysis problems, Computational Materials Design (CMD) emerges.

In general, there are three major components in computational materials design – design representation, design evaluation and design optimization, and they all have existing challenges. The emphasis of this dissertation is to develop a microstructural design methodology that addresses these challenges and effectively design microstructural materials. In the remainder of this section, we will elaborate the existing challenges of the three components in computational materials design, and briefly introduce the proposed design methodology.

1.3.1 Challenges in Design Representation

The first challenge in CMD is how to effectively represent the object being studied using a set of design variables. In the context of microstructural materials design, the object to be represented is the microstructure. In microstructural materials design, microstructures are typically stored in the format of 2D or 3D images. This representation is of high-dimension and it is infeasible to apply any optimization method directly on this high-dimensional space. Therefore, it is desired to develop a set of low-dimensional representations that could effectively describe microstructures
of great dispersive variations without losing a lot of dispersive or geometric information. A typical practice of developing such representation is to utilize microstructure characterization techniques. This is because microstructure characterization essentially creates a mapping from microstructure image space to the low-dimensional representation space. While there are a lot of microstructure characterization approaches available as the candidates, there are several limitations associated with them to be applied in microstructural materials design. For instance, some MCR approaches (Gaussian Random Field (GRF) [35] or Markovian Random Field (MRF) [36], Deep Belief Network-based method[37] and Transfer learning-based methods[38]) have no parameters available to serve as design variables. In addition, while methods such as two-point correlation functions, physical descriptor-based approach or spectral density function based method are applicable for material microstructural design, their efficacy is limited by the potential information loss (i.e. loss of either dispersive or geometrical characteristics) in microstructure representation and/or dimensionality reduction. In microstructure representations, some approximations such as taking radial averages in two-point correlation function or spectral density function or approximating cluster shapes with ellipses with physical descriptor-based method could result in the loss of microstructural characteristics. Dimension reduction is often needed in microstructure optimization due to the high-dimensional representation of microstructures. A common practice is to conduct a transformation of microstructure representations (e.g. using Principal Component Analysis (PCA) [39]) and remove some insignificant dimensions. Information loss would also occur in the removal process.

To overcome the problems of the existing MCR approaches in microstructural materials design, it is necessary to develop a new approach to learn microstructure representation while minimizing the information loss. Since low-dimensional representation is always desired in design
optimization, it would be beneficial if the dimensionality could be controlled. In this dissertation, a deep adversarial learning based approach utilizing the state-of-the-art deep generative models is developed to learn latent variables (a.k.a. representations) of a dataset of microstructures.

1.3.2 Challenges in Design Evaluation

Design evaluation refers to the process of evaluating the performance of a certain design. In context of microstructural materials design, design evaluation is the process of simulating the material property of a given design. A common practice of estimating the material properties is firstly reconstructing microstructure from a certain set of design variables, then Finite Element simulations are then conducted to estimate the material properties. While this two-step process is capable of evaluating the material properties, the computational cost is always significant. In the first step, in most of the existing microstructure reconstruction methods, there is always an iterative optimization process, which is computationally costly. For example, when utilizing physical descriptor-based approach, simulated annealing is used for allocating the cluster centroids. For the highly-loaded composites, there might be hundreds of clusters and thus it may take a very long time to properly allocate all the cluster centroids via optimization. In the second step, each of the Finite Element simulations could be costly. Therefore, it is infeasible to conduct a grid search on a great number of design candidates.

This dissertation aims to solve these two problems in design evaluation using generative model and surrogate model respectively. Specifically, a generative model to rapidly produce microstructure images from design variables is trained by deep adversarial learning, while the structure-property relationship which used to be simulated by Finite Element Analysis is inferred via Gaussian Process meta-modeling.
1.3.3 Challenges in Design Optimization

In traditional material design, it is tended to downplay the role of microstructure in material design. A lot of works are rooted in understanding the processing-property relation, which relies on the empirical studies and have huge uncertainty in this mathematical relation due to the lack of sufficient knowledge. The import role of microstructure needs to be fully recognized due to its capability of tailing material property/performance. Not only depending on atomic bonding and atomic/molecular structure of individual material constitutes, the material property is also influenced by the morphology of multiple phases and interphases/interfaces that determine the interactions of material constituents.

The emphasis of this dissertation is to develop a general framework that is applicable for optimizing a wide range of microstructural materials. Existing design optimization approaches are mostly designed according to the microstructure characterization techniques, and its application would be very limited to the material system in which the microstructure characterization technique is applicable. For instance, when descriptor-based microstructure characterization is used in the optimization framework, the design variables are the areas of clusters, orientation angles and nearest center distances. For microstructures which cannot be described by these descriptors, this framework is not applicable. The proposed optimization framework aims to provide a generic off-the-shelf solution for a variety of microstructural materials.

1.4 Research Tasks

The processing-structure-property paradigm proposed by Olson [5] has driven a lot of successes in materials science so far. In previous years, Liu, Siad et al. [40] and McDowell [41] developed hierarchical modeling frameworks for property analysis and stochastic constitutive
relations. However, these conceptual frameworks for computational design of materials system using physical multiscale models lack the usage of standard design languages, a formal computational framework and real implementations. Xu et al. [16] formulated and developed a computational design framework according to this need. However, their framework only includes the latter part, structure-property relations, but not the processing-structure mappings. Therefore, the first task of this dissertation is to complete the processing-structure-property loop under the descriptor-based representation frameworks. The second task of this dissertation, to improve the Finite Element analysis for modeling the interphase of polymer nanocomposites. In addition, given that generality is becoming a major concern nowadays in exploring new material systems, approaches that are applicable to a wide range of material systems, including microstructure reconstruction method and materials design approach, would be developed. Detailed research tasks are elaborated as follows:

**Task 1.** Processing-structure modeling using energy-mediated descriptors: in this task, the primary focus would be developing a descriptor-based quantitative tools to describe the processing-structure relationship for polymer nanocomposites.

**Task 2.** Gradient interphase modeling via Finite Element Analysis: in this task, it is aimed to develop a new gradient interphase representation for modeling the viscoelastic property of polymer nanocomposites. The interphase representation would be explored by utilizing the currently available experimental data of local interphase property and the effects of the new interphase representation would be numerically studied.

**Task 3.** Generic microstructure reconstruction via transfer learning: in this task, the generality problem of microstructure reconstruction techniques would be improved by introducing a transfer learning-based approach. It would be demonstrated that the approach is applicable for a wide range
of material systems while retaining the reconstructing accuracy. Additional knowledge about the model hierarchy would be also leveraged in developing structure-property predictive model for polymer nanocomposites.

**Task 4.** Microstructural materials design via deep adversarial learning: in this task, an end-to-end off-the-shelf solution for designing microstructural materials would be developed. It is shown that this approach is capable of handling complex microstructure characteristics, reducing the dimensionality of microstructure representations as prescribed, and optimizing microstructures to achieve desired material properties.

1.5 Dissertation outline

![Figure 1-3 Dissertation outline](image)

The outline of this dissertation is illustrated in **Figure 1-3**. Chapter 1 introduces the problems that this dissertation aims to address, followed by the review of the related technical
background in Chapter 2. Chapter 2 provides technical background of the related works, including but not limited to the quantification of processing procedures, Finite Element Analysis, microstructure characterization and reconstruction (MCR), deep learning and its applications, to facilitate the further presentation of the proposed approaches. After that, Chapters 3-6 present the details of the developments regarding the four research tasks respectively. Specifically, Chapters 3-4 emphasize on the completion of the processing-structure-property paradigm using descriptor-based approach for polymer nanocomposites, while Chapter 5-6 present generic deep learning based approaches for microstructure reconstruction, structure-property predictions and microstructural materials design. From the perspective of contents, Chapter 3-5 focus on the development in assessing the processing-structure-property paradigm of polymer nanocomposites, while Chapter 6 emphasize the developments in materials design. However, if viewed from the perspective of primary techniques, Chapter 3-4 pursues descriptor-based approach while Chapter 5-6 investigate extensively in the field of deep learning (demonstrated in Figure 1-3). Last but not the least, we draw conclusions and present potential research directions upon this dissertation in Chapter 7.
Chapter 2 Technical Background

This chapter provides the technical backgrounds associated with the four research tasks in this dissertation. First, an overview of a popular processing technique for manufacturing polymer nanocomposites, namely polymer extrusion, is presented, followed by a review of quantitative method for describing this processing technique. After that, in Section 2.2, a review of stochastic microstructure characterization and reconstruction (MCR) algorithms is provided. In particular, physical descriptor-based approach, which is closely related to the first two research tasks, are emphasized in the discussion. In addition, in Section 2.3, Finite Element models for studying the structure-property relationship of polymer composites are reviewed. Moreover, Section 2.4 presents some fundamentals of deep learning, including the building blocks such as convolutional neural networks and optimization techniques such as stochastic gradient descent. Lastly, we cover the fundamentals of generative models, which have been one of the most popular research areas recently in deep learning at the end.

2.1 Polymer extrusion and its quantification

While there are a great variety of processing techniques, such as resin transfer molding [42-45], injection molding [46-49] and compression molding [50, 51], to manufacture polymer nanocomposite, polymer extrusion [52, 53] is probably the easiest and the most popular one that has been widely applied. In the category of polymer extrusion, a lot of variations have been developed in order to fulfill the needs of the property of polymer nanocomposite. Examples of polymer extrusion techniques include but not limited to single screw extrusion [54] and twin screw extrusion [55]. In addressing the first research task in this dissertation, single screw extrusion is considered.
Single screw extrusion is a process used for producing polymer nanocomposite by forcing the mixture of fillers and melted polymers through an extruder. Figure 2-1 gives a simple illustration of a single screw extruder. In early years, the studies on the effects of processing conditions are primarily qualitative and the major focus is not to quantify the effects of processing conditions on microstructures being produced. For instance, White[55] conducts a series of experimental studies to study extrusion. His emphasis lays in developing a mathematical model to estimate the local pressure distribution along the screw but lack the analysis of processing-structure relationships. As the experimental data accumulates, analytical or semi-analytical models are progressively developed to quantify the processing procedure and to guide the improvement of screw design and processing conditions. Lafleur et al. [56] is a promising example of this category of works. In their work, they divide the whole extrusion into four distinct zones: solids conveying zone, melting delay zone, melting zone and metering zone. They analyze these zones of the extruder individually and present a general model that integrates the mathematical models for each individual zone. However, they fail to correlate the processing conditions to microstructures quantitatively. Another set of works on single screw extrusion is to improve the mixing performance by introducing new techniques. For example, Kim et al. [57] introduces the chaotic mixing into single screw extrusion to improve its mixing performance. However, their works only emphasize the improvement of the flow in the extruder but does not check the improved flow’s impacts on the final dispersion.

Figure 2-1An illustration of the single screw extrusion
As the significance of microstructure is being recognized, a lot of recent studies on the effects of processing conditions on the microstructure emerge. For instance, it is found qualitatively that, in order to reduce the nanoparticle agglomerate size, the agglomerate cohesive strength must be overcome [58]. In addition, it is also observed that with increasing shear energy input, the agglomerate size can be further reduced [59]. While these qualitative studies reveal some intrinsic relationship between processing conditions and microstructure dispersions, it is still unclear that how to precisely control the processing condition to achieve the desired microstructure dispersion without a rigorous quantitative analysis.

In this regard, quantitative analysis of the processing-structure relationships has emerged in recent years. For instance, Kasaliwal et al.[58] developed a power law rule for the dependence of the dispersion of CNT agglomerates on the specific energy, and Natarajan et al. [60] developed a quantitative relationship between interfacial energy and microstructure dispersions. Noticing that the interfacial energy parameter in Natarajan et al. [60] does not take into account the impact of processing conditions, in this dissertation, we extend their work by presenting an energy-mediated representation approach to describe the processing conditions. In addition to the interfacial energy, another processing descriptor, processing energy is introduced to synthesize the contributions of individual processing parameters. Detailed explanation of the energy-mediated descriptors for representing the processing procedure of single screw extrusion will be elaborated in Chapter 3.

2.2 Microstructure characterization and reconstruction

It has been well recognized that microstructures play a significant role in determining the material properties. Realizing that in most material system the corresponding microstructure embodies some degree of randomness (e.g. grain size distribution in crystal materials or particle
distribution in fibrous composites), it is evident that statistical characterization of microstructure would be a powerful tool that, on one hand captures the pattern hidden in the randomness of microstructures, and on the other hand extract microstructural features to be correlated with processing conditions and material properties. The characterized information, in return, can be then used to computationally reconstruct new microstructures to augment the available image data or even guide future experiments. In addition, reconstructing statistically equivalent microstructure would also provide sufficient microstructural data to analyze the uncertainty associated with the structure-property prediction model (via statistical learning or Finite Element analysis).

From the perspective of computational materials design, microstructure characterization and reconstruction are also of great importance. In defining the design space of material microstructures, typically a proper microstructure characterization method is chosen to convert the high-dimensional image representation of the microstructure into a lower-dimensional representation. This space of this reduced representation is then utilized as the design space. In contrast, microstructure reconstruction, is always used in three scenarios in computational materials design.

The first scenario is design evaluation. In design evaluation, the material property corresponds to the given design needs to be evaluated. Therefore, it is necessary to first reconstruct microstructure images from design space, and conduct physical simulations such as Finite Element Analysis on these reconstructed microstructures. The second scenario is the retrieval of microstructures from optimal design. After design optimization, an optimal design would be obtained. However, it is usually desired to visualize this design by displaying the corresponding microstructure, or to validate the optimality of the design using physical simulation with reconstructed microstructure. In both these two scenarios, microstructure reconstruction is an
indispensable component in the loop of materials design. Therefore, developing microstructure reconstruction method that has the correspondence to characterization method becomes a must. The third scenario of using microstructure reconstruction is when 3D microstructures are needed for physical simulation while only images of 2D slices are available. In this case, the 2D slices could be viewed as projections of 3D microstructure, and assumptions need to be made for the third dimension. Once the 3D microstructure is obtained, it could be fed into physical simulation such as Finite Element analysis or statistical analysis such as in Hu et al.[29]. A comprehensive review of the existing microstructure characterization and reconstruction techniques could be found in Bostanabad et al. [34].

2.2.1 Microstructure characterization

Microstructure characterization refers to the statistical representation of a material’s morphology via a finite set of characteristic functions, models or features. In the last decades, a lot of efforts have been devoted in developing microstructure characterization methods that are suitable for different material systems.

1) **Statistical function-based approaches**: among the variety of microstructure characterization approaches, statistical functions are probably the most popular choice in quantifying microstructure dispersion. Statistical functions capture the degree of spatial correlation among different locations in a probabilistic sense. Often, a single statistical function is not sufficient to capture all the microstructural information and usually it is required to use multiple statistical functions of different orders to fully represent microstructural dispersion. Examples of these statistical functions includes N-point correlation functions [61], lineal-path function [62] and cluster correlation function [63].
2) **Gaussian random field-based approach** [35]: Gaussian random field based approach models the spatial distribution of material phases using Gaussian random fields. Specifically, instead of viewing the microstructure images as a vector or matrix, this approach treats it as a sequence of signals in which the stages of the signals correspond to material constituents. It also imposes the local invariant assumption so that radial distance function kernel could be applied.

3) **Spectral density function-based approach** [64]: Spectral density function-based approach first converts microstructure into its Fourier space, then takes the radial average of the Fourier magnitude. It is very suitable for studying optical material systems since the material property is also frequency dependent.

4) **Physical descriptor-based approach** [15]: Different from statistical function based approach and spectral density function, in which microstructural features are represented by a continuous (or high-dimensional) function, and Gaussian random field based approach, which is essentially a model-based approach and does not provides usable features to be correlated to processing conditions or material properties, physical descriptor-based approach capture microstructural information from three different length scale: geometry, dispersion and constitution. Examples of the descriptors within these three categories are: geometry \(\rightarrow\) size of the agglomerates, dispersion \(\rightarrow\) nearest center distance of the agglomerates, and constitution \(\rightarrow\) volume fraction of the nano-fillers. In essence, all the physical descriptors directly reflect different aspects of microstructure characteristics, and they are almost the collection of key microstructural features being considered in the former experimental studies. Given the direct correlation between the physical descriptors and their direct correspondence to microstructure characteristics, the descriptors are referred to be “physically meaningful”. The advantages of this approach are demonstrated in prior works such as [15-17, 29, 30].
In this dissertation, the material system of interest is polymer composite, which features spherical or elliptical shaped clusters in microstructures. Therefore, descriptor-based approach is suitable for analyzing such material system. Upon Xu et al. [15], this dissertation aims to extend the current structure-property by including processing descriptors. Eventually, a descriptor-based processing-structure-property linkage could be completed and the knowledge learned in this study could be utilized in accelerating new advanced material discovery. In addition, as it is observed that local interphase property is closely related to one of the dispersive descriptors – nearest boundary distance, physical descriptor-based approach would also be utilized extensively in establishing the gradient interphase representation in Chapter 4.

2.2.2 Microstructure reconstruction

Microstructure reconstruction refers to the process of generating or retrieving microstructure images in 2D or 3D format from microstructure characteristics including statistical models, functions or features. There are primarily three applications of microstructure reconstruction: 1) Data augmentation: Collecting microstructure images through Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Atomic Force Microscope (AFM) is expensive and time-consuming. However, a large amount of image data is always desired for training statistical learning or pattern recognition models, or assessing the uncertainty of structure-property models. In this regard, microstructure reconstruction techniques could produce statistically equivalent microstructures to the experimental ones so that the amount of data is augmented. 2). Microstructure retrieval from design: Usually the design optimization of microstructural materials is conducted on design space. At the end of design optimization, it is usually desired to visualize the microstructure that corresponds to the optimal design and draw
some understandings of the optimized microstructures. In this case, microstructure reconstruction techniques could be applied to convert microstructural design representations back to the image format for the ease of further analysis. 3). 3D microstructure reconstruction: microstructure imaging techniques such as SEM, TEM and AFM operate on slices of composite samples. In other words, all the collected microstructures by these techniques are presented in 2D format. However, there are scenarios that 3D microstructures are needed. For instance, simulating the damping behavior of rubber composite takes 3D microstructures as the inputs. By appropriately making the assumption of the third dimension (e.g. isotropic), 3D microstructure could be produced based on the microstructural characteristics.

There is always correspondence between the characterization methods and the reconstruction methods. For instance, to reconstruction microstructures from two-point correlation function, simulated annealing based Yeong and Torquato method (aka. YT method) to interchange the pixels in the microstructure images. In contrast, Gaussian Random Field and Spectral Density Function based approach pursue a Volume Fraction-driven level cutting strategy. In physical descriptor-based microstructure reconstruction, the cluster centroids are allocated through simulated annealing, then cluster geometries are sampled and assigned to each centroid.

It should be noted that, all the aforementioned microstructure characterization and reconstruction approaches are developed specifically for one or a few material systems that share similar microstructural characteristics. The usage of these approaches requires knowledge of the assumptions of the characterization methods as well as heuristics of the material system. There is not, by far, a general microstructure characterization and reconstruction method that could apply to a wide range of material systems. In this dissertation, a generic transfer learning based
microstructure characterization and reconstruction approach is proposed to provide an off-the-shelf solution for materials scientists to explore new advanced material systems.

2.3 Numerical modeling approaches for assessing the structure-property relationship

In the prior studies of polymer nanocomposites, it is always of great interest to predict the material property from one or a few microstructures. In addition to directly measuring the property of experimental samples, there are primarily three categories of approaches to access this structure-property relationship.

1) **Analytical approach:** this category of approaches contains the early works that develop the structure-property relationship via mathematical functions. Review articles by Hashin[20] and Christensen[21] cover most of the mathematical models for modeling composite material behaviors, including the popular Mori-Tanaka method[22]. Fisher and Brinson [23] further extend the Mori-Tanaka method into 3D and conducted a rigorous comparison with Benveniste’s method [24]. The primary limitation of this category of approaches is their feasibility to be applied to complex microstructure without the aids of computational tools.

2) **Molecular Dynamics** (MD): different from FE modeling approaches, MD approaches access the structure-property relationship of polymer nanocomposites in a smaller scale. Essentially, MD specifies the interactions between molecules are specified by the potentials (e.g. Lennar-Jones potential) and emphasizes on understanding the underlying physics in nano-scale. Examples of using MD approaches to understand the intrinsic principle of polymer nanocomposite includes [65-67].

3) **Finite Element Analysis:** Promoted by the developments of modern computers, Finite Element (FE) modeling provides an inexpensive alternative to the traditional experimental
approaches. A plethora of successes using FE methods to study the effects of interphase has been achieved. For instance, Zhu et al. [25] developed a FE model for predicting elastic property of polymer nanocomposites and the simulated property agreed with the reported experimental measurements. Another promising example is Read et al. [26], in which a FE model for predicting the viscoelastic property of polymer blends was presented. Some other works [27-31] also illustrated FE models to study effects of interphase on viscoelastic property of polymer nanocomposites.

In Chapter 4 of this dissertation, a new gradient interphase representation inspired by experimental observations is presented. After that, FE modeling is utilized them to numerically validate and study the effects of interphase representation on the bulk composite property.

2.4 Deep learning

In era of big data, deep learning emerges as one of the hottest research domains that impulse the rapid developments of artificial intelligence. In recent years, a lot of notoriously difficult artificial intelligence tasks such as object recognition, face recognition, self-driving vehicles and object tracking in movies have been well addressed by deep learning models. The concept of stacked neural network was originally proposed in 1980s, but due to the limitation of computational resources at that time, the training of such hierarchical model was infeasible. As other machine learning models such as Support Vector Machines, Gradient Boosted Tree attracted people’s attention in 1990s and 2000s, the developments of deep neural networks have been in nearly hibernation stage. In 2006, Hinton et al. revived deep learning models by presenting a breakthrough in handwritten digits recognition using Restricted Boltzmann Machines (RBM) [68]. Starting from then, the developments of deep learning algorithms and the corresponding
computational hardware (primarily Graphic Process Unit) have greatly impulse the growth of the deep learning applications. Another milestone of deep learning is the launch of ImageNet competition [69]. ImageNet is a large-scale image classification competition features millions of labelled images. The availability of such large dataset greatly motivated the research community of deep learning, and a series of deep learning models [70-72] are then developed to quickly improve the classification accuracies. The popularity and the great performance of deep neural network have also promoted their applications in fields other than computer vision. For instance, the application of deep reinforcement learning improves the performance of dialogue generation in [73], and the usage of recurrent neural network leads to a significant success in image captioning [74].

While the aforementioned successes are all in the category of supervised learning, a lot of works have been accomplished in semi-supervised learning or unsupervised learning. Hinton’s RBM model, as an example, is an unsupervised learning strategy that aims to extract useful features of handwritten digits. Among these deep learning-based unsupervised learning approaches, deep generative models are probably the most popular ones in recent years. Instead of trying to convert original data into a lower-dimensional representation, deep generative models start from a pre-defined low-dimensional vector and produce artificial data to mimic the real ones. Deep generative models overcome the limitations of traditional maximum likelihood paradigm in training unsupervised learning model, and they have demonstrated successes in a wide range of applications [75, 76]. In the recent development of deep generative models, generative adversarial network is probably the most popular one. Originated from game theory, generative adversarial network has two competing networks – generator and discriminator. During the training, generator network is improved to produce more realistic data which approximates the probabilistic
distribution of the real data set, while the discriminator is trained to distinguish the artificial ones from the real ones. After training, Nash equilibrium is achieved so that the generator could fool the discriminator. Then the lower dimensional signal that stimulates the generation would be treated as latent variables. The successes of generative adversarial networks have been demonstrated in a lot of applications [77, 78].

In this dissertation, transfer learning of deep convolutional neural network and generative adversarial networks would be used for microstructure reconstruction and materials design respectively. In Section 2.4.1-2.4.3, some basics of these models would be introduced.

2.4.1 Fundamentals of deep learning

In this section, some fundamentals of deep learning would be introduced. The introduction starts from a simple neuron unit and then extends to hierarchical stacking of such units. After that, back-propagation, which is the major concepts in optimizing the weights in the deep neural networks would be introduced.

![Neuron unit](image)

**Neuron unit:** Figure 2-2 illustrates the simplest neuron unit. In this neuron, $z$ is a linear weighted combination of $x_1$ and $x_2$ as
\[ z = w_1 x_1 + w_2 x_2 + b_0 \]  

where \( w_1 \) and \( w_2 \) are the weight parameters while \( b_0 \) is the bias. A linear or nonlinear mapping function \( f(\cdot) \) then transform \( z \) into \( y \), which is the output of this neuron unit. Candidate of the transformation function includes but not limited to identity function, sigmoid function and tanh function.

**Deep neural network**: Deep neural network is essentially hierarchical stacking of simple neuron units. Shown in Figure 2-3 is a two-layer fully connected network (the count of layers does not include input layer). In this hierarchical structure, each unit of the hidden layer, \( h_i \), performs a linear combination of input units \( x_j \) and a nonlinear transformation. Then the values of \( h_i \) is further integrated to produce the output \( y \). In the state-of-the-art deep neural networks, the input \( X \) might be of thousand dimensions (e.g. images or audio signals), and there might be tens of hidden layers with thousands of units. Other operations such as convolutional filtering or skip connections also appear in these models.

![An illustration of deep neural network](image)

**Gradient descent and back-propagation**: To build an accurate mapping from the input \( X \) to the output \( Y \), the weight and bias parameters need to be correctly assigned. To obtain the proper
values for the weights and biases, the parameters are randomly initialized and an optimization process is conducted to update the values using the available data. In training deep learning models, gradient descent is favored because of its simplicity and practical efficiency. In each iteration, the gradient of the total loss (e.g. cross-entropy between the true label of $y$ and predicted value $y'$) with respect to the weights and the biases are computed, and a small step along the negative gradient direction is taken to update the parameters.

The gradient descent algorithm raises a critical question: how to effectively compute the gradient? The answer is *back-propagation*. The back-propagation algorithm was originally introduced in the 1970s, but its importance wasn’t fully appreciated until a famous 1986 paper by Rumelhart, Hinton and Williams [79]. That paper described several neural networks where backpropagation works far faster than earlier approaches to learning, making it possible to use neural networks to solve previously unsolvable problems. As is well recognized, back-propagation is the workhorse in training deep learning models nowadays.

Back-propagation essentially computes the gradients through chain rule. By taking the simplest neuron unit demonstrated in Figure 2-2 as an example, the relationship between $y$ and $X$s could be represented by,

$$y = f(z) = f(w_1 x_1 + w_2 x_2 + b_0)$$  \hspace{1cm} (2.2)

By following the chain rule, the gradient of $y$ with respect to $w_1$ could be computed as,

$$\frac{\partial y}{\partial w_1} = \frac{\partial y}{\partial z} \cdot \frac{\partial z}{\partial w_1} = f' \cdot x_1$$ \hspace{1cm} (2.3)

The gradient with respect to other parameters $w_1$ and $b_1$ could also be computed in the similar manner. After the gradient for each parameter is obtained, a small step would be updated on each of these parameters on the negative gradient direction.
2.4.2 Deep Convolutional Neural Networks

In the early stage of the developments of deep learning models, fully-connected neural networks were used for addressing problems such as recognizing hand-written digits in the MNIST dataset [68]. However, these models do not take into account the spatial correlation in the data, which is usually critical in image data. In this regard, LeCun et al. [80] developed the convolutional filtering that gathers spatial information from images. **Figure 2-4** is a simple illustration of how 2x2 convolutional filter works on a 3x3 matrix. The output of the convolution is essentially the sum of the values being filtered and in this case, the output layer could be viewed as a summary of local information of the input layer. It should be noted that, other hyper parameters such as filter size, strides and padding could make the convolution more complex.

![An illustration of convolutional filtering](image)

**Figure 2-4** An illustration of convolutional filtering

Using the convolutional filters as building blocks, deep convolutional network has demonstrated plethora of successes in computer vision tasks. The first significant success of deep convolutional network is AlexNet [70], which was the winning model for ImageNet competition in 2012. Szegedy et al. [71] developed a deeper convolutional network to further improve the performance of the classification. The specialty of Szegedy’s model is that, in addition to the loss function produced by the outputs of the network, they also inject some loss functions in the middle of the model hierarchy to prevent the gradient from vanishing or saturating. He et al. [72] made a
breakthrough in ImageNet in 2016 by introduction the residual network. They showed that adding skip connection in the deep convolutional network, the classification accuracy could be improved while the number of parameters could be tremendously reduced.

2.4.3 Deep generative models

Deep generative models are an emerging class of deep learning models which has gotten a lot of attention in recent years. Different from traditional discriminative deep neural networks which aim to classify instances or to determine a sequence of actions, deep generative models are essentially a class of unsupervised deep learning models that learn the true data distribution so as to generate new data instances with some variations. Variational Auto-encoder (VAE) and Generative Adversarial Networks (GAN) are two major branches of the state-of-the-art deep generative models.

Variational Auto-encoder is a variant of auto-encoder. As illustrated in Figure 2-5, in auto-encoder, the encoder converts the original data into a low-dimensional code, and the decoder retrieves back the original data from the “code”. In comparison, the encoder in VAE tries to estimate a mean value and a standard deviation value. Then these two values would be used to generate a different data points that shares the same contents as the original one. In other words, auto-encoder emphasize the capability of data retrieval while VAE focuses on new data generation. However, VAEs suffer from a well-recognized issue of the maximum likelihood training paradigm when combined with a conditional independence assumption on the output given the latent variables. It is found that they tend to distribute probability mass diffusely over the data space and tend to generate blurry images.
In contrast to VAE, GAN is advantageous that it does not share the same training paradigm. GAN is comprised of two networks, a generator network and a discriminator network. The role of the generator is to produce artificial data to approximate the joint distribution of the real data, while the discriminator’s job is to identify the “fake” data from the real ones. Goodfellow et al. [81] provides a vivid analogy to GAN: the generator could be viewed as a group of criminals trying to produce fake currency while the discriminator is the police trying to distinguish the fake currency from the authentic ones. An illustration of GAN is shown in Figure 2-6.
2.4.4 Applications of deep learning models in computational materials science

While deep learning models have achieved significant accomplishments in research fields such as computer vision (CV), natural language processing (NLP) and human-computer interactions (HCI), they are not directly applicable for problems in computational materials science without carefully investigating the intrinsic relationships between these research problems. In other words, for apply deep learning models to address a specific problem in computational materials science, it is of great significance to a) identify the research objectives of the problems, b) search for the most similar application scenario in traditional CV/NLP/HCI fields and the corresponding state-of-the-art deep learning solutions to the problem of interest, and c) modify the deep learning models and apply them to the computational materials science problem of interest. In this dissertation, two research challenges are of great interests: stochastic microstructure reconstruction and microstructural materials design. In this section, the process of identifying the deep learning approach for solving these two research problems are elaborated.
First, both two research problems are image-based: stochastic microstructure reconstruction takes one image of the original microstructure and produces multiple realizations of statistically equivalent reconstructions, while microstructural materials design essentially optimizes the microstructure image. Therefore, it is straightforward that the most similar deep learning applications to these two problem would be computer vision tasks. Convolutional filters, which is the key component that comprises convolutional neural networks and their variants (e.g. mixture of recurrent network and convolutional network), has become the popular choice to handle the high dimensionality of images in computer vision problems. Therefore, it is natural to consider convolutional filtering in addressing the two image-based materials science problems in this dissertation.

Second, while we have narrowed our discussion to the scope of convolutional networks, there are still a great amount of available deep learning models as our candidates. Therefore, more specific requirements/objectives from the research problems are utilized to further determine the deep learning models to be applied. On one hand, for stochastic microstructure reconstruction, only one original microstructure is supplied. In other words, there is not a great amount of data for training a deep learning model. In this case, the strategy of transfer learning, which utilizes a pre-trained model on a similar task, is applied. Detailed formulation of the transfer learning approach would be elaborated in Chapter 5. On the other hand, for microstructural materials design, a large amount of microstructure images is available to identify the common characteristics of the material being studied, and it is expected to generate new microstructure designs during the design optimization process. In this regard, deep generative models, which is trained on dataset and is capable of generating similar data instance (i.e. microstructure with similar characterizes in the context of microstructural materials design), are taken as the solution. In Chapter 6, a deep
generative model, namely generative adversarial network, is utilized to identify the proper microstructure presentation and to conduct design optimization. The advantages of the selected generative adversarial network over other deep generative models would be further elaborated in Chapter 6.
Chapter 3 Developing a quantitative processing-structure relationship for polymer nanocomposite

3.1 Introduction

Even though many outstanding properties of polymer nanocomposites (PNC) have been demonstrated in the literature [82-88], commercial use is often limited because the processing is either expensive or difficult. One primary challenge is in controlling nanoparticle dispersion, which is often crucial for obtaining optimized properties [89-92]. Furthermore, tailoring the properties of nanocomposites is typically a trial and error process because the development of quantitative process-structure-property relationships is limited [53, 93, 94]. For example, the interfacial energy mismatch between the filler and matrix is often tailored, but a quantitative relationship between interfacial energy and processing parameters is not well developed. To obtain efficient development of nanocomposites, a modeling approach is needed that can incorporate the particle/surface chemistry and the processing required to achieve a specific nanofiller dispersion. With such a predictive model, the number of iterations required using experimental exploration can be reduced, and the design and optimization of materials to achieve desired properties will be accelerated.

Prior work has demonstrated a quantitative relationship between interfacial energy and dispersion under equilibrium conditions [60]. When the filler and the polymer are thermodynamically compatible, the filler is well dispersed. Agglomeration increases when the work of adhesion between the fillers exceeds the work of adhesion between the filler and the polymer [13]. The surface energy also determines the mobility of the interphase, which is significant for properties like glass transition temperature [60].
Most processing methods result in a kinetically trapped microstructure that is not in equilibrium and thus it is important to develop quantitative relationships to predict dispersion under those conditions. An example of a non-equilibrium processing method is extrusion. Extrusion is an inexpensive, fast and simple method to produce polymer products [95] and it is the most important process in the polymer industry [95, 96]. Therefore, extrusion processing is analyzed in this section. It is well known qualitatively that to reduce the nanoparticle agglomerate size, the agglomerate cohesive strength must be overcome [94]. With increasing shear energy input, the agglomerate size can be further reduced [59]. The details of the dispersion process are more complex. To deagglomerate nanoparticles in an extruder and maintain particle separation, several processes have to take place[59, 94, 97-101]:

1. incorporation of the filler in the matrix,
2. wetting of the filler with matrix material,
3. infiltration of the matrix into the agglomerate,
4. breaking up of the agglomerates and erosion of nanoparticles from the agglomerate surface,
5. distribution within the matrix,
6. re-agglomeration due to particle collisions during mixing

These processes depend on 9 factors:

a. surface energies of the components,
b. viscosity of the polymer,
c. packing density of the agglomerate,
d. chain stiffness of the polymer,
e. shear stress,
f. specific energy input during processing,
g. agglomerate size,

h. crystallinity,

i. agglomerate strength.

The quantitative dependence of some of the listed processes and factors have been studied in the literature and the interdependencies are complex. For example, wetting of the filler by the matrix (point 2) depends on the surface energies (point a) and the polymer viscosity (point b). Impregnation (point 3) of the filler agglomerates with polymer melt depends on the porosity and the density of the agglomerates (point c), the surface energy (point a), the polymer structure (point d) [102], and the polymer viscosity (point b) [94] [103-105]. The packing density (point c) of the agglomerates not only influences the penetration time of the matrix in the agglomerate (point 3), but also the agglomerate strength (point i) [106-108]. Infiltration of the agglomerate with polymer (point 3) increases the distance between particles, which facilitates deagglomeration [12]. After infiltration, the particles have to be dispersed and distributed to realize single primary nanoparticles. The dispersion (point 4) process is mainly controlled by the shear stress (point e) and processing energy (point f), which increases with increasing polymer viscosity (point b). Furthermore, the particle-matrix interaction (point a) plays an important role during deagglomeration, because the shear stress (point e) has to be transferred from the matrix to the agglomerate [109]. The initial agglomerate size (point g) can also influence the final distribution: Larger agglomerates are easier to distribute, but individual particles are clearly not well dispersed. Furthermore, for large residence times, re-agglomeration (point 6) can occur [107]. In addition, during crystallization (point h) (only occurring in semi-crystalline polymers) both agglomeration and de-agglomeration can occur (point 6) [110].
In this study, surface energy, polymer viscosity, shear stress and processing energy (point a, b, e and f) are studied. Although the other factors could have significant impact on dispersion and distribution, their impact is not considered because of either the limited number of composites systems in this study (e.g. for studying the chain stiffness and the crystallinity) or difficulty in gaining the needed information during the applied process (e.g. for investigating the packing density and size of the agglomerates).

In previous studies, Kasaliwal et al. found a power law rule for the dependence of the dispersion of CNT agglomerates on the specific energy input [94]. But Kasaliwal et al. did not take into account the interfacial energy of the components (CNT in Polycarbonate). In this work, we take both the interfacial energy and processing energy into account.

This chapter is divided into several sections beginning with the description of experimental processing of polymer nanocomposites using extrusion. The next section presents the descriptors for predicting the dispersion of nanocomposites under non-equilibrium processing conditions. In particular, the definition of two key parameters that capture the mixing energy are firstly presented, followed by microstructure descriptor analysis including image analysis, microstructure characterization and key descriptor identification. Correlations between processing and microstructural descriptors are then established, and the impacts of the processing descriptors on the microstructural dispersion are shown.

### 3.2 Energy-mediated descriptors for representing processing conditions

#### 3.2.1 Experimental settings

**Material**
Monofunctional siloxanes were procured from Geleste Inc. and used as received. The siloxanes purchased were octyldimethylmethoxysilane (ODMMS: \(\text{CH}_3-(\text{CH}_2)_7-\text{Si}(\text{CH}_3)_2-\text{O}-\text{CH}_3\)), chloropropyldimethylethoxysilane (CPDMES: \(\text{Cl}-\text{C}_3\text{H}_6-\text{Si}(\text{CH}_3)_2-\text{O}-\text{C}_2\text{H}_5\)), and aminopropylidimethylethoxysilane (APDEMS: \(\text{NH}_2-\text{C}_3\text{H}_6-\text{Si}(\text{CH}_3)_2-\text{O}-\text{C}_2\text{H}_5\)). Due to the monofunctionality of the silanes, a monolayer of silanes is ensured. The colloidal silica had a primary particle size of 15 nm and was supplied in methyl ethyl ketone by Nissan Inc. The trade name was MEK-ST. Matrix polymers were in powder form. The polystyrene (PS) (grade number 339-341-70) was purchased from Goodfellow Corporation. The PS powder had a particle size of 30-300 \(\mu\text{m}\), and a \(T_g\) around 100 °C. The polypropylene (PP) was tHC001A-B1 from Borealis. The PP powder size was 200-600 \(\mu\text{m}\) and \(T_g\) is around -5 °C. The poly(methyl methacrylate) (PMMA) was purchased from Scientific Polymer Products, Inc. (catalog number 037B). The powder size of the PMMA was 200-650 \(\mu\text{m}\) and \(T_g\) is around 98 °C.

The surface modification was according to Natarajan et al. [60]. 50 ml tetrahydrofuran (THF) and 16 ml of the silica nanoparticles in solvent were refluxed at 70 °C for 24 h under nitrogen atmosphere. The mixture was cooled to room temperature. Then the amount of THF was reduced to 20 ml in a rotor evaporator in order to reduce the amount of needed hexane. The mixture was precipitated in 200 ml of hexane. The particles were then centrifuged at 10,000 rpm for 10 min at 10 °C. After that, the particles modified with ODMMS and CPDMES were re-dispersed in ethanol, APDEMS-modified silica was redispersed in THF. The nanoparticles in ethanol were then mixed with the adequate amount of PP and PS polymer powder to gain a particle content of 2 wt%. Note: the PP and PS did not dissolve in the ethanol. The APDEMS-modified silica in THF was either mixed with the adequate amount of PP or precipitated out in water. The organic solvent was evaporated and the water-particle suspension was mixed with PS or PMMA resulting in 2 wt%
particle content. For PMMA the ODMMS- and CPDMES-modified silica was also precipitated out by pouring the solution in water. The ethanol was evaporated and the remaining silica in water was mixed with an adequate amount of PMMA. After evaporation of the water or ethanol, the nanoparticle-polymer mixture was dried in a vacuum oven for 12 h. The mixtures were then milled in a jet milling machine in order to reduce the starting agglomerate size. These mixtures were used for further extrusion.

The interfacial energy of the silane-modified silica and the polymer matrix was reported elsewhere [60, 111-113] and is given in **Table 3-1**. The surface energy was measured by building a monolayer of the silanes on a silicon wafer and measuring the contact angle with water, formamide and diiodmethane [60]. We assume here that the distribution of the molecular weight and its effect on the polymer interfacial energy can be neglected [114].

**Table 3-1** Interfacial energies of the used silane-modified silica and the polymers

<table>
<thead>
<tr>
<th>Filler</th>
<th>Interfacial energy</th>
<th>dispersive (mJ/m$^2$)</th>
<th>polar (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octyl-mod-silica [13]</td>
<td>31.00</td>
<td>28.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Chloro-mod-silica [13]</td>
<td>36.21</td>
<td>30.46</td>
<td>5.76</td>
</tr>
<tr>
<td>Amino-mod-silica [13]</td>
<td>43.64</td>
<td>37.85</td>
<td>5.79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Interfacial energy</th>
<th>dispersive (mJ/m$^2$)</th>
<th>polar (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene [113]</td>
<td>29.8</td>
<td>29.8</td>
<td>0.01</td>
</tr>
<tr>
<td>Polystyrene [112]</td>
<td>42</td>
<td>41.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Poly(methyl methacrylate) [112]</td>
<td>40.2</td>
<td>35.8</td>
<td>4.4</td>
</tr>
</tbody>
</table>

**Composite Synthesis**

The extruder was from Randcastle Extrusion Systems, Inc. single screw extruder (type RC-0500). The screw length was 342.9 mm, the screw diameter was 12.7 mm and the channel width
was 9.8 mm. The inner diameter of the screw increased from 0.56 mm to 11.4 mm from the main hopper to the polymer output. The extruder die was disassembled in order to reduce its influence on particle dispersion. The nanoparticle-polymer powder mixture was extruded at 180 °C and at different rotation speeds (20 rpm, 195 rpm for all the composites and 100 rpm only for amino-modified Silica samples).

**TEM and Microtoming**

To observe the dispersion of the nanoparticles in the polymer matrix, the materials were embedded in an epoxy matrix and slices of ~50 nm were sectioned at room temperature in an ultramictrotome using a diamond knife. The sections were collected on a copper grid and imaged in a JEOL-2010 transmission electron microscope (TEM).

**Thermo-Gravimetric Analysis**

The particle content of the nanocomposites was determined with thermo-gravimetric analysis (TGA). The samples were first heated at 10 K/min up to 700 °C and then the temperature was kept at 700 °C for 5 min.

**Viscosity**

The viscosity of the samples was measured in a parallel-plate rheometer. The samples were pressed at 180 °C. The sample size was 25 mm and the gap was set to 2 mm. The shear-rate was changed in the rotation mode at a temperature of 180 °C for PP; 200 °C, 210 °C, 220 °C for PS; and 220 °C, 230 °C for PMMA. For samples with high viscosity that could not be measured at 180 °C, the samples were measured at higher temperature and the viscosity at 180 °C was calculated according to the Arrhenius [95, 115] as,

\[
\eta(T) = \eta(T_0) \cdot \exp \left( \frac{\Delta E}{R} \cdot \left( \frac{1}{T} - \frac{1}{T_0} \right) \right)
\]  

(3.1)
where \( R \) is the Avogadro constant and \( E \) the activation energy.

### 3.2.2 Interfacial Energy Descriptors

The final dispersion state when extruding nanocomposites depends on the deagglomeration and reagglomeration of the nanoparticles during processing. The dominant enthalpic factor in dispersion was simulated by Starr et al. [116]. The result shows the importance of the interaction strength between the particle and polymer and the interaction strength between particles. Below a critical value (when the particle-polymer interaction was weaker than the particle-particle interaction) the particles agglomerated abruptly. Therefore, Natarajan et al. [60] and Koshkava et al. [113] used the ratio of the work of adhesion between filler and polymer and the work of adhesion of filler to filler \((\frac{W_{PF}}{W_{FF}})\) to capture the contact angle of the filler on the polymer. Stöckelhuber et al. [117] and Wang et al. [118] also found that the stability of the initial dispersion after processing and annealing is driven by the relative work of adhesion. The contact angle can be calculated using Eqn. (3.2) [119, 120].

\[
\cos \theta = \begin{cases} 
-1 + 2 \sqrt{\frac{\gamma_p^d \gamma_F^d}{\gamma_F^p}} + 2 \sqrt{\frac{\gamma_p^p \gamma_F^p}{\gamma_F^d}}, & W_{PF} \frac{W_{PF}}{W_{FF}} < 1 \\
1, & W_{PF} \frac{W_{PF}}{W_{FF}} \geq 1 
\end{cases}
\]  

(3.2)

where \( \gamma_p^p \), \( \gamma_p^d \), \( \gamma_F^p \) and \( \gamma_F^d \) are the polar and dispersive components of the polymer and the filler, respectively. \( \gamma_F \) is the total filler interfacial energy, which is given by \( \gamma_F = \gamma_F^p + \gamma_F^d \) [121], as Fowkes approximated that the polar and dispersive component make additive contributions. This expression assumes that the particles are the wetting component. It must be noted that in this equation, the contact angle \( \theta \) is truncated to 0 for the case \( W_{PF}/W_{FF} \geq 1 \). Eqn. (3.2) indicates that
the particles can wet the polymer better and are less likely to form agglomerates [13]. In contrast, when \( \frac{W_{PF}}{W_{FF}} < 1 \) (\( \theta \) increases above \( 0^\circ \)) the particles are inclined to agglomerate.

**Table 3-2** gives the results of \( W_{PF}/W_{FF} \) from Eqn. (3.1) and Eqn. (3.2) for the respective polymers and fillers given in **Table 3-1**. The only compatible material combinations \( (W_{PF}/W_{FF} \geq 1) \) in this work are octyl- and chloro-modified silica with PS and PMMA. The PP combinations and the amino-modified silica in PS and PMMA are not compatible \( (W_{PF}/W_{FF} < 1) \).

Table 3-2 Descriptors describing the interfacial energy of the various material combinations. The compatible combinations are given in light grey

<table>
<thead>
<tr>
<th>Silica modification</th>
<th>Polymer</th>
<th>PP</th>
<th>PS</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octyl-mod-silica</td>
<td>( W_{PF}/W_{FF} )</td>
<td>0.94</td>
<td>1.15</td>
<td>1.12</td>
</tr>
<tr>
<td>Chloro-mod-silica</td>
<td>( W_{PF}/W_{FF} )</td>
<td>0.84</td>
<td>1.04</td>
<td>1.05</td>
</tr>
<tr>
<td>Amino-mod-silica</td>
<td>( W_{PF}/W_{FF} )</td>
<td>0.78</td>
<td>0.95</td>
<td>0.96</td>
</tr>
</tbody>
</table>

3.2.3 Processing Descriptors

In order to develop microstructure/processing relationships, the specific shear energy was evaluated. The shear stress in the screw channel depth of an extruder \( H(L) \) can be calculated according to the shear stress in the space between two cylinders [122]. When the channel depth \( H \) is changing along the extruder, it is dependent on the length of the screw \( L \). The shear rate is determined by Eqn. (3.3) with the channel depth \( H(L) \), the screw diameter \( d \) and the screw speed \( N \).

\[
\dot{\gamma} = \frac{\pi (d - 2H(L))N}{H(L)}
\] \hspace{1cm} (3.3)
The shear stress \( \tau \) (Eqn. (3.4)) can be calculated using the viscosity \( \eta_P \) of the polymer and the shear rate \( \dot{\gamma} \) from Eqn. (3.3).

\[
\tau = \eta_P \cdot \dot{\gamma}
\]  

The viscosity of the materials was estimated with the Cross law (Eqn. (3.5)) (\( \eta_{P,lim} \) is the viscosity at infinite shear rate, \( \eta_{P,0} \) is the viscosity at zero shear rate and \( \alpha \) is a fitting-factor) and the Einstein equations (Eqn. (3.6)) for filled polymers (\( f \) is the filler fraction, \( \eta_F \) is the viscosity of the filled polymer and \( \eta_P \) is the viscosity of the neat polymer) [115].

\[
\eta_P = \eta_{lim} + \frac{(\eta_{P,0} - \eta_{P,lim})}{1 - \alpha \cdot \dot{\gamma}^{2/3}}
\]  

\[
\eta_F = \eta_P + f \cdot 2.5 + f \cdot 21.4^2
\]  

A number of Finite Difference Method (FDM) or Finite Element Method (FEM) based models have been proposed for analyzing the conveying and mixing process for single screw extrusion [123-128]. These methods are mathematically complex and computational costly. Lai [129] has proposed a fast track algorithm where no partial differential equations are included to simplify the analysis without losing much accuracy. In Lai’s model, the processing energy consumption in a circular segment with infinitesimal length along the screw length direction, \( dw \), is defined as,

\[
dw = \frac{\pi D \Omega}{60} dF_{by}
\]  

where \( D \) is the screw diameter, \( \Omega \) is the screw speed and \( dF_{by} \) is the tangent component of the traction on the screw barrel surface. With Eqn. (3.7), the power consumed on an infinitesimal area of the barrel surface can be obtained. By integrating \( dw \) over the screw surface, the total power consumption, \( w \), is obtained. The total power consumption is then divided by the throughput to synthesize the descriptor,
where \( q_m \) is the mass throughput in the processing. Note that the unit of this descriptor \( E_y \) is J/s which indicates that this descriptor represents the energy consumption on each unit of composites during the processing. This term, \( E_y \), provides a simple way to represent the complicated processing procedure and it is then taken as a processing descriptor in our later discussions. The two processing descriptors discussed in this section, \( W_{PF}/W_{FF} \) and \( E_y \), representing the compatibilities of the constituents and the processing energy consumption respectively, will be used as the representations of the processing. The descriptor for the geometric aspects of the composite is developed in Section 3.3 with the analysis of the microstructure.

3.3 Descriptor-based microstructure characterization

In addition to the interfacial energy (\( W_{PF}/W_{FF} \)) and processing descriptors (\( E_y \)) discussed in Section 3.2, it is also important to quantitatively describe the nanofiller dispersion (microstructure) of the nanocomposites. To obtain an accurate and representative description of the microstructure, an image pre-processing method, statistical characterization technique, and machine learning algorithm were applied to TEM images of nanocomposites. At least 10 TEM images with a magnification of 60,000 were taken from one nanocomposite-slice of 50 nm in order to analyze the microstructure.

3.3.1 Image preprocessing and Niblack binarization

Before statistical characterization of the microstructure, a pre-processing step, image binarization, was applied to the TEM images to identify the gray-scale pixels as either nanoparticles (fillers) or polymer matrix. Typically, a global threshold, \( T \), determined by some statistical criterion, is used
as the decision boundary for this binary classification problem [15, 130-133]. For example, if the portion of the desired fraction in the image is known (for example, the volume fraction is prescribed for the Statistical Representative Volume Elements (RVE) [15]), a level can be selected such that just the filler pixels are above the threshold. And if the histogram of the gray-scale values is bimodal, where two comparable intensity peaks are distinctly separated, the threshold can be set at the minimum point in the valley between the peaks [133]. These global threshold-based techniques were originally proposed for recognizing texture from a gray-scale document page, in which case a small portion of misclassification or noise does not influence the identification results. In our study of TEM images of polymer nanocomposites with low volume fraction, however, small areas of uneven background brightness, especially shadows created by voids, wrinkles, or uneven thickness can be misclassified into the incorrect phase and result in significant error. To address this problem, instead of using a global threshold method, local threshold algorithms based on a sliding window were employed. Several pixel-wise threshold algorithms [134] have been evaluated on the TEM images of our polymer nanocomposites with both small volume fraction (around 1%) and small areas of uneven brightness. The Niblack algorithm [135] was found to perform the best among these algorithms. In the Niblack algorithm, the pixel-wise threshold is computed as follows:

\[
T_{\text{Niblack}} = m + k \left( \frac{\sum_i p_i^2}{N_p} - m^2 \right)
\]

(3.9)

where \( m \) is the local gray-scale mean of the pixel’s neighbor area, \( i \) enumerates all the pixels in the neighbor area (in the sliding window), \( p_i \) is the gray-scale value of pixels and \( N_p \) is the total number of the pixels in the neighbor area chosen based on the area of uneven brightness (\( k \) is an empirical constant that is set to -0.2 by the authors [134, 135]). Figure 3-1 illustrates the
comparison of binarization results using the global and Niblack local thresholding. In this example, the volume fraction in the global thresholding algorithm is assigned the same value as that obtained from Niblack algorithm for fair comparison. It can be found that the dark matrix area (zone B) was incorrectly recognized as a large cluster by the global thresholding algorithm, resulting in the omission of the real clusters in zone A. In contrast, using the Niblack algorithm, the grayscale image is well binarized and undesired misidentifications can be minimized. As Niblack algorithm is found to be a more accurate binarization algorithm to process TEM images of polymer nanocomposites, this binarization tool has been integrated in the open-source online database for polymer nanocomposites, named NanoMine [136].

Figure 3-1 The comparison of global and Niblack local thresholding based binarizations (a)

Original grayscale TEM image (b) Binary image processed using global thresholding (using the same VF=0.0173 as obtained from Niblack algorithm (c). Binary image processed using Niblack algorithm

3.3.2 Microstructure characterization on 2D microscopic images

In the statistical characterization and design of heterogeneous material systems, three main categories of microstructure characterization and representation approaches have been proposed: 1) the physical descriptor-based method [16, 137-141], in which the material microstructure is
represented by physically meaningful descriptors; 2) The correlation function-based approach, where the microstructure is expressed by an infinite-dimensional function [137, 142-144]; and 3) The random field method for which the microstructure is modeled by random fields [137, 145-147]. Xu et al. [16] found that among these three approaches, the descriptor-based approach is the most computationally efficient without losing significant accuracy. Additionally, the variables used in the latter two approaches lack physical meaning, preventing insight into the morphology of the microstructure and its impact on material response. Furthermore, the infinite dimensionality of the correlation function and random field based approaches hinders further design and optimization of the microstructure. Thus, the descriptor-base characterization tool is integrated into NanoMine [136] and descriptor-based representation approach is adopted in this work.

In the descriptor-based design representation approach for nanocomposites [15, 16], the descriptor set for microstructure consists of 13 statistical descriptors (their first 4 statistical moments are measured), and 3 deterministic descriptors. In addition to these 55 descriptors, other research includes one additional statistical descriptor, area weight equivalent radius \(r_{aw}\) (the nearest center distance \(r_{ncd}\) is also considered in their work, but it is already included in our original set), when determining the impact of the interfacial energy on dispersion [60]. In this work, we include this interfacial energy related descriptor (its first 4 statistical moments) for a total of 59 descriptors, shown in Table 3-3. Although the dimension of microstructure representation is significantly reduced by replacing multiple TEM images with a set of descriptors, the number of descriptors is large and will be addressed in the next section.
Table 3-3 Descriptors studied in the microstructure characterization, divided into three physically based categories

<table>
<thead>
<tr>
<th>Category</th>
<th>Descriptor</th>
<th>Definition</th>
<th>Type</th>
<th>Number of moments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Category 1: Composition</td>
<td>$VF$</td>
<td>Volume fraction</td>
<td>Deterministic</td>
<td>1</td>
</tr>
<tr>
<td>Category 2: Dispersion</td>
<td>$r_{ncd}$</td>
<td>Cluster’s nearest centroid distance</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$r_{nbd}$</td>
<td>Cluster’s nearest boundary distance</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\theta$</td>
<td>Principle axis orientation angle [148]</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$I_{filler}$</td>
<td>Surface area of filler phase</td>
<td>Deterministic</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>Number of clusters</td>
<td>Deterministic</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Local$VF$</td>
<td>Local Volume fraction of the Voronoi cell [149]</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td>Category 3: Geometry</td>
<td>$r_c$</td>
<td>Cluster’s Equivalent radius</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$r_p$</td>
<td>Inscribed circle radius</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$r_{aw}$</td>
<td>Area weighted equivalent radius ($r_{aw} = r_c/A$)</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$A$</td>
<td>Cluster area</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\delta_{cmp}$</td>
<td>Cluster’s compactness</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\delta_{rmd}$</td>
<td>Cluster’s roundness</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\delta_{ecc}$</td>
<td>Cluster’s eccentricity</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\delta_{asp}$</td>
<td>Cluster’s aspect ratio</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\delta_{rect}$</td>
<td>Cluster’s rectangularity</td>
<td>Statistical</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\delta_{tort}$</td>
<td>Cluster’s tortuosity</td>
<td>Statistical</td>
<td>4</td>
</tr>
</tbody>
</table>

Since the images studied from the TEM slices of nanocomposites are not necessarily RVEs but are Statistical Volume Elements (SVEs) [150], a single TEM is not representative. In order to obtain representative statistics for each sample, an assembly step is applied after characterizing TEM images individually. By assuming that all the clusters have been fully captured within the TEM images, and all the magnitudes of the nearest neighbor vectors are small enough to ensure that a cluster’s nearest neighbor lies in the same TEM image scale, the characterized statistics from each single image are weight averaged.
3.4 Supervised learning based key descriptor identification

We aim to build a predictive model between interfacial descriptors ($W_{PF}/W_{FF}$), processing descriptors ($E$) and microstructure descriptors to relate the impacts of processing conditions on the microstructure. However, the large number of potential microstructure descriptors limits our ability to develop a useful model. Two challenges can be identified: 1) Since the set of 59 descriptors are collected from the studies on different aspects of microstructure for different material systems, are they all significant in representing the microstructures in this work? 2) Is it possible to simplify the model without losing too much accuracy to facilitate our intuitive understanding? These challenges are addressed using a supervised learning based algorithm to identify the most significant descriptors among the 59 candidates and correlating the significant set of descriptors with the interfacial and processing descriptors discussed in Sections 3.1 and 3.2 [151]. In this identification process, three commonly used correlation functions that describe different aspects of the microstructures (two-point correlation, surface correlation and linear path correlation functions) are selected, as we believe that these functions are complementary to each other, and together they may be able to fully represent the high-dimensional microstructures. The significance of the 59 candidate descriptors are determined by analyzing their average impact on the first 250 points of the correlation functions (corresponds to 342 nm) for all the samples using the RRelief algorithm [151]. The descriptors that influence the correlation functions the most, receive a higher significance score than the ones that have little impact the correlation function (e.g. the higher the significance level is, the representative the descriptor is). The learned significance levels by the supervised learning algorithm are then normalized to make the sum of the descriptors’ significances equal to one. The top ten significant descriptors obtained from this
analysis and their corresponding significance levels are shown in Table 3-4. The significant levels are used as the criteria to select the representative descriptors for the microstructures in this work.

Table 3-4 Top 10 significant descriptors from Table 3 as identified by supervised learning (The subscripts following the descriptors are the number of their statistical moments)

<table>
<thead>
<tr>
<th>Rank</th>
<th>Descriptor</th>
<th>Significance</th>
<th>Rank</th>
<th>Descriptor</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$I_{\text{filler}}$</td>
<td>0.0505</td>
<td>6</td>
<td>$A_{1}$</td>
<td>0.0360</td>
</tr>
<tr>
<td>2</td>
<td>$r_{\text{aw}1}$</td>
<td>0.0500</td>
<td>7</td>
<td>$r_{c2}$</td>
<td>0.0345</td>
</tr>
<tr>
<td>3</td>
<td>$VF$</td>
<td>0.0500</td>
<td>8</td>
<td>$N$</td>
<td>0.0328</td>
</tr>
<tr>
<td>4</td>
<td>$r_{\text{aw}2}$</td>
<td>0.0432</td>
<td>9</td>
<td>$r_{p1}$</td>
<td>0.0324</td>
</tr>
<tr>
<td>5</td>
<td>$r_{c1}$</td>
<td>0.0370</td>
<td>10</td>
<td>LocalVF$_1$</td>
<td>0.0321</td>
</tr>
</tbody>
</table>

In Table 3-4, none of the third and fourth moments of the statistical descriptors is identified as one of the top 10 significant ones. Therefore, the supervised learning results show that, for the composites we study, the third and fourth statistical moments of the microstructural descriptors can be neglected for representation of nanoparticle dispersion. Also, according to Table 3-4, the three most significant descriptors are selected, one from each of the predefined categories (Table 3-3), to be correlated with the processing energetics: Composition $\rightarrow$ $VF$, Dispersion $\rightarrow$ $I_{\text{filler}}$ (Surface area of filler phase) and Geometry $\rightarrow$ $r_{\text{aw}1}$ (Area weighted equivalent radius ($r_{\text{aw}} = r_c/A$)). In the previous work of microstructure reconstruction [151], the significant descriptors selected are treated sequentially because multiple single-objective optimizations applied sequentially are more favorable than one multi-objective optimization. However, in this case there is no sequence among the selected descriptors since each descriptor represents a separate and parallel aspect of the microstructure. Thus we choose a model that considers the three descriptors simultaneously.
Note that even though the three descriptors are selected from three physically based categories, they are not necessarily independent from each other. For instance, with the same volume fraction, the larger the area weighted equivalent radius ($r_{aw1}$), the lower the filler interphase area ($I_{filter}$). Considering these dependences between the microstructure descriptors, any of them has to be expressed in terms of not only the processing descriptors, but also the other microstructure descriptors (e.g. $r_{aw1} = g(E_y, W_{PF}/W_{FF}, I_{filter}, VF)$). With both the microstructure and processing descriptors on the right side of the expression, it is hard to intuitively understand how the processing descriptors contribute to the dispersion.

To establish a simple expression that is easily interpreted, we introduce an intermediate descriptor, volume fraction normalized filler surface area ($I_{filter} = I_{filter}/VF$) to represent the compound effects of the three selected microstructure descriptors so that only the processing descriptors are on the right hand side of the correlation. We omit $r_{aw}$ in this intermediate descriptor because $r_{aw1}$ has highly linearly negative correlation with $I_{filter}$ (the correlation coefficient is -0.89). Once the correlation between processing descriptors and $I_{filter}$ is established, the relations for $r_{aw}$ can be easily derived. Working with the intermediate descriptor has two other advantages. First, it helps to rule out the effect of different VFs of the constituents in the samples from the processing-structure correlation. Our model aims to demonstrate the impact of the processing energy descriptors on the dispersion, regardless of the ratio of constituents in the composites. Second, the intermediate descriptor $I_{filter}$ inherits the ability of the descriptor-based representation in that its physical meaning is easy to interpret. In the studied polymer nanocomposites where the volume fractions are very similar, a larger $I_{filter}$ indicates a better dispersion in the microstructure. Considering the advantages listed above, we chose $I_{filter}$ as the single descriptor to represent the
dispersion of the microstructures and correlate it with the processing and interfacial descriptors ($E_Y$ and $W_{PF}/W_{FF}$) in the next section.

3.5 Data-driven quantification of processing-structure relationship

The processing and interfacial descriptors, $E_Y$ and $W_{PF}/W_{FF}$, and the microstructure descriptor $I_{filter}$ are characterized from 17 samples with at least 10 images for each (249 images in total), following the steps described in Section 3.4. The results are presented in Table 3-5 and analyzed in this section.

Table 3-5 Descriptor values of the composite samples

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Particle surface modification</th>
<th>$W_{PF}/W_{FF}$</th>
<th>$E_Y$ (J/g)</th>
<th>$I_{filter}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Octyl</td>
<td>1.15</td>
<td>34.52</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>85.73</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Chloro</td>
<td>1.04</td>
<td>33.18</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>85.66</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Amino</td>
<td>0.95</td>
<td>33.28</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>104.34</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>85.76</td>
<td>0.12</td>
</tr>
<tr>
<td>PP</td>
<td>Octyl</td>
<td>0.94</td>
<td>0.65</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.03</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Chloro</td>
<td>0.84</td>
<td>0.58</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.53</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Amino</td>
<td>0.78</td>
<td>0.65</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.16</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.08</td>
<td>0.12</td>
</tr>
<tr>
<td>PMMA</td>
<td>Amino</td>
<td>0.96</td>
<td>103.10</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>964.16</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>410.92</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Recall that a larger value of $I_{filter}$ indicates a better dispersion. The materials with the best compatibility (e.g. highest values of $W_{PF}/W_{FF}$) show the best dispersion (octyl-modified silica
and PS) (Figure 3-2) as indicated by the larger volume fraction normalized interface area. The dashed line indicates the threshold of 1, beyond which materials have a wetting angle of 0° and the particles wet the polymer.

![Figure 3-2](image)

**Figure 3-2** The impact of the filler-matrix compatibility descriptor ($\frac{W_{PF}}{W_{FF}}$) on the microstructure dispersion ($\bar{I}_{filler}$)

The microstructure dispersion descriptor $\bar{I}_{filler}$ also depends on the processing energy descriptor $E_p$ (Figure 3-3). In Figure 3-3, samples with the same type of polymer and surface modification method are grouped together and marked with the same symbol. Figure 3-3 implies that, the dispersion of the samples with same polymer and surface modification could be improved by increasing the processing energy.
Figure 3-3 The impact of processing energy descriptor ($E_\gamma$) on the microstructure dispersion ($\bar{I}_{filler}$) in log scale. The polymer types and the surface modification methods that correspond to the data points could be found in Table 3-5.

Note that Figure 3-3 is plotted with a logarithmic scale, so the processing energy, $E_\gamma$, has a relatively smaller impact on the more compatible composites (e.g. the composites that have relatively greater $W_{PF}/W_{FF}$ values), even the slopes of each sample set seems very similar in Figure 3-3. For example, the octyl-modified silica with PS shows the best compatibility with a $W_{PF}/W_{FF}$ of 1.15. Those materials also have the best dispersion quality, $\bar{I}_{filler}$. But the influence of the processing energy, $E_\gamma$, on the octyl-modified silica with PS is less pronounced, even though materials show a slight increase with increasing compounding energy. Natarajan et al. [60], who used solvent mixing, found a very abrupt aggregation of nanoparticles when the compatibility of the nanoparticles with the polymer matrix goes from compatible (e.g. $W_{PF}/W_{FF} \geq 1$) to not compatible (e.g. $W_{PF}/W_{FF} < 1$). The results in this research show that the aggregation of the
nanoparticles with a $W_{PF}/W_{FF} < 1$ is less abrupt than it has been found by Natarajan et al. for solvent mixed nanocomposites [60]. This effect of the more compatible composites is because the materials that are melt processed do not reach equilibrium compared to the materials that are produced with solvent mixing [60] and also start out with larger agglomerates.

These results indicate that dispersion quality, $\tilde{T}_{\text{filter}}$, can be correlated to both the material compatibility ($W_{PF}/W_{FF}$) and the processing energy ($E_y$). The relationship between these variables was further developed using data mining techniques to provide a mathematical expression, which could be used in further analyses and prediction schemes. The results for the three types of polymer matrix are shown in Figure 3-4, where the $R^2$ values indicate that $\tilde{T}_{\text{filter}}$ is linearly correlated with the combined energetic terms.
According to Figure 3-4, the given linear regression model fits the characterized data set well for both the PP, PS and PMMA composites. This figure reveals that 1. nanoparticles may be easier to disperse in PP by slightly increasing the compatibility or the shear energy input; 2. nanoparticles need more energy input or a better compatibility to be well dispersed in PS and PMMA due to the smaller slope. The difference between the slopes of the regression models implies that some properties of the polymer matrix type will have a large influence on the dispersion. The same result has been found in [102], where the influence of surface energies on the dispersion of CNT in different polymer matrices was analyzed. PS did not follow the general trend and the authors assume that the stiff polymer backbone of PS leads to a worse dispersion than expected from the surface energetics. Similarly, we can suggest that PP allows a larger increase of dispersion with increasing processing energies and polymer-particle compatibility because of the flexible polymer
backbone and lack of side groups. PMMA is also a stiffer chain than PP and has a similar slope as the PS.

In addition, as is discussed in section 1, there are 9 factors that may influence the 6 processes during deagglomeration in the extruder, but some of these factors (c, d, g and i) were not considered because of insufficient data. To consider the potential significance of these factors that may be discovered in the future, we include these factors (point c, d, g and i) in our processing-structure model by addition of a single polymer matrix-dependent term, $f(matrix)$, in the processing-structure correlation. This matrix-dependent term provides the flexibility for the regression model to be extended to take the detailed effected of the unconsidered factors into account.

Based on the results in Figure 3-4 and the comments above, a general linear regression model is proposed as

$$\tilde{I}_{filter} = f(matrix) \sinh^2(2W_{PF}/W_{FF} - 1)\log(E_\gamma + 1) + C_0$$

(3.10)

where the term $f(matrix)$ represents the effect of the matrix polymer and $C_0$ is the expected volume fraction normalized interphase area if no processing energy is applied ($E_\gamma = 0$). The results for Figure 3-4 are shown in Figure 3-5.
Figure 3-5 Regression of both polymer matrices within one model with the help of a matrix-dependent term \( f(\text{matrix}) \). Here \( f(\text{PP}) \), \( f(\text{PS}) \) and \( f(\text{PMMA}) \) are set as 15.120, 1.0 and 0.759 respectively to account for the difference of the regression slopes in Figure 3-4

Based on the proposed model, a quantitative relationship between the dispersion of the materials (expressed with \( \bar{I}_{\text{filler}} \)), the mixing conditions (expressed with processing energy \( E_{\gamma} \)) and interfacial energies of the components \( (W_{PF}/W_{FF}) \) have been established. In the future, the expression of the term \( f(\text{matrix}) \) may be studied in details by applying similar analyses across nanocomposites with various types of polymer matrix or by exploring similar experimental data via NanoMine [136]. For instance, the explicit inclusion of additional factors such as the influence of the stiff polymer chain of the PS [102] (point d) or the crystallinity (point h), might lead to more complicated expressions in \( f(\text{matrix}) \), to account for the different polymers [102, 110]. Also, as only the agglomerate size after mixing is studied in this work, the agglomerate size before and during the compounding, which indicates how easy it is to break-up the agglomerates, can be considered. Furthermore, the polymer matrix changes during the compounding process by insertion of mechanical and thermal energy or chemical reactions like branching. This change may
influence the polymer properties, such as molecular weight distribution, viscosity or surface energy. Additionally, the temperature dependence of surface energy may be another factor to explore. Other factors (point c and d) that may influence the infiltration of the polymer would be also considered.

3.6 Summary

In the processing-structure-property paradigm of advanced materials development, the microstructure plays a significant role in determining the material properties. In polymer nanocomposites it is essential to predict and control the dispersion of the nanofiller. This prediction requires a thorough understanding of the effects of interfacial energy and processing conditions on the nanoparticle dispersion. This section represents a significant step toward gaining such knowledge. Targeted experiments were performed on a set of nanocomposites composed of three different polymer matrices and 3 functionalizations of nanoparticles, processed under various mixing energies. The resulting compounds had different interfacial energies and dispersions, which were quantified. Dispersions were analyzed by binarization of TEM images using pixel-wise neighborhood-dependent Niblack thresholding algorithms and the dispersion was statistically captured using physically meaningful descriptors. Supervised learning revealed that the cluster surface area is the most significant descriptor representing the dispersion of nanoparticles in a polymer matrix. The interfacial energy was described by the ratio of the work of adhesion of filler to polymer to the work of adhesion of filler to itself \( (W_{PF}/W_{FF}) \), which also represents the compatibility of the filler-matrix combination. The mixing energy input, \( E_y \), was taken as the processing descriptor. This coordinated set of data show that the dispersion is strongly influenced by the interfacial compatibility \( (W_{PF}/W_{FF}) \) of particle and matrix. The larger the work of adhesion
of filler to polymer and the smaller the work of adhesion of filler to itself, the better the dispersion of the resulting nanocomposites. Processing also plays an important role for the dispersion of nanoparticles where dispersion is improved with increasing input of mixing energy. An empirical quantitative relationship was developed expressing the dispersion descriptor as a function of the processing descriptor (mixing energy) and the interfacial energy descriptor. To generalize the expression, an additional term $f(matrix)$, was included to represent the influence of the inherent polymer chain properties such as chain stiffness and crystallinity which are not considered in this work. This section provides a basis for the prediction of nanocomposite process-structure-property relationships and the possibility to simulate and design nanocomposites. By far, the first research task in Section 1.4 has been addressed.
Chapter 4 Gradient Interphase Representation for Modeling Viscoelastic Property

4.1 Introduction

Polymer nanocomposites have attracted much attention in materials science due to their superior properties and great potential in engineering applications. Prior studies [152-159] have shown that in polymer nanocomposites, the incorporation of a small amount of nanoscale inclusions renders significant enhancements of their mechanical, dielectric and thermal properties, while retaining low density and ease of processing. This combination of multi-property enhancement and facile manufacture make polymer nanocomposites a promising multi-functional material in industry. A variety of constituents (e.g. silica[160], clay[161] and graphite[162]) and morphologies (e.g. spherical particle[27] or nanotube[163]) of nano-inclusions have been investigated to meet different engineering demands in prior works.

In addition to attributes offered to the composite by the nano-inclusions themselves, the region of polymer near the particles, termed the interphase, contributes dramatically to the overall material response. Both geometric and chemical constraints at the nanofiller-polymer interface alter the mobility of the local and interconnected polymer chains, resulting in significant changes to the physical properties of this interphase domain[18, 164-166]. Most notably, even in nanocomposites with very low loadings (e.g. 1 wt % filler), the percolating nature of polymer chain response can lead to a substantial interphase volume fraction, and thereby contribute to the bulk composite properties. For example, it is demonstrated in [27] that the existence of ~2 vol% well dispersed nanotubes will produce 81.4 vol% interphase areas assuming an interphase thickness 3 times the diameter of nanotube.
In recent years, experimental efforts have been devoted to studying effects of interphases on the bulk properties of polymer nanocomposites. For instance, Seiler et al. [18] applied Electric Force Microscopy (EFM) to verify the existence and to estimate the thickness of interphase in silicon nanocomposites. Ciprari et al. [19] utilized data from thermal gravimetric analysis (TGA), transmission electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) to study the structure and density of interphase for six nanocomposite systems. In addition to such experimental investigations, theoretical models have also been proposed to analyze the impacts of interphase for composites. Review articles by Hashin[20] and Christensen[21] cover fundamental mathematical models developed in early years for composite material behaviors without considering interphase, including the popular Mori-Tanaka method[22]. Fisher and Brinson[23] further improve the combination of the Mori-Tanaka method and Benveniste’s method[24] by assuming an interphase region between filler aggregates and polymer to investigate the mechanical property of viscoelastic composite. Other analytical approaches for analytically modeling the interphase includes Deng et al. [167], in which the particle-interphase regions are mechanically equated to effective particles by applying a volume fraction weighted super-position of particles and matrix, and Ji et al. [168] where a simple linear gradient change of elastic moduli in the interphase was assumed. While having demonstrated the success in evaluating the structure-property relationship of polymer nanocomposites, the existing models are limited by only considering the microstructure in a coarse or average sense.

Promoted by the developments of modern computational methods, Finite Element (FE) modeling provides an inexpensive alternative to the traditional experimental approaches and micromechanics models. A number of works have utilized FE methods to study the effects of interphase in composites. For instance, Zhu et al. [25] developed a FE model to predict the elastic
properties of polymer nanocomposites and showed good agreement with experimental measurements. In Boutaleb et al. [169], a micromechanical analytical interphase model, in which interphase regions are also assumed, is proposed for studying and modeling the stiffness of polymer composites via Finite Element Analysis. Another promising example is Read et al. [26], which presents a FE model for predicting the viscoelastic property of polymer blends whose polymer constituents are immiscible and the property distribution is discrete. Our earlier works [27-31] also illustrated FE models to study effects of interphase on viscoelastic property of polymer nanocomposites. In one pair of papers, [27, 28] we presented a FE model in which uniform interphase properties are assumed, and the effects of interphase volume fraction and particle agglomeration, respectively, are explored. Built upon this uniform interphase FE model, studies regarding choice of Representative Volume Element (RVE) [29], statistical assembly of Statistical Volume Elements [30] and inference of appropriate interphase parameters from experiments [31] have been pursued. Despite these successes, it is noteworthy that in these works [27-31], the effective interphase property has been modeled by one or two uniformly distributed interphase layers surrounding the filler aggregates. This simplified assumption of the interphase domain is made due to lack of local measurements of interphase properties.

In recent years, the development of Atomic Force Microscopy (AFM) nano-indentation instrumentation has provided a feasible solution to measure the mechanical property of interphase domains in the nanoscale. In Downing et al.[170], it is illustrated that the size of the interphase and its stiffness could be measured using phase imaging AFM. In addition, Cheng et al.[32] demonstrated the feasibility of using AFM nano-indentation to characterize local elastic modulus on a film-substrate model composite. Zhang et al. [33] created a set of substrate-polymer-substrate samples, varying the distances between substrates, and discovered both the interphase gradient
decay and interactions between interphases produced by different substrates. The availability of AFM data, together with the recent development of statistical tools for analyzing and quantifying microstructures [15], make it feasible to describe interphase behaviors continuously (in contrast to the discretized/uniform representations as used in prior works) and take the spatial effects of interphase and microstructural dispersions into account. In this regard, this work presents a new descriptive interphase representation for modeling the properties of polymer nanocomposites, with an explicit implementation for viscoelastic material response. The approach, however, is general and applicable to other physical properties. The proposed interphase representation disentangles the complex interphase behavior into two continuous interphase functions, namely the single-body interphase gradient and the multi-body interphase compound effect. The single-body interphase gradient describes the spatial distribution of the material property within the interphase created by one single filler aggregate, while the multi-body interphase compound effect quantifies the interacting behavior of interphases created by different aggregates. The functional formulations of these interphase functions are learned via mining a set of AFM data in [33], and they are implemented into a pixelated plain strain FE model. Numerical studies are conducted to investigate the effects of each interphase function on the bulk viscoelastic property of the polymer composites. By a comparative study with prior simulation work [27-29], the advantage of the proposed interphase representation and the corresponding FE model is demonstrated.

The remainder of the chapter is organized as follows: in Section 4.2, the proposed interphase representations are first defined. We then illustrate how the proposed interphase representation can be implemented in FE modeling of the viscoelastic properties of polymer nanocomposites. In addition, a Bayesian Inference (BI) approach, which is an essential tool for inferring the interphase representation mathematically, is introduced. In Section 4.3, the explicit functional forms of the
interphase representation are identified via data mining, followed by a series of numerical studies to demonstrate the effects of the interphase representations. The advantages of the proposed interphase representation are then studied via a comparative study with the prior interphase modeling work [27]. Moreover, by utilizing a set of experimental data, the spatial distribution of local viscoelastic property is investigated via solving the inverse problem by Bayesian Inferences. In Section 4.4, we draw conclusions and discuss future work.

4.2 Gradient Interphase Representation

While it is well recognized that the existence of interphase significantly contributes to the bulk viscoelastic properties of polymer nanocomposites, there is not a descriptive interphase representation that takes the spatial distribution of interphase properties into account. This deficiency is primarily because: 1). In early years, local measurements of the polymer properties at 10’s of nanometer resolution were not available and thus there was insufficient experimental evidence to support a detailed interphase representation, and 2). The interphase effects on the polymer nanocomposites are a coupled interaction of both spatial property distribution and microstructural dispersions. Therefore, it is difficult to exclude the influence of complex microstructural dispersions and isolate the interphase spatial distribution alone. To address this entanglement, Cheng et al. [32] manufactured a special film-substrate structured “model” composite sample and utilized AFM to study the local property of interphase created by single filler aggregates. Zhang et al. [33] extended this work by producing a series of substrate-film-substrate model composite samples with different film thicknesses. These works eliminated the effects of microstructure dispersion and demonstrated that 1) the stiffness of the interphase decays as the distance from the filler interface increases. 2) closer pairs of substrates result in an increased stiffness in the interphase region, beyond simple superposition of two single-surface effects. In the
light of these experimental observations, in this work, we propose a new gradient interphase representation for modeling the viscoelastic property of polymer nanocomposites. Specifically, two interphase functions, namely single-body interphase gradient and multi-body interphase compound effect, are proposed to reflect and quantify the experimental findings.

![Figure 4-1 Illustration of interphase functions. (a) Single-body interphase gradient. (b) Multi-body compound effect. The blue dashed line represents the single-body interphase gradient created by one single aggregate and the red curve shows how the compound effect makes an impact on the resultant interphase property.](image)

4.2.1 Single-body Interphase Gradient

It is found in Cheng et al. [32] and Zhang et al. [33] that the local elastic property of interphase decays as the distance from filler surface increases. Based on this observation, we propose the first component of interphase representation, namely single-body interphase gradient, to describe the dependence of interphase property on the distance from a single filler aggregate.
As shown in Figure 4-1(a), the single-body interphase gradient describes the gradually decaying effects in the interphase created by one single filler aggregate. No interaction between interphases created by different aggregates are considered in the single-body interphase assumption. For the elastic property, the single-body interphase gradient is expressed as,

\[ E_d = F(d; \Phi), \quad d \leq L_0 \] (4.1)

where \( E_d \) is the elastic modulus at a distance \( d \) from filler surface, \( F(\cdot) \) is the functional form of the interphase gradient defined by a set of hyper-parameters \( \Phi \), and \( L_0 \) is the interphase thickness which is usually determined by some threshold value on the mechanical property enhancement.

To identify the functional form of the single-body interphase gradient function for viscoelastic properties, while recent works [171, 172] have shown the feasibility of directly measuring the local viscoelasticity via AFM, the methodologies to capture quantitative viscoelasticity from AFM instrumentation is still under development. Additionally, in [173] the microstructural geometries used are too complex to disentangle the coupling effects of microstructure and interphase gradient. Therefore, the analogy between the elastic modulus and the magnitude of the complex modulus is utilized in this work to extend the interphase gradient from elasticity as in [33] to viscoelasticity.

The functional form of the single-body interphase gradient function \( F(\cdot) \) can be expressed as,

\[ \frac{|E_{d,f}^*|}{|E_{+\infty,f}^*|} = F(d,f; \Phi), \quad d \leq L_0 \] (4.2)

where \( E_{d,f}^* \) is the complex modulus of the interphase at a distance \( d \) from the filler aggregate, \( |E_{d,f}^*| \) represents the magnitude of the complex modulus, and \( |E_{+\infty,f}^*| \) indicates that modulus normalized by the magnitude of the complex modulus of the matrix \( |E_{+\infty,f}^*| \). In addition, \( f \) is the frequency at which the viscoelasticity is measured, and \( L_0 \) is the interphase thickness and \( \Phi \) is a set of hyper-parameters in the functional form of the interphase decay. For the examples in this
work, elastic AFM data is used, such that the $F$ determined is independent of frequency and the frequency dependence for $|E_{\alpha_f}^{\epsilon}|$ arises solely due to the matrix viscoelastic modulus. However, as reliable viscoelastic AFM data becomes available, the interphase gradient function $F$ can be revised to contain frequency dependencies explicitly as indicated in Eqn. (4.2).

4.2.2 Multi-body Compound Effect

In defining the single-body interphase gradient, it is prescribed that only the interphase created by one single aggregate is considered. While it seems that this definition could quantify the experimental findings in [32], it would fail to describe the interacting effects of interphases observed by Zhang et al. [33]. The single body gradient would also fail to capture interaction effects in complex microstructure dispersions, where every particle has many close neighbors and thus many potential interaction effects. Therefore, we propose the second component of interphase representation, namely *multi-body (interphase) compound effect*, to describe the interaction phenomenon in the interphase areas that are affected by multiple filler aggregates. The multi-body interphase compound effect decays to the single body effect if the filler aggregates are sufficiently far from each other, and it occurs when the interphases created by different aggregates interact as depicted in Figure 4-1(b). The multi-body interphase compound effect is not limited to simply additive response and an extended interphase region for interacting particles can be larger than that for isolated particles, as observed in [33]. To model the viscoelasticity of the interphase for multi-body effects, the analogy between the elastic modulus as in [33] and the magnitude of the complex modulus introduced in Section 4.1.1 is utilized again and the form of the multi-body compound effect $G(\cdot)$ is expressed as,
\[ |\overline{E_{x,f}}| = g\left(|\overline{E_{d_1,f}}|, \ldots, |\overline{E_{d_n,f}}|; \Omega\right) \]  

where \(|\overline{E_{x,f}}|\) is the normalized magnitude of the complex modulus at location \(x\), \(f\) is the frequency at which the viscoelasticity is measured, \(d_i(i = 1, 2, \ldots, n)\) represents the nearest distances from location \(x\) to the filler aggregate \(#i\), \(n\) is determined by a user-specified, sufficiently large cut-off distance, and \(\Omega\) is a set of hyper-parameters in the functional form of the compound effect.

### 4.3 Implementing the Proposed Interphase Representation in Finite Element Modeling

#### 4.3.1 Finite Element Model

To examine the influences of the proposed interphase representation functions (i.e. single-body interphase gradient and multi-body compound effect), a pixelated viscoelastic 2D plain strain model is developed. Different from our prior work [27] in which a conforming mesh is utilized, the pixelated model in this work discretizes the microstructure with elements of rectangular shapes, which as a consequence avoids potential meshing errors and provides higher flexibility in assigning complex interphase property distributions. In addition, periodic boundary conditions are applied in assigning the interphases (shown in **Figure 4-2**) and constraining the boundary displacements as,

\[
\begin{align*}
\mathbf{u}(X_1, 0) + U_2 &= \mathbf{u}(X_1, L) \\
\mathbf{u}(0, X_2) + U_1 &= \mathbf{u}(L, X_2)
\end{align*}
\]

where \(L\) is the length of the square edge, \(\mathbf{u}(i,j)\) is the displacement at location \((i,j)\), and \(U_1\) and \(U_2\) depend on the particular loading applied on the cell.
4.3.2 Interphase property

In prior numerical simulations for polymer nanocomposites [28, 29, 31, 146, 174], the effective property of the interphase is often assumed to be directly related to the property of the polymer matrix. Therefore, the interphase property is modeled by applying a transformation on the master curve of matrix. For instance, to simulate the dielectric property of polymer composites [174], the interphase property has been obtained through a transformation process controlled by five parameters, while to model the viscoelastic property [27, 29], a shifting and/or broadening conversion of the matrix property has been assumed. In this work, we assume that in the interphase created by a single filler aggregate, the local viscoelastic property of an infinitesimal area in the interphase is related to the bulk property by a shift of $S$ decades in relaxation time, and the shifting factor $S$ is dependent on the distance away from the filler surface. For the interphase locations affected by multiple filler aggregates, the interphase property is determined using the multi-body compound effect to combine the theoretical single-body interphase properties. Figure 4-3 illustrates these assumptions of interphase viscoelastic property conceptually.
Figure 4-3 The illustration of the assumptions of the interphase viscoelastic properties (a) left – the two locations A and B in the interphase are identified; right – the corresponding viscoelastic properties (\(\tan\delta\) peak) for A and B. Since A is closer to the filler than B, the shifting factor \(S_A\) is greater than \(S_B\). (b) left – location A again experience a single-body effect from the left filler, but point P, at the same distance from the left filler as point A, is located also close to the right filler in the interacting interphase region. For point P, the distances from two filler aggregates \(d_C\) and \(d_D\) are identified and used to determine the resultant property using single-body and multi-body effects; right – the “virtual” property for point P is found by first inferring single-body interphase gradient by \(d_C (S_C)\) and \(d_D (S_D)\). \(S_{\text{compound}}\) for point P is then determined using the multi-body compound effect function \(G(\cdot)\) in Eqn. (4.3).

It should be also noted that according to the guideline suggested by Cheng et al. [32], the interphase thickness, \(L_0\), is defined as the distance from substrate surface to the point where the interphase property drops to 105% of the matrix property. This definition of interphase thickness
$L_0$ is also utilized in this work when the interphase representation is implemented in FE model. In other words, a particular location is considered as interphase if its magnitude of the complex modulus is greater than 105\% of that of the matrix. Using this criteria, locations which are outside the range of single-body interphase thickness from the aggregates can still be inside the range for the multi-body effect.

4.3.3 Bayesian Inference (BI) for identifying the hyper-parameters in the interphase representation

For polymer nanocomposites, techniques such as DMA for acquiring the bulk viscoelastic properties are comparatively mature and inexpensive while probing the local viscoelastic properties within the interphase using AFM is still under development, time consuming and relatively rare. Therefore, in this work, we apply a Bayesian Inference based approach [31] to inversely infer a reasonable distribution of properties within the interphase region. In this approach, AFM data on “model” composites is firstly utilized to learn the functional forms of the two interphase functions, in which the values of hyper-parameters ($\Phi, \Omega$) are unknown. The functional forms of the interphase representation are then implemented into the FE model and Bayesian Inference is conducted to identify the values of ($\Phi, \Omega$) that best match the simulated bulk composite property with the objective property. In a first demonstration, a virtual target property is computed using the prior uniform interphase model and is used as the objective to identify the equivalent gradient interphase representation. In the second demonstration, the gradient interphase modeling approach is applied to experimental data to investigate the spatial distribution of interphase properties. The first demonstration serves as a validation of the algorithms developed while the second demonstration shows the ability of the approach to describe experimental composite data with continuous interphase functions as developed in this chapter.
Figure 4-4 The workflow of the Bayesian Inference approach for identifying the values of the hyper-parameters $\Phi$ and $\Omega$.

Figure 4-4 illustrates the workflow of the Bayesian Inference approach to identify the hyper-parameters’ values in the gradient interphase representation. Before the inference process, the properties of individual constituents (particle aggregates and polymer matrix), the bulk property of the composite and its microstructural dispersion is known, and the functional forms with unknown parameters $(\Phi, \Omega)$ of the single-interphase gradient and multi-body interphase compound effect are identified via data mining on the AFM data. The objective of the Bayesian inference is to identify the appropriate values of $(\Phi, \Omega)$ that match the simulated bulk composite property with experimental data. The Bayesian Inference starts with the specification of the ranges of the hyper-parameters $\Phi$ and $\Omega$, which in the context of interphase modeling confines the strength of single-interphase gradient property and interphase interactions. After that, the initial values $\Phi_0$ and $\Omega_0$, which determines the corresponding single-body interphase gradient and multi-body compound effect, are randomly generated from the prescribed ranges. The interphase representation is then fed into FE analysis to simulate the viscoelastic property. While it is theoretically possible to conduct a full grid search on all possible solutions $X = (\Phi, \Omega)$ and
evaluate the difference between the simulation property and the objective property (we denote the difference as $\mathbf{y}$), it is computationally cheaper to infer the relationship of $\mathbf{X}$ and $\mathbf{y}$ via Gaussian Process metamodeling.

Gaussian Process model, also known as Kriging model, is a statistical model that interpolates the observations and supplies quantification of uncertainty for the metamodel prediction at each estimation point. Essentially, Gaussian Process models the data points $\{\mathbf{X}, \mathbf{y}\}$ and the estimations $\{\mathbf{X}', \mathbf{y}'\}$ using

$$
\begin{bmatrix}
\mathbf{y}'
\end{bmatrix} \sim \mathcal{N}
\left(
0, 
\begin{bmatrix}
\text{Cov}(\mathbf{X}, \mathbf{X}) & \text{Cov}(\mathbf{X}, \mathbf{X}') \\
\text{Cov}(\mathbf{X}', \mathbf{X}) & \text{Cov}(\mathbf{X}', \mathbf{X}')
\end{bmatrix}
\right)
$$

(4.5)

in which $\text{Cov}(\mathbf{A}, \mathbf{B})$ represents the covariance matrix between $\mathbf{A}$ and $\mathbf{B}$, defined by $\text{Cov}(\mathbf{A}, \mathbf{B}) = \mathbb{E}(\mathbf{A}\mathbf{B}^T) - \mathbb{E}(\mathbf{A})\mathbb{E}(\mathbf{B}^T)$. Conditioning on the data $D = \{\mathbf{X}, \mathbf{y}\}$, the posterior $P(\mathbf{y}'|\mathbf{X}, \mathbf{X}', \mathbf{y})$ yields a Gaussian distribution where,

$$
\mu = \text{Cov}(\mathbf{X}, \mathbf{X}')\text{Cov}(\mathbf{X}, \mathbf{X}')^{-1}\mathbf{y}
$$

$$
\Sigma = \text{Cov}(\mathbf{X}', \mathbf{X}') - \text{Cov}(\mathbf{X}, \mathbf{X}')\text{Cov}(\mathbf{X}, \mathbf{X}')^{-1}\text{Cov}(\mathbf{X}', \mathbf{X})
$$

(4.6)

Gaussian Process metamodeling establishes a surrogate model that quantifies the statistical mean and uncertainties in the unexplored region. By considering the mean estimation and the uncertainties, the next candidate point $\mathbf{X}_{t+1}$ that could potentially improve the performance would be identified based on the current dataset $(\mathbf{X}_{0:t}, \mathbf{y}_{0:t})$. In proposing the next candidate point, several criterion have been used. For instance, [31] utilizes Expected Improvement (EI) while Li and Yang et al. [175, 176] applies the GP-Hedge criteria which combines three scores -- EI, lower confidence bound (LCB) and probability of improvement (PI). In this work, EI is utilized to propose the next candidate point $\mathbf{X}_{t+1} = (\Phi_{t+1}, \Omega_{t+1})$ to explore.
4.3 Results

Utilizing the ideas and the related techniques presented in the prior section, the detailed analysis for identifying the functional forms of interphase gradients is demonstrated in this section. Specifically, the functional forms with unknown parameter set \((\Phi, \Omega)\) of the interphase gradients are firstly explored via data mining on AFM data (Section 4.3.1). Then the correspondence between the interphase gradient and shifting factors in the frequency domain for viscoelasticity is illustrated in Section 4.3.2 to demonstrate how the proposed interphase gradient is implemented into Finite Element modeling. Lastly, Section 4.3.3 presents the numerical analysis of the impacts of \((\Phi, \Omega)\) parameters, as well as the numerical validations using Bayesian Inference by taking the prior uniform interphase model and an experimental data as optimization objectives.

4.3.1 Data mining to identify the functional forms of interphase representation

Experimental data on model samples provides clear, quantitative data on interphase gradients near surfaces \([32, 33]\), and even illustrates a compound interaction effect. Herein we utilize the AFM data in \([33]\) to identify appropriate functional forms of the interphase representation.

**Single-body interphase gradient**

Zhang et al.\([33]\) present AFM data on modulus gradients on carefully designed model composites with variable spacing between substrates. Four PMMA samples with distances of 520nm, 256nm, 156nm and 60nm between the silica substrates were used. It is found that 520nm is sufficiently large to ensure that interphases created by the two substrates do not interact with each other. Therefore, the data of the 520nm sample is utilized to probe the functional form of single-body interphase gradient in this work. Data analysis reveals that the single-body interphase gradient follows an exponential decay and its functional forms could be expressed as:
\[ \overline{E_d} = \alpha'e^{-\beta'd} + 1 \]  

(4.7)

where \( \overline{E_d} \) is the normalized modulus, \( \alpha' \) and \( \beta' \) are hyper-parameters and \( d \) is the distance from filler surface. The fits of the data are illustrated in Figure 4-5.

![Figure 4-5](image)

Figure 4-5 Regressions of the AFM experimental data. The regression of 520 nm sample is utilized for investigating the functional form of the single-body interphase gradient (\( \alpha' = 5.14, \beta' = 0.079 \)), while the 156nm sample (\( \alpha' = 7.07, \beta' = 0.077 \)) would be utilized later in the study of multi-body compound effect.

In order to extend these data on elastic interphase values into modeling the viscoelastic properties, we utilize the analogy between elastic modulus and the magnitude of complex modulus. The normalized magnitude of the complex modulus of the interphase in polymer nanocomposite is thus expressed as,

\[ \frac{|E^*_{d,f}|}{|E^*_{+\infty,f}|} = ae^{-\beta d} + 1 \]

(4.8)

where \( |E^*_{d,f}| \) is the normalized magnitude of the complex modulus at distance \( d \) from the filler under frequency \( f \), and \( |E^*_{+\infty,f}| \) is the magnitude of complex modulus of polymer matrix. It is also noted that in this extension from elasticity to viscoelasticity, it is assumed that the frequency
dependence of the interphase property $E_{d,f}^*$ is identical to that of the matrix property $E_{+\infty,f}^*$. This functional form explicitly specifies the hyper-parameters defined in Eqn. (4.2) by $\Phi = (\alpha, \beta)$. It should be noted that, while both Eqn. (4.7) and Eqn. (4.8) are exponential, the hyper-parameters $(\alpha, \beta)$ and $(\alpha', \beta')$ are not necessarily identical. In a later section we will utilize the concept of relaxation time shift factors to relate the complex modulus parameters obtained from the elastic experiments to corresponding changes in the full viscoelastic properties of the material.

**Multi-body compound effect**

The compound effect describes the phenomenon that when two filler aggregates are close to each other, their interphases could interact providing additional enhancement of the property of the interphase area between the aggregates. The work by Zhang et al. [33] quantitatively demonstrates this effect and in this work we use data from the 520 nm and 156nm sample to mathematically describe the multi-body compound effect.

As per [33], the filler substrates in the 520nm sample is considered to be far enough to avoid interphase interaction, while the 156nm sample is observed to have increased interphase property incurred by interphase interaction. Therefore, Eqn. (4.7) is first used to learn the single body interphase gradient from the 520nm sample, defined as $E_d^* = F(d)$ as in the previous section. For the 156 nm sample, for a location which has a distance of $d_1$ from the left substrate, the distance from the right substrate is $(156 - d_1)$ nm. At this location, the theoretical normalized elastic moduli affected by either side are $E_{d_1}^* = F(d_1)$ and $E_{d_2}^* = F(d_2) = F(156 - d_1)$ respectively. At the same time, using the data from the 156nm sample and Eqn. 7, an exponential decay function (shown in **Figure 4-5**) $E_d^{\text{compound}} = E_d^{156\text{nm}} = H(d) = G(F(d))$ is also obtained.
It is noted that \( H(d) \) reflects the observed experimental effects of single-body interphase gradient \( F(\cdot) \) and two-body compound effect \( G(\cdot) \), and it is directly dependent on the distance \( d \) from the substrate surface in the AFM sample. In contrast, \( G(\cdot) \) is the mathematical function of compound effect that is not observable from experiments and is not distance dependent. Because of the symmetry of the substrate-polymer-substrate model composite sample, it is straightforward to take \( H(d) \) as the compound property when \( 0 < d \leq 78nm \), and take \( H(156 - d) \) when \( 78 < d < 156nm \). By varying \( d_1 \), a dataset \( \left( \overline{E_{d_1}}, \overline{E_{d_2}}, \overline{E_{d_1}}^{\text{compound}} \right) = \left( \overline{E_{d_1}}, \overline{E_{d_2}}, \overline{E_{d_1}}^{156nm} \right) \) is collected and the compound effect \( G(\cdot) \) could be learned by \( \overline{E_{d_1}}^{\text{compound}} = G(\overline{E_{d_1}}, \overline{E_{d_2}}) \).

While the compound effect is learned from the AFM experimental data in which only two filler substrates are included, it is desired to develop a generalized form for describing the interphase impacted by multiple \((n>2)\) filler aggregates. In this generalization, the functional form of the compound effect \( G(\cdot) \) (Eqn. 3) should satisfy some constraints: 1) the functional form has to be symmetric with respect to \( \overline{E_{d_1}}, \overline{E_{d_2}}, \ldots, \overline{E_{d_n}} \). Otherwise, interchanging \( \overline{E_{d_1}} \) and \( \overline{E_{d_j}} \) \((i \neq j)\) would result in different compound properties. 2) The functional form should be monotonically decreasing with respect to distances \( d_i \) from aggregates. 3) The inclusion of the single-body interphase gradient \( \overline{E_{d_i}} \) created by aggregate \#i should lead to the enhancement of compound property. Mathematically, this latter constraint is expressed as,

\[
G\left(\overline{E_{d_1}}, \overline{E_{d_2}}\right) < G\left(\overline{E_{d_1}}, \overline{E_{d_2}}, \overline{E_{d_3}}\right) < G\left(\overline{E_{d_1}}, \overline{E_{d_2}}, \ldots, \overline{E_{d_n}}\right) \tag{4.9}
\]
Several mathematical forms that satisfy these three constraints (e.g. the sum or the sum of the squares of the normalized elastic modulus) are extracted and the relationship between these features and the compound property is analyzed. A linear relationship (Figure 4-6) between the compound normalized elastic modulus and the term $\sum_{i=1}^{n} (E_{d_i} - 1)$ is identified as,

$$\frac{E_{x^{\text{compound}}}}{E_{x}} - 1 = \eta' \sum_{i=1}^{n} (E_{d_i} - 1) + \xi'$$

(4.10)

where the location $x$ determines the surface distances $d_i$, while $\eta' = 1.08$, $\xi' = 0.06$ and $n = 2$ for the fitted regression. Conceptually, $(E_{d_i} - 1)$ represents the virtual enhancement of elastic modulus produced by filler aggregate #i, and $(\frac{E_{x^{\text{compound}}}}{E_{x}} - 1)$ indicates the combined enhancement of the elastic modulus above the matrix property by all the surrounding filler aggregates. $\eta'$ is a parameter describing the interactive behavior between interphases created by
different aggregates and $\xi'$ is a compensating factor to correct the under/over-estimation. By analogy, the compound effect for viscoelastic property is assumed to be,

$$|E_{\text{compound},f}^*| - 1 = \eta\left[\sum_{i=1}^{n} (|E_{d_{,i},f}^*| - 1)\right] + \xi$$

(4.11)

With this formulation, the parameter set $\Omega$ in Eqn. (4.3) is specified by $\Omega = (\eta, \xi)$.

4.3.2 Determination of the shifting factors at each location in the interphase

To implement the FE simulations of the composite properties using a gradient interphase concept, we must determine the shifting factor at each location of the polymer material. This shifting factor at any location in the interphase is determined by: 1) identifying the number of aggregates $N$ that may affect this location. 2). For each filler aggregate #i $(i=1…N)$, computing the theoretical single-body interphase gradient $|E_{d_{,i},f}^*|$ using Eqn. (4.8), 3). Applying the compound effect (Eqn. (4.11)) to combine $|E_{d_{,i},f}^*|$ to obtain $|E_{\text{compound},f}^*|$, and 4) as illustrated in Figure 4-7, $|E_{\text{compound},f}^*|$ is essentially the vertical enhancement of the normalized magnitude of complex modulus at frequency $f$. The corresponding shifting factor can then be identified according to $|E_{\text{compound},f}^*|$ as illustrated in Figure 4-7.
Figure 4-7 An illustration of the conversion between the normalized magnitude of complex modulus and shifting factor for interphase. $E^*_\text{compound,f}$ is the normalized magnitude of complex modulus at frequency estimated by multi-body compound effect and $S_{\text{intph}}$ is the corresponding shifting factor.

4.3.3 Numerical studies of the interphase effects

In the prior sections, the proposed interphase representation is first presented, followed by a data-driven exploration of the mathematical forms of the representations. In this section, we first explore the parametric influences of the hyper-parameters in the proposed interphase representations. After that, we study the equivalent spatial distributions of the interphase representations for a prior numerical model with uniform interphase assumption, by applying a Bayesian Inference method. Last, the proposed interphase representation is applied to describe the spatial distribution of interphase property of an experimental sample of polymer composite.

The effects of single-body interphase gradient

The effects of single-body interphase gradient are first investigated. Using the circle packing algorithm in [64], a dilute microstructure (Figure 4-8(a)) is generated to prevent the
interactive between interphases created by different filler aggregates – in this case only the single interphase effect will be relevant around each particle. The values of the two parameters $\alpha$ and $\beta$ from Eqn. 8 in the single-body interphase gradient are altered individually and the comparisons between the simulated viscoelastic properties by altering $\alpha$ and $\beta$ are shown in Figure 4-9(a) & (b). It is observed that $\beta$, the term in the exponent in Eqn. 8, has greater effects on the bulk property than $\alpha$. This effect is explained by Figure 4-9(c) & (d), where the distributions of shifting factors are shown. The contour plots of shift factor magnitude demonstrate that increasing the value of $\alpha$ only affect the property of the interphase regions closely surrounding the filler aggregate, and thus making slight difference in the bulk composite property. In contrast, varying $\beta$ value can substantially extend the interphase region (Figure 4-9(d)) and thus affect the bulk composite property significantly.

![Microstructures](image)

Figure 4-8 Microstructures used for studying the effects of interphase representation. (a) a dilute microstructure (VF=0.29%) for studying single-body interphase gradient, (b) a moderately loaded microstructure (VF=1.77%) for studying multi-body compound effect, (c) Transmission
Electron Microscopy (TEM) image of Polystyrene-silica composite, and (d) the binarized image (VF=1.83%) of (c) using Niblack algorithm[177, 178].

Figure 4-9 Effects of single-body interphase gradient. (a) the comparison between the simulated viscoelastic properties by different $\alpha$, (b) the comparison between the simulated viscoelastic properties by different $\beta$, (c) the distribution of shifting factor magnitude when altering $\alpha$, and (d) the change of shifting factor distribution when altering $\beta$. The color map represents the value of the shift factor, $S$ (see Figure 3); e.g. in (c) a shift of 1 decade from the matrix properties is reflected by a color value of 1.

The effects of multi-body interphase compound effect

With the effects of single-body interphase gradient as a baseline, the influence of multi-body interphase compound effect is also investigated. In this numerical study, a moderately loaded microstructure (Figure 4-8(b)) is generated and different settings of interphase compound effect are tested. Specifically, the generalization of compound effect from two filler AFM experimental samples to multiple filler geometries is applied to allow the interaction between multiple filler
aggregates. The cut-off radius for considering a specific location impacted by a filler is set to 100 pixels for this example (half length of the microstructure), while the exponential form of the single-body interphase gradient (Eqn. 7 & 8) indicate that only the closest particle will have significant impact to the property at a given material point. The use of a large potential influence window (defined by the cut-off distance) in the algorithm is more general and allows the interaction functions to effectively handle the level of influence of closer and more distant particles. Figure 4-10(a) & (b) show the comparisons between the simulated composite properties with different $\eta$, $\xi$ values. From Figure 4-10(a) & (b), it is found that increasing $\eta$ could lower the magnitude of the tan (\(\delta\)) peak and shift it to lower frequency. In contrast, altering $\xi$ could only shift the tan (\(\delta\)) curve but not able to change its magnitude. This effect could be explained by Figure 4-10(c) & (d): (c) shows that increasing $\eta$ could enhance the interactions between interphases, which could affect the tan (\(\delta\)) curve in both horizontal and vertical directions. In comparison, changing $\xi$ result in an increment of shifting factor magnitude, which leads to a shifting of the bulk property.
Figure 4-10 Effects of multi-body interphase compound effect. (a) the comparison between the simulated viscoelastic properties by different $\eta$, (b) the comparison between the simulated viscoelastic properties by different $\xi$, (c) the distribution of shifting factor magnitudes when altering $\eta$ and (d) the distribution of shifting factor magnitudes when altering $\xi$. The color map represents the value of the shift factor, $S$ (see Figure 3); e.g. in (c) a shift of 1 decade from the matrix properties is reflected by the color value indicated for 1.

**Numerical comparison to uniform interphase modeling**

In our prior work [27], without the access to the experimental measurement of local mechanical property, it was assumed that the interphase property was related to the matrix property in frequency domain by a simple two decade shift in relaxation times. In this section, a comparative
study is conducted to demonstrate that the proposed gradient interphase representation could not only predict the bulk property of the composite as the prior one but also supply additional interphase information. First, a microstructure of Polystyrene(PS)-Silica composite is chosen (Figure 4-8(d)) and the master curve of PS referenced at 120C degree is utilized as the matrix property. We assume that the functional forms of the interphase representations that we learned from earlier analysis is applicable to this example. The target bulk viscoelastic property is simulated by the prior uniform interphase model, in which interphase property is assumed to be shifted from matrix property by 2 decades. In this simulation, the thickness of interphase is set as 30 pixels (146nm, while the particle diameters are 40nm on average). Second, we iteratively run the FE model with gradient interphase under the Bayesian Inference framework to achieve the equivalence. In these simulations, 100Hz is used as the reference frequency $f$ in Eqn. (4.8) and Eqn. (4.11) for estimating the shifting factor for each location in the interphase. In addition, the ranges for the hyper-parameters are specified as $\alpha \in [4, 6.5], \beta \in [0.06, 0.1], \eta \in [0.8, 1.2]$ and $\xi \in [-0.5, 0.5]$ and the objective function is set as,

$$
\varepsilon = \sum_{i=1}^{n} [\tan(\delta)_{\text{uniform}} - \tan(\delta)_{\text{gradient}}]_{f=f_i}^2
$$

(4.12)

where $f_i$s are the frequencies that the viscoelastic property is evaluated at, and the number of frequencies to evaluate, $n$, is set as 30 in this numerical study.

Then the values of $(\Phi, \Omega)$ that minimize $\varepsilon$ are identified using the Bayesian Inference approach for 50 iterations, as illustrated in Section 4.2.4.
Figure 4-11 The comparison between the FE models using uniform interphase and gradient interphase via Bayesian Inference. (a) the distribution of shifting factor magnitude for the uniform interphase FE model. The interphase property is uniformly distributed and shifted from matrix property by 2 decades, (b) the distribution of shifting factor magnitudes for the proposed gradient interphase FEA model, (c) the comparison between the matrix property and the simulated properties of the two models, and (d) the history of Bayesian Inference.

After the Bayesian Inference, it is found that the values of \((\alpha, \beta, \eta, \xi)\) to achieve the model equivalence (error = 0.03) are (4.22, 0.09, 0.80, -0.50) respectively. Key observations from these simulations are: 1) compared to the previous uniform interphase model (Figure 4-11(a)), the proposed gradient interphase representation (Figure 4-11(b)) can effectively model the interphase property with physically realistic gradients, while achieving the same bulk composite property (Figure 4-11(c)). 2) The Bayesian Inference approach is capable of exploring the optimal solution efficiently and reducing the number of FE simulations (Figure 4-11(d)). 3) From Figure 4-11(b), it is found that the interphase areas that affected by many filler aggregates are significantly strengthened. 4) Using Eqn. (4.8) and the criteria of interphase thickness determination (105% of the matrix property) described in Section 4.2.2, the interphase thickness in the proposed model is
obtained as 54.84 pixels. The total interphase thickness in the gradient interphase case is larger than that of the uniform interphase model because single-body interphase gradient drops exponentially as the distance increases, naturally extending its domain.

**Numerical Verification with Experimental Data**

In the previous discussion, the prior uniform interphase modeling approach is utilized to produce a virtual objective of the material viscoelastic property, and the equivalent gradient interphase representation is learned via Bayesian Inference. In this section we demonstrate the descriptive capability of the proposed interphase representation by directly utilizing experimental data for a composite in [179] and investigate how the proposed gradient interphase representation could describe the distribution of local properties within the microstructure.
Figure 4-12 The results of numerical validation of the proposed gradient interphase representation on experimental data from [179]. (a) Microstructure image gathered from [179] (b) binary image of the microstructure. (c) the distribution of shifting factor magnitudes for the proposed gradient interphase FEA model. (d) the comparison between the matrix property, experimental measurements of the composite property and the simulated property. (e) the history of Bayesian Inference.

In this validation, the microstructure of the composite (Figure 4-12(a)) is extracted and binarized (Figure 4-12(b)). Meanwhile, the temperature sweeps of the viscoelastic properties of the matrix and composite in that work are also converted to frequency dependent spectrums (the green and the blue curves in Figure 4-12(d)) using Williams-Landel-Ferry equation[180]. These data, together with the proposed interphase gradient representations, is then fed into the Bayesian Inference framework discussed previously to match the simulated bulk property to the
After the Bayesian Interference computations, the functional forms of the interphase representations are identified and the spatial distribution of local properties within the microstructure can be visualized. It is also noted that, since the microstructure in this numerical validation has different length scale from the previous one, the ranges of the hyper-parameters in the Bayesian optimization are adjusted accordingly as $\alpha \in [1.5, 6.5]$, $\beta \in [0.12, 0.25]$, $\eta \in [0.5, 1.1]$ and $\xi \in [-1.5, 1.0]$, and Eqn. (4.12) is kept as objective function.

As shown in Figure 4-12(d), after employing the Bayesian Inference method, the simulated property of the composite agrees well with the experimental measurements (error = 0.04). The corresponding values of the hyper-parameters are $(\alpha, \beta, \eta, \xi) = (2.37, 0.15, 0.5, 0.0185)$. Figure 4-12 demonstrates that 1). the proposed FE model can effectively model the spatial distribution of the local properties in the microstructure (Figure 4-12(c)), while matching of the experimental viscoelastic property data. 2). The Bayesian Inference framework can efficiently explore the space of the hyper-parameters and identify these values of hyper-parameters. 3) Using Eqn. (4.7) and the criteria of interphase thickness determination (105% of the matrix property), the interphase thickness in the proposed model is obtained as 26.10 pixels, which corresponds to 166nm. While this interphase thickness identified in this work is of the same magnitude as found in our prior work (~100 nm in [32]), it is slightly greater than that in [32]. This finding could be due to 1) the difference between elastic and viscoelastic properties: the interphase thickness in [32] was inferred using elastic property while in this work the magnitude of complex modulus is utilized. Different properties could perform slightly differently in reflecting the interphase thickness. 2) Numerical error introduced by coarsened meshing: in our FE model, the original microstructure which has a resolution of 700x700 pixels is coarsened to a voxelated meshing (200x200) for computational efficiency, and this coarsening process may introduce numerical errors.
It should be also noted that while the functional form of the compound effect is learned based on the experimental data with two overlapped interphases, our method can handle the interaction between interphases produced by multiple particle aggregates. **Figure 4-13** illustrates the distribution of the number of overlapped interphase in the microstructure for the two validations conducted in this work. It is observed that, in the region that many particle aggregates are densely distributed, it is possible that a particular location is affected by more than 10 nearby aggregates. This again verifies the capability of our method in handling multi-body (greater than 2) compound effect and complex microstructure dispersions.

![Figure 4-13](image)

**Figure 4-13** The distributions of the number of overlapped interphases in the two test cases of this work. (a) & (b) correspond to the microstructures in Figure 4-11 & 4-12 respectively.

**Tackling computational limits with cut-off distance**

Different from the traditional definitions of interphase, in which an interphase thickness ranging from tens to hundreds of nanometers is prescribed, the proposed interphase representation does not require such a thickness to be defined in advance. While applying the single-body interphase gradient, it is presumed that a filler aggregate could potential impact all the material
points within the microstructure. Since the single-body interphase gradient is monotonically decreasing, the closer a material location is to the filler aggregate, the greater the interphase effect would be. After the single-body interphase gradients created by different filler aggregates are applied on the entire microstructure, multi-body compound effect is then utilized at each material point to combine the “virtual” interphase impacts together. For a microstructure of size L-by-L with n distinct filler aggregates, it takes $O(nL^2)$ to propagate single-body interphase gradients to the entire microstructure. In addition, it takes $O(nL^2)$ to apply the multi-body compound effect to each material points. Therefore, the total computational cost is $O(nL^2)$. It is noted that, this computational cost increases in a quadratic manner with respect to the size L of the microstructure. Therefore, it would be very computationally expensive to apply the proposed interphase representation on a very large microstructure. To tackle this computational problem, herein we introduce the cut-off distance as briefly discussed in the prior discussions.

The cut-off distance defines a window around the filler aggregate out of which the impact from the filler aggregate is negligible. Unlike traditional interphase definitions which aim to ensure every point in the interphase has significantly difference in its property from the matrix, the window defined by the cut-off distance here only ensure that the material points outside the window are impacted insignificantly. In other words, it is possible that, under the definition of the cut-off distance, some material points within the window could have similar property to the matrix. With the introduction of cut-off distance D, the computational cost of applying the single-body interphase gradient reduces to $O(nD^2)$, while that for compound effect is trimmed to $O\left(n \frac{D^2}{L^2} L^2\right) = O(nD^2)$. Therefore, the total computational cost is reduced to $O(nD^2)$ no matter how large the microstructure is. With this setting, the user could easily determine the cut-off
distance D based on the computational capability of their machines and thus avoid potential computational problems such as memory overflow.

In all the computational examples in this chapter, the cut-off distance is set to 100 pixels consistently (subject to the computational capability of our server). Table XX illustrates that, the interphase enhancement has decreased to less than 1% of the matrix property before reaching the boundary of the cut-off window. Therefore, this setting would have negligible impact in the modeling results of the bulk property of the material.

Table 4-1 Cut-off distances and their equivalent physical length for each computational example in this chapter

<table>
<thead>
<tr>
<th>Example</th>
<th>α</th>
<th>β</th>
<th>Distance where single-body interphase gradient decreases to 101% of matrix property (nm)</th>
<th>Cut-off distance (pixel)</th>
<th>Equivalent physical length of the cut-off distance (nm)</th>
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</thead>
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<td>0.06</td>
<td>88.3</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.06</td>
<td>99.9</td>
<td>100</td>
<td>250</td>
</tr>
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<td>106.6</td>
<td>100</td>
<td>250</td>
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<td>4</td>
<td>0.04</td>
<td>149.8</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.08</td>
<td>74.9</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
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<td>100</td>
<td>250</td>
</tr>
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<td>67.2</td>
<td>100</td>
<td>480</td>
</tr>
<tr>
<td>Figure 4-12</td>
<td>2.37</td>
<td>0.15</td>
<td>36.5</td>
<td>100</td>
<td>636</td>
</tr>
</tbody>
</table>

4.4 Summary

Based upon AFM experimental observations of local polymer interphase properties, we proposed here a new gradient interphase representation. The proposed interphase representation contains two components, single-body interphase gradient, which represents the effects of single filler aggregates, and multi-body compound effect, which describes the interaction between interphases created by multiple filler aggregates. The proposed interphase representation is
implemented in Finite Element simulation and numerical studies are conducted to investigate the effects of each interphase representation components. In addition, the proposed interphase representation is compared numerically with previously developed uniform interphase model via FE modeling and Bayesian Inference. It is demonstrated that the proposed interphase can achieve the equivalent property prediction capability as the prior method, and also supply more reasonable interphase gradient information. In addition to the numerical validation on virtual material property, it is also shown that the proposed interphase representation could facilitate the exploration of spatial property distribution within the interphase by utilizing Bayesian Inference on experimental measurements.

While this work presents the complete process of utilizing AFM experimental measurements of local interphase properties in inferring spatial distribution of interphase via Finite Element modeling, several potential directions could be pursued to further extend this work. First, in this work, the mathematical form of compound effect is learned from the AFM experimental data in which only two filler substrates are included, and the generalization of the compound effect for multiple (n>2) interphase interaction is not rigorously validated. AFM model composites with a great variance of complex geometries, if available, would reveal the impacts of microstructural descriptors for multiple interphase cases, and they would potentially lead to a more precise functional form of the compound effect. Then this sophisticated interphase representations could be utilized to predict the properties of given composites in addition to the inference of interphase properties presented in this work. Second, while the discussion in this work is limited to modeling the viscoelastic property of polymer nanocomposites, similar interphase representation could also be developed in the similar manner for other material properties of interest (e.g. dielectric property...
if local dielectric property within interphase is available). Lastly, the proposed interphase representation could be implemented in 3D FE modeling.
Chapter 5 A transfer learning based approach for microstructure reconstruction and structure-property prediction

5.1 Introduction

Under the Materials Genome Initiative (MGI)[181], materials informatics has become a revolutionary interdisciplinary research area fundamentally changing the methods to discover and develop advanced materials. In past success using materials informatics, *stochastic microstructure reconstruction* – the process of generating one or a few microstructures with morphology embodied by a set of statistically equivalent characteristics – has demonstrated its significance in both processing-structure-property modeling[5, 182, 183] and computational materials design[184, 185]. Therefore, the prescription of these microstructural characteristics is crucial in determining the effectiveness of microstructure reconstruction. Existing approaches for quantifying microstructure characteristics can be roughly classified into three major categories, i.e., approaches that are statistical modeling-based, visual features-based and deep learning-based.

Statistical modeling-based approaches employ statistical models or attributes (e.g., mean particle size) to quantify microstructure morphology or features. These methods are widely used, yet their application to microstructure reconstruction is often limited to certain types of material systems and cannot be generalized. For instance, while N-point correlation functions[186] are theoretically sound for microstructure characterization, it is computationally intractable to use high-order correlation functions (e.g., 3-point correlation and above) for microstructure reconstruction. The physical descriptor-based approach[15] is often limited to characterizing and reconstructing microstructures with regular geometries (e.g., spherical clusters) but is not applicable to material systems with irregular inclusions (e.g., ceramics or copolymer blends).
Another set of examples of statistical models are approaches based on Gaussian Random Fields[35] and Markovian Random Fields[36, 187]. A limitation of these approaches is the assumption that locally invariant properties always hold throughout microstructures, which is not always the case.

In the last decade, visual features used for object classification or face detection in the field of computer vision have been utilized by material scientists to characterize microstructures and to study structure-property relationships. For instance, DeCost et al. [188] used bag of visual features such as Scale-Invariant Feature Transform (SIFT) to collect a “visual dictionary” for describing and classifying microstructures. Chowdhury et al.[189] utilized visual features such as histogram of oriented gradients (HoG) and local binary patterns (LBP) to distinguish between micrographs that depict dendritic morphologies from those that do not contain similar microstructural features. Despite these successes, the use of visual features-based approaches in microstructure reconstruction is unexplored and potentially limited because these visual features are essentially low-order abstractions of microstructures, thereby rendering reconstruction of statistically equivalent microstructures using only these abstractions in the absence of high-order information difficult.

Revived from near pseudoscience status during the “AI winter”[68], deep neural networks, which feature large model capacities and generalities, have stimulated a plethora of applications across different disciplines[70, 190-195] (including materials science) in recent years. Existing deep learning-based approaches in materials science fall into two categories: material-system-dependent or -independent. Material-system-dependent approaches train deep learning models based on collected materials data, with their subsequent applications are often limited to the material system used for training. For instance, Cang et al.[196] extracted microstructure representations for alloy systems using convolutional deep belief networks. Their model[196] was
trained with 100 images of size 200 x 200 pixels. While their model generated satisfactory reconstruction results for the chosen alloy material, their model was highly constrained to the type of alloy system used for the training set. Li et al. [197] developed a Generative Adversarial Network (GAN)-based model to learn the latent variables of a given set of synthetic microstructures, but their model needs to be retrained for application to a set of microstructures with significantly different dispersion. In contrast to these material-system-dependent approaches, transfer learning provides an alternative to capture microstructure characteristics without the need for training with a set of materials data (i.e., it is material-system-independent). Transfer learning[198-200] refers to the strategy of migrating knowledge for a new task from a related task that has already been learned[201]. In the context of microstructure analysis, deep-learning models trained for benchmark tasks using computer vision are fully or partially adopted to quantify microstructures or to address other complex challenges. For instance, DeCost et al. [202] utilized a transferred deep convolutional network to capture hierarchical representations of microstructures and then used these representations to infer the underlying annealing (i.e., processing) conditions. Lubbers et al. [203] adopted the VGG-19 model[204], trained on ImageNet[205], and used the activations of its network layers as microstructure representations to identify physically meaningful descriptors (e.g., orientation angles) via manifold learning. Nevertheless, none of these newly developed transfer learning-based approaches has addressed the challenge of microstructure reconstruction, where the extracted features from a network need to be reproduced in a statistically equivalent way. It should be noted that in Lubbers et al. [203], a prior texture representation based on the activations of deep convolutional layers previously developed by Gatys et al.[206] was implemented to synthesize visually similar microstructures with the same texture representation. However, the more challenging problem of achieving statistical equivalency of microstructures, which could not be
guaranteed by visual similarity, was not addressed in their work. It is also noteworthy that, in the prior transfer learning-based works such as Lubber et al.[203], the transferred neural network model is considered as a “black box” and there lacks understandings of the relationship between the network layers and the microstructure characteristics.

In the present study, a generalized transfer learning-based, training-free approach is proposed for reconstructing statistically equivalent microstructures from arbitrary material systems using a single given target microstructure. The input microstructure with labeled material phases is first passed through an encoding process to obtain a 3-channel representation in which material phases are distantly separated. In the meantime, the initial 3-channel representation of the reconstructed microstructure is randomly generated as the initialization. In each iteration of the reconstruction process, both of the 3-channel representations of the original and reconstructed microstructures are fed into a pre-trained deep convolutional network, VGG-19[204], and a loss function is utilized to measure the statistical difference between the original and the reconstructed microstructures. The gradient of the loss function with respect to each pixel of the reconstructed microstructure is computed via back-propagation and is then utilized in gradient-based optimization to update the reconstructed microstructure. Finally, the updated 3-channel representation of the reconstructed microstructure is propagated through a decoding stage via unsupervised learning to obtain the reconstructed microstructure with labeled material phases. In addition to visual similarity, statistical equivalence of the reconstructed microstructure is achieved by the encoding-decoding pair, which ensures sharp phase boundaries with correct labeling for the phase of each pixel. In addition, to ensure the computational viability of the proposed approach, model pruning is conducted on the transferred deep convolutional network. For validation, microstructures generated by differently pruned models are evaluated via visual inspection, numerical validation,
and the calculation of receptive fields, which are defined as the regions in the input space that influence a particular convolutional neural network feature. The correlation between network layers and microstructure dispersion is also concurrently analyzed. Finally, as an extension, the knowledge learned in model pruning is utilized in determining the architecture and initialization conditions in developing a structure-property predictive model. A numerical validation using a small dataset of microstructures and their optical properties is conducted in order to verify the proposed structure-property modeling approach.

5.2 Microstructure reconstruction via transfer learning

5.2.1 The workflow of the proposed approach

The proposed transfer learning-based approach for microstructure reconstruction migrates a pre-trained deep convolutional network model [204] created using ImageNet [205] – an auxiliary dataset which contains millions of regular images – and adds encoding-decoding stages before and after the deep convolutional model, as illustrated in Figure 5-1.
1) **Encoding**: The transferred deep neural network has very strict requirements for data entry in terms of the image size and 3-channel representation alignment. Therefore, we encode the original microstructure in which each pixel is labeled with material phases into 3-channel representations so that the dimensionality of the input image fits the requirements of the transferred deep convolutional model. For ease of distinguishing individual phases after reconstruction, we employ maximize-minimum (maximin)[207] distance mapping from phase labels to the 3-channel representations.

2) **Gradient-based microstructure reconstruction**: Three steps are applied in transferring the deep convolutional neural network into microstructure reconstruction. a) **Removal of highest network layers**: It is well recognized that higher-level layers, particularly the last fully connected layer, are discriminators tuned specifically for the image classification task. For our new task of microstructure reconstruction using the transferred VGG-19 model based on non-material images, we eliminate the highest 7 layers (3 fully-connected and 4 convolutional layers with the associated

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Figure 5-1 The workflow of the proposed microstructure reconstruction approach
pooling and dropout layers) (see details in the “Model Pruning” section below). b) **Gram-matrix computation**: Gram-matrix[206], which is usually used for measuring the differences in textures between images, is taken as the measurement of statistical equivalence between the original microstructure and the reconstruction. We implement its forward and backward computations (i.e. the calculation of Gram-matrix and its gradient) by customizing a computation unit and integrating it with the transferred model. On each layer of the convolutional deep network, first the Gram-matrices of the original and reconstructed microstructures are computed based on the activation values, then the differences of the Gram-matrices on the corresponding layers between the original and reconstructed microstructures are added as the optimization objective. c) **Gradient computation via back-propagation**: The state-of-the-art deep learning platform provides a fast and handy way of gradient calculation via back-propagation through the computation graph. The gradient of the objective (Gram-matrix difference) with respect to reconstruction image pixels is thus calculated via back-propagation. The gradient is then fed into nonlinear optimization (either L-BFGS-B[208] or Adam[209]) to update the reconstruction iteratively until convergence is found. It is noted that stochasticity of the microstructure reconstructions is achieved by random initialization of the microstructure image before the back-propagation operation.

3) **Decoding**: after obtaining the 3-channel representation of the reconstruction, an unsupervised learning approach is used to convert the 3-channel representation back to the desired representation: images with labeled material phases. Furthermore, considering that volume fraction (VF) is a critically important microstructural descriptor, a Simulated Annealing-based VF matching process is exercised at the end to ensure the reconstructed image has the same VF as the original through erosion or dilation.
5.2.2 The detailed implementation of the proposed workflow

**Encoding via Maximizing Minimum Distance**

Microstructures are typically represented as \( NxM \) matrices (where \( N \) and \( M \) correspond to the height and width of the microstructure image, respectively). The first step is to convert the \( NxM \) matrices to the 3-channel representations that can be fed into the transferred deep convolutional model. While there are a variety of mapping methods for this conversion, here we suggest an encoding strategy that maximizes the minimum Euclidian distance between the encoded phase coordinates. This encoding strategy is chosen for the ease of distinguishing individual phases after the gradient-based optimization for reconstruction in the encoded space is carried out.

Maximization of the minimum distances between a number of points in the feature space has been solved typically by gradient-based search algorithms or stochastic search algorithms such as simulated annealing [210]. It can also be formulated as an NP-complete, independence in geometric intersection graphs problem, which can be addressed by approximate algorithms [207]. However, given that in most cases, the number of different material phases in an original microstructure is not large, it is not necessary to pursue the farthest separations as long as the phase clusters after reconstruction can be properly distinguished. Therefore, for material systems which have no more than three (3) material phases such as in this work, we take a simpler approach – Latin Hyper-cube Sampling [211] (LHS). Specifically, by setting the number of sampling points to be equal to that of distinct material phases in the original microstructure, LHS samples with maximin distance criteria would create a 3-vector representation for each material phase. Then, for each pixel in the \( NxM \) microstructure, we replace the original scalar phase label by the 3-vector, which leads to \( NxMx3 \) matrix representations.
Deep Convolutional Characterization and Reconstruction

While a lot of models have been developed for the ImageNet task such as GoogleNet[212] and ResNet [72], the VGG-19 model [204] is selected in this work because of its structural simplicity and regularity. The original VGG-19 [204] model has 19 layers (3 fully connected layers and 16 convolutional layers). In transferring this model, all layers beyond the 2\textsuperscript{nd} highest pooling layer are first eliminated (i.e. 1 fully-connected layer, 1 pooling layer and 3 convolutional layers). Both the network structure and the network parameters from the VGG-19 model are inherited as the transferred deep convolutional model in this work.

Microstructure reconstruction using the transferred deep convolutional model is essentially a gradient-based optimization process. The objective function to be minimized is the sum of Gram-matrix differences on the selected neural network layers, and the variables to be optimized are the pixel values in the microstructures. The optimization process can be decomposed into three steps: 1) Initialization: an NxMx3 matrix is initialized randomly with uniform distribution for each entry in the microstructure. Different initializations will result in different statistically equivalent microstructure reconstructions. 2) Forward-propagation: At each iteration of optimization, the values in NxMx3 representations of the original and the reconstruction are forward-propagated simultaneously through the deep learning network, creating corresponding activation values on each layers. 3). Back-propagation: Gram-matrix [206] on selected layers are matched between the reconstruction and the original microstructure to find the difference (i.e., loss). The gradient of the loss with respect to each pixel in reconstruction is then computed via back-propagation using GPU, and it is then fed into a nonlinear optimization algorithm to update the pixel values of the microstructure reconstruction. Steps 2) and 3) are then executed iteratively until the solution converges to a local optimal state of the microstructure reconstruction.
The convolutional deep neural network in the present approach is composed of two sets of computation units: regular units (convolutional operation, Rectified Linear Unit transformation, and pooling operation) and customized units (Gram-matrix related computations). While the back-propagation of regular units are well integrated in the popular deep learning platforms, the Gram-matrix related derivations are still needed for the implementation in customized units. Here we demonstrate the derivation briefly. Let $x$ and $\bar{x}$ denote the original and reconstructed microstructure in the encoded space at iteration $n$, respectively. $x$ and $\bar{x}$ are first passed through the transferred convolutional network for activating feature maps $F^i$ of layer $i$. Then in each layer $i$ of the network, $x$ and $\bar{x}$ will activate a stack of feature maps $F^i, F^i \in \mathbb{R}^{N_t \times M_t}$, where $N_t$ is the number of filters and $M_t$ is the size of the vectorized feature maps in layer $i$. Let $F^i_{jk}, \bar{F}^i_{jk}$ denote the activations of the $j^{th}$ filter at position $k$ in layer $i$ for $x$ and $\bar{x}$. The Gram matrix [206] of both microstructures is defined as the inner product between feature map $p$ and $q$ in layer $i$:

$$G_{pq}^i = \sum_r F^i_{pr} F^i_{qr}$$  \hspace{1cm} (5.1)

$$\bar{G}_{pq}^i = \sum_r \bar{F}^i_{pr} \bar{F}^i_{qr}$$  \hspace{1cm} (5.2)

The contribution of the loss in layer $i$ is:

$$E_i = \frac{1}{4N_t^2M_t^2} \sum_{j,k} (G_{jk}^i - \bar{G}_{jk}^i)^2$$  \hspace{1cm} (5.3)

The total loss is:

$$L = \sum_i E_i$$  \hspace{1cm} (5.4)
Next, a gradient-based optimization with the aim of minimizing the total loss between the original and the reconstructed microstructures is utilized in order to update the reconstructed microstructure. The gradient $\frac{\partial L}{\partial x}$ is decomposed by the chain rule as:

$$\frac{\partial L}{\partial x} = \frac{\partial L}{\partial E} \cdot \frac{\partial E}{\partial \bar{F}} \cdot \frac{\partial \bar{F}}{\partial x}$$  \hspace{1cm} (5.5)$$

where

$$\frac{\partial L}{\partial E_i} = w_i$$  \hspace{1cm} (5.6)$$

$$\frac{\partial E_i}{\partial \bar{F}_{jk}} = \left\{ \begin{array}{lr} \frac{1}{N_i^2 M_i^2} \left[ (\bar{F}_i)^T (G^i - \bar{G}^i) \right], & \text{if } \bar{F}_{jk}^i > 0 \\ 0, & \text{otherwise} \end{array} \right.$$  \hspace{1cm} (5.7)$$

and $\frac{\partial \bar{F}}{\partial x}$ is automatically handled by back-propagation in Caffe. The gradient $\frac{\partial L}{\partial x}$ is then fed into the Limited-memory Broyden-Fletcher-Goldfarb-Shanno algorithm [208] with bound constraints of $[0, 255]$ (L-BFGS-B) or Adam optimizer [209] on each encoded dimension to minimize the total loss $L$. At the end, convergence at local minimum is achieved and each pixel will be assigned a 3-vector by L-BFGS-B. In other words, at the end of the optimization, a $N\times M\times 3$ matrix will be obtained for the next step of decoding.

**Decoding Reconstruction via Unsupervised Learning and Simulated Annealing**

The reconstructed microstructure in the encoded space obtained from the previous step is essentially an $N\times M\times 3$ matrix with each entry ranging from 0 to 255. To generate a microstructure image that is compatible to further numerical analysis such as Finite Element simulations, it is critical to convert the $N\times M\times 3$ image back to the $N\times M$ image with each pixel appropriately labelled with material phases. In other words, for each location in the microstructure, its current
representation of 3-vector needs to be replaced by a scalar label that indicates material phase. Since the reconstruction in the encoded space obtained by L-BFGS-B or Adam optimization is a local minimum, there is no guarantee that the 3-vectors of the reconstructed pixels are still exactly at the coordinates we sampled in the encoding step. Nevertheless, it is observed that 3-vectors of pixels for the same material phase are still clustered. Hence, we apply an unsupervised learning approach (K-means clustering) to separate the reconstructed pixels into K groups, where K is the number of material phases counted in the encoding process.

It should be noted that K-means clustering does not enforce the ratio of pixels’ partition for each material phase, so it is possible that the volume fraction of each cluster is slightly different from that of the original microstructure. Considering that volume fraction (VF) is a key feature for material systems, such as polymer composites or carbonates, the last step of the algorithm is to compensate the discrepancy of VF between the original and the reconstructed microstructures by switching pixels’ phase label on the boundary. Herein we utilize a stochastic optimization approach, simulated annealing (SA), to match the phase VFs with those in the original microstructure.

5.2.3 Results

A dataset of microstructure images obtained by state-of-the-art microstructure imaging techniques, covering carbonate, polymer composites, sandstone, ceramics, a block copolymer, a metallic alloy and 3-phase rubber composites (the 1st row in Figure 5-2) has been collected for demonstration and validation of the proposed MCR approach. Given the great variety of microstructural morphologies, this dataset provides a comprehensive test-base for comparing our proposed approach to other MCR approaches. Among all test samples, special attention is given
to two challenging systems – 2-phase block copolymer and 3-phase rubber composites. The block copolymer sample has a fingerprint-shaped microstructure, in which anisotropy is observed locally whereas isotropy holds globally. In contrast, the rubber composite sample has higher local isotropy, yet its three-phase nature is difficult to capture using any prior approach.

The quality of microstructure reconstruction is assessed both quantitatively based on numerical metrics and qualitatively through visual inspection. As the two-point correlation function is the most commonly used statistical function to evaluate microstructure reconstructions[15, 36], we adopt it as one of the quantitative evaluation metrics in the present work. However, per Torquato [213], the two-point correlation function itself is not sufficient in evaluating the statistical equivalence of microstructures. In this work, the lineal-path correlation function[62] is used as an additional metric to quantify the statistical similarity between the original and reconstructed microstructures [36]. Since most statistical functions are reduced representations of microstructures, they cannot reveal the microstructure characteristics completely. To this end, visual inspection was also conducted as a complementary validation to the numerical comparisons.
Figure 5-2 The comparison of the original microstructures and their corresponding reconstructions using different approaches. The proposed transfer learning approach reconstructions are presented in the second row, highlighted in red. N/As represent the cases where the microstructure in that column cannot be reconstructed by the approach specified for that row.

As depicted in Figure 5-2, in addition to the proposed transfer learning-based approach (Row 2), four existing MCR approaches (i.e., decision tree-based synthesis[36], Gaussian Random Field[35, 137, 147], two point correlation[186, 214], and physical descriptor[15]) are applied to each of the microstructures in the collected data, except for the three-phase rubber composite sample in the last column since none of the commonly used approaches can process the multi-
phase microstructure of the rubber composite (three materials phases). The discrepancy between the correlation functions of the original microstructure and those from reconstructions is measured by

\[ \varepsilon = \frac{s_1}{s_2} \times 100\% \]  

where \( s_1 \) is the area between the two correlation functions and \( s_2 \) is the area under the correlation function of the original microstructure. The error rates of the reconstruction for each method in each material sample are illustrated in Table 5-1 and Table 5-2. It should be noted that in the copolymer and ceramic samples, the white material phase is almost all connected, and thus it is inappropriate to apply the physical-descriptor based approach. In addition, for the alloy material system (Fig. 2, column 6), the proposed approach is significantly better than other microstructure reconstruction approaches in generating visually satisfactory reconstructions. Since visual similarity between the original and reconstructed microstructures is a necessary qualitative criterion to validate the equivalence of microstructures, we do not conduct further numerical validation for the alloy material system in the later part of this chapter.

From Table 5-1, we find that the proposed transfer learning based approach for using convolutional deep networks outperforms all other reconstruction approaches in four out of the five material systems being numerically evaluated. For the sandstone sample, the accuracy of reconstruction using the proposed approach is just slightly lower than that of the two-point correlation function based approach. One may expect that the error evaluated using the two-point correlation function should be the smallest when the two-point correlation approach is used for reconstruction because the metric is directly used as an objective. However, the two-point correlation function based reconstruction uses simulated annealing, which yields difficulty in
converging to the global minimum, leading to poorer performance. Moreover, while the reconstructions from the GRF and two-point correlation function based approaches on the copolymer material system achieve a relatively low error rate (0.85% and 1.20%, respectively), those reconstructions are visually different from the original microstructure. This again verifies Torquato’s proposition \cite{213} that two-point correlation only partially reveals the statistical equivalence of the original microstructure and its reconstructions. Finally, the error rates for the polymer composite material system are observed to be higher than those of other systems. For the low-loading polymer nanocomposite material system, the values of $s_2$ in Eqn. (5.8) are lower than those for the other material systems studied in this work. Therefore, a slight difference between the correlation functions ($s_1$) would lead to a significantly larger error rate.

Table 5-1 Error rate (%) of two-point correlation function for reconstructions using different approaches for various material systems (bold font indicates the method with the lowest error rate for each material system). The method presented in this work is highlighted in red.

<table>
<thead>
<tr>
<th>Method</th>
<th>Material</th>
<th>carbonate</th>
<th>ceramics</th>
<th>sandstone</th>
<th>copolymer</th>
<th>Polymer comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transfer Learning</td>
<td></td>
<td>3.91</td>
<td>1.00</td>
<td>1.74</td>
<td>0.78</td>
<td>6.8</td>
</tr>
<tr>
<td>Decision tree</td>
<td></td>
<td>4.76</td>
<td>1.09</td>
<td>8.51</td>
<td>1.62</td>
<td>13.71</td>
</tr>
<tr>
<td>GRF</td>
<td></td>
<td>9.62</td>
<td>2.06</td>
<td>2.58</td>
<td>0.85</td>
<td>30.53</td>
</tr>
<tr>
<td>Two-point correlation</td>
<td></td>
<td>5.16</td>
<td>1.13</td>
<td>1.17</td>
<td>1.20</td>
<td>13.2</td>
</tr>
<tr>
<td>Physical descriptor</td>
<td></td>
<td>6.92</td>
<td>N/A</td>
<td>6.47</td>
<td>N/A</td>
<td>12.51</td>
</tr>
</tbody>
</table>

Table 5-2 illustrates the error rate evaluated using the lineal-path correlation function. Three major findings are summarized from this comparison. 1) The transfer learning-based approach achieves a low error rate (<8%) in all five samples, while the performance of the other four methods varies significantly across different material systems. 2) While the two-point correlation function based approach reaches very low error rates in Table 1, its error rates of the lineal-path function is very large. This result is reasonable since the two-point correlation function based
approach applies pixel-switching in its reconstruction process, but the connectivity in the clusters is not guaranteed. 3) While the transfer learning-based approach demonstrates superiority in terms of generality, the decision-tree based approach is a very competitive also achieves very low error rates in three of the five samples.

Table 5-2 Error rate (%) of lineal-path correlation function for reconstructions using different approaches for distinct material systems (bold fond indicates the lowest error rate, red highlight indicates the proposed method.)

<table>
<thead>
<tr>
<th>Method</th>
<th>Material</th>
<th>carbonate</th>
<th>ceramics</th>
<th>sandstone</th>
<th>copolymer</th>
<th>Polymer comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transfer learning</td>
<td>7.63</td>
<td>1.31</td>
<td>3.61</td>
<td>6.38</td>
<td>3.58</td>
<td></td>
</tr>
<tr>
<td>Decision tree</td>
<td>3.26</td>
<td>1.69</td>
<td>3.10</td>
<td>50.30</td>
<td>14.71</td>
<td></td>
</tr>
<tr>
<td>GRF</td>
<td>59.38</td>
<td>49.28</td>
<td>47.79</td>
<td>27.41</td>
<td>59.58</td>
<td></td>
</tr>
<tr>
<td>Two-point correlation</td>
<td>45.59</td>
<td>37.92</td>
<td>24.19</td>
<td>8.09</td>
<td>30.65</td>
<td></td>
</tr>
<tr>
<td>Physical descriptor</td>
<td>18.08</td>
<td>N/A</td>
<td>28.11</td>
<td>N/A</td>
<td>12.86</td>
<td></td>
</tr>
</tbody>
</table>

While the error rates of the proposed transfer learning-based convolutional network approach and the two-point correlation based approach are very close in a few cases (e.g. copolymer), their reconstructions could significantly differ from visual inspection. This again implies that while lower-order statistical functions can capture lower-order statistical equivalence, high-order metrics are needed to completely assess the statistical equivalence.

Since both the two-point correlation function and lineal-path correlation function are low-order representations of microstructures, they do not fully capture the high-order characteristics of the original and reconstructed microstructures. To this end, we also visually inspected the reconstructions of different material systems (Figure 5-2) and compared our findings to the results in Table 5-1 and Table 5-2. In general, the visual similarity between the original microstructures and the reconstructed ones agrees with the error rates in Table 5-1 and Table 5-2, with the exception of the block copolymer reconstruction using the two-point correlation function based
approach. In this case, the reconstruction achieves 1.20% error rate in the two-point correlation function and 8.09% error rate in the lineal path correlation function. However, the reconstruction looks like a random white noise image by visual inspection. This finding again confirms Torquato’s proposition [213] that low-order statistical functions are not capable of representing the microstructure completely.

In addition to demonstrating the advantages through quantitative comparative studies (Figure 5-2, Table 5-1 and Table 5-2), we demonstrate the versatility of the proposed approach through analyzing complex microstructures, such as those in block copolymer and 3-phase rubber composite samples. As illustrated in Figure 5-3, the original fingerprint-shaped copolymer sample has very different local anisotropy at different locations, whereas the global isotropy holds. The proposed deep convolutional network-based approach can accurately reproduce this characteristic in its reconstruction, while the decision tree-based approach generates a diagonally oriented anisotropic reconstruction.

![Figure 5-3](image)

(a) Original  (b) Deep Convnet  (c) Decision Tree

Figure 5-3 Original microstructure of block copolymer sample and its reconstructions using the proposed deep convolutional network-based approach and decision tree based approach.

Advantages of the proposed approach are also demonstrated in Figure 5-4 by analysis of a rubber composite sample that consists of two rubber phases (Butadiene rubber (BR, white) and
Styrene-Butadiene rubber (SBR, blue) with one filler phase (carbon black (CB, cyan)), at two different carbon black compositions. Given the multiphase nature of this material, the statistical equivalence of the original microstructures (Figure 5-4 (a) & (c)) and their reconstructions (Figure 5-4 (b) & (d)) is evaluated using the two-point correlation function in the one-vs-rest manner: specifically, the three-phase microstructure is first binarized into three binary images (BR vs. the rest, SBR vs. the rest and CB vs. the rest). Then the correlation function is applied to the binary images in order to validate the statistical equivalence. Using this method, the statistical equivalence of the original microstructures and their reconstructions are validated (Table 5-3).

Table 5-3 Error rate (%) of the two-point correlation function for reconstructions on three-phase rubber composite samples in Figure 5-4 using the proposed deep convolutional network-based approach.

<table>
<thead>
<tr>
<th>Image</th>
<th>Composite #1 (Fig 4(a) &amp; (b))</th>
<th>Composite #2 (Fig 4(c) &amp; (d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR-vs-rest</td>
<td>0.77</td>
<td>0.80</td>
</tr>
<tr>
<td>SBR-vs-rest</td>
<td>2.25</td>
<td>1.99</td>
</tr>
<tr>
<td>CB-vs-rest</td>
<td>3.67</td>
<td>5.25</td>
</tr>
</tbody>
</table>

Figure 5-4 Original microstructures of 3-phase rubber composite and their reconstructions using the proposed deep convolutional network-based approach. (a&b) Original and reconstructed microstructures of BR(35.7 wt%)/SBR(35.7 wt%)/CB(28.6 wt%) sample. (c&d) Original and reconstructed microstructures of BR(41.7 wt%)/SBR(41.7 wt%)/CB(16.6 wt%) sample. Color
map: Butadiene rubber (BR, white color), Styrene-Butadiene rubber (SBR, blue color), carbon black (CB, cyan color).

5.3 Numerical pruning and understanding the network model hierarchy

5.3.1 Quantification of model complexity

While it is shown that the proposed approach is capable of reconstructing statistically equivalent microstructures accurately for a wide range of material systems, the application of the proposed approach is potentially limited because of its high computational cost (primarily GPU memory consumption and the number of operations in back-propagation.) In our experiments, the loading of full VGG-19 model consumes 11541MB GPU memory on a Nvidia GeForce Titan Xp graphic card and leads to a significant amount of back-propagation operations. Therefore, in this section, model reduction is studied by eliminating some network layers to increase computation efficiency and viability. Noticing that, different computational platform may have very different computational performance for the same model, in this study, the number of weight parameters is used to measure the model complexity.

The model pruning in this work is achieved by first gradually eliminating high-level layers, followed subsequently by elimination of low-level layers from the transferred deep convolutional network. This sequence in layer removal not only keeps the lower part of the network architecture intact, but also aligns with the understanding of network architectures presented by Yosinski et al.[215] In other words, higher-level layers are likely to be high-level concept discriminators for specific tasks. Thus, their elimination may impact the reconstruction less significantly than the removal of lower-level layers (i.e., the ones close to the image), which are usually interpreted as general local feature extractors similar to Gabor filters[216] or color blobs. In the vanilla version
of the proposed approach, the first convolutional layer and the first four pooling layers are included in the loss function. The inclusion of these five layers essentially requires the loading of the first 12 convolutional layers, which introduce 10,581,696 parameters (not counting the biases). The removal of the highest pooling layer (pooling_4 in VGG-19) of the five layers reduces the number of included convolutional layers to 8, which have 2,324,160 parameters (21.96% of the previous one). Further elimination of the other pooling layers (pooling_3, pooling_2 and pooling_1) would reduce the number of convolutional layers to 4, 2 and 1 respectively, which corresponds to 259,776/38,592/1,728 weight parameters (2.45%, 0.36% and 0.02% of the first one), respectively.

5.3.2 Investigating model hierarchy via inspecting reconstructions

Figure 5-5 illustrates the reconstructions using different selections of layers. From this comparison, we find three important results. 1) The elimination of the highest pooling layer has an insignificant impact on the reconstruction results. This result is expected, as those higher pooling layers are discriminators specifically tuned for the original AI task (i.e. image classification for ImageNet dataset). 2) From the comparison (Figure 5-5 A-3 & A-4, B-3 & B-4), the removal of the third pooling layer results in the loss of long-distance dispersion equivalence. Specifically, in Figure 5-5 (A-4) global variation of local anisotropies is lost, while variation of cluster-cluster distances is decreased in Figure 5-5 (B-4). 3) From the comparison (Figure 5-5 A-4 & A-5, B-4 & B-5), the elimination of the lowest pooling layer leads to significant loss of short-distance (local morphological) equivalence. Our observations further validates our hypothesis that in transferring deep learning models, the highest neural network layers (i.e. layers higher than pooling_3) may be eliminated because they are discriminators for the original ImageNet [69] image classification task but are not useful for microstructure reconstruction. In contrast, network layers lower than
pooling_3 need to be retained to keep dispersive characteristics in the reconstructed microstructure. **Figure 5-5** (C&D) illustrates the reconstruction error rates (Eqn. (5.8)) computed using two-point correlation function and lineal-path correlation function. It is observed that removal of pooling_3 and pooling_2 would not affect the reconstruction accuracy significantly. Noticing that neither of the two correlation functions could fully capture microstructure characteristics, in determining the optimal pruned network architecture, we still retain the layers that are necessary for both visual similarity and statistical equivalence (i.e. layers lower than pooling_3).

![Microstructure reconstructions for copolymer and carbonate using different selections of neural network layers in Gram-matrix matching. (Figure index: A ~ copolymer, B ~ carbonate, 0 ~ original microstructure, 1 ~ 4 lowest pooling layers + lowest convolutional layer,](image_url)

Figure 5-5 Microstructure reconstructions for copolymer and carbonate using different selections of neural network layers in Gram-matrix matching. (Figure index: A ~ copolymer, B ~ carbonate, 0 ~ original microstructure, 1 ~ 4 lowest pooling layers + lowest convolutional layer,
2 ~ three lowest pooling layers + lowest convolutional layer, 3 ~ two lowest pooling layers + lowest convolutional layer, 4 ~ the lowest pooling layer + lowest convolutional layer, 5 ~ lowest convolutional layer only). C. Comparison of the reconstruction errors of each pruned model for copolymer sample using correlation functions. D. Comparison of the reconstruction errors of each pruned model for carbonate sample using correlation functions.

5.3.2 Investigating model hierarchy via receptive fields

In addition to the numerical study illustrated above, the model pruning is also analyzed from the perspective of receptive fields. A receptive field is a significant concept in deep convolutional networks and is defined as the region in the input space that influences a particular convolutional neural network feature. As all the convolutional filters in the VGG-19 model are 3x3 pixels, it is relatively straightforward to compute the receptive fields for each layer (*Table 5-4*). The sizes of the receptive fields could be interpreted as follows: for the lowest convolutional layer (conv_1-1), varying each entry of its output can affect a small region of 3x3 pixels, while altering the output of the pooling_4 layer leads to the influence of a large area of 160x160 pixels (the full microstructures in this work are 256x256 pixels). The sizes of the receptive fields for each layer also reveal their individual roles in controlling the microstructure reconstruction. Specifically, higher-level layers (e.g. pooling_3) control the long-distance dispersion in the microstructure, while lower-level layers (e.g. conv_1-1 and pooling_1) specify local geometries. This again validates our findings in the comparison of reconstructions in *Figure 5-5*. For the two material systems in *Figure 5-5*, a 72x72 pixel window from the microstructure is capable of capturing most of the statistical characteristics; therefore, layers higher than pooling_3 could be eliminated while retaining the quality of the microstructure reconstruction.
Table 5-4 Receptive field for each layer used for computing loss function in the proposed approach

<table>
<thead>
<tr>
<th>Layer</th>
<th>Conv_1-1</th>
<th>Pooling_1</th>
<th>Pooling_2</th>
<th>Pooling_3</th>
<th>Pooling_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Receptive field</td>
<td>3x3</td>
<td>10x10</td>
<td>28x28</td>
<td>72x72</td>
<td>160x160</td>
</tr>
</tbody>
</table>

5.4 Structure-property prediction by leveraging the knowledge of model hierarchy

5.4.1 Transfer learning-based strategy for developing structure-property predictive model

In addition to using deep learning for microstructure reconstruction, a natural extension is to employ the architecture of deep convolutional networks for analyzing structure-property relationships of advanced materials. It has been found by Yosinski et al.[215] and LeCun et al.[195] that transfer learning (i.e. using pre-trained weights to initialize the network) improves the stability and accuracy of the predictive model. Despite these successes, there is no rule to determine how many layers to transfer, thereby introducing subjective choice. Typically, the inclusion of more pre-trained layers increases the flexibility of the network model but increases the associated computational cost and the likelihood of over-fitting. To resolve this issue, the model pruning investigated in the previous section is used to identify the necessary pre-trained layers for describing dispersive characteristics in microstructures and thus provides a guideline for this determination. Specifically, we propose the general rule of determining the number of transferred layers as follows: the remaining layers in the pruned microstructure reconstruction model are regarded as necessary ones to describe microstructure characteristics; therefore, they also need to be adopted in developing structure-property predictive models. In the context of VGG-19 models, all the layers beyond pooling_3 are discarded in pruning and the remaining 8 convolutional layers and 3 pooling layers are utilized to initialize the neural network for structure-property predictions.
5.4.2 Dataset

To justify the validity of the proposed strategy, an additional dataset consisting of structure-property pairs was obtained by generating 5,000 microstructure patterns using the Gaussian Random Field [35](GRF) method (a popular and computationally efficient choice to generate microstructures of optical materials) with a wide range of correlation parameters, followed by subsequent simulation of their light absorption rates at a wavelength of 600nm using Rigorous Coupled Wave Analysis (RCWA). RCWA is a Fourier space-based algorithm that provides the exact solution to Maxwell’s equations for electromagnetic diffraction. While we set the diffraction order in RCWA such that each simulation takes less than 5 minutes to complete, more accurate simulation solutions can be obtained by choosing higher diffraction orders.

5.4.2 Numerical validation

To demonstrate the effectiveness of this approach, a numerical study is conducted to develop a structure-property predictive model for optical microstructural materials. 250 microstructures of size 128x128 pixels are generated using the Gaussian Random Field approach[35], and their corresponding optical absorption properties (a scalar value between 0 and 1) are simulated using Rigorous Couple Wave Analysis [217] (RCWA). This dataset is split into 200 and 50 microstructures for training and testing, respectively. Figure 5-6 shows several examples of the generated microstructures. The architecture of the neural network is constructed using the layers lower than the pooling_3 layer in VGG-19. The output of the pooling_3 layer is flattened, followed by two fully connected layers of size 2048 pixels and 1024 pixels with Rectified Linear Unit (ReLU) and dropout (p=0.5) operations. The weights in the transferred layers are initialized using the pre-trained weights in the VGG-19 model while the remaining ones are initialized randomly.
Two additional experiments are also conducted as control groups: **group 1** – instead of adopting layers lower than pooling_3, we only transfer the ones below pooling_2, and the rest of the settings are kept the same as the proposed approach; **group 2** – layers lower than pooling_4 are adopted, and the same settings for fully connected layers are used. Adam optimizer (learning rate = 0.0005, beta1=0.5, beta2=0.99) is used to fine-tune the parameters. The mini-batch size is set as 50 and the number of epochs is 4,000. For each group, the training is repeated 15 times to investigate accuracy and stability.
Figure 5-6 Examples of the generated microstructures for developing structure-property predictive model.

Figure 5-7 The comparison of the mean-squared-error (MSE) and the mean-absolute-error (MAE) between the proposed approach and two control groups.

**Figure 5-7** shows the results of the proposed approach and two control groups. Comparing to the proposed approach, the control group 1 is observed to be under-fitted (i.e., higher mean error and larger variance of the error), while the control group 2 shows a higher likelihood of overfitting (i.e., more outliers with large associated error). This comparison validates the significance of the
knowledge learned from microstructure reconstruction model pruning, and it also validates the proposed structure-property modeling approach.

5.5 Summary

Microstructure reconstruction and structure-property prediction are two challenging but advantageous tasks in computational materials science. In this work, a transfer learning based approach for reconstructing microstructures is first proposed. A comprehensive comparison of results for multiple materials between the proposed approach and existing approaches is conducted to demonstrate the accuracy and generality of the proposed approach. To reduce the computational cost, the transferred deep convolutional network is pruned, and the understanding of the correspondence between neural network layers and long/short-range dispersions in microstructures are drawn by visual inspection and analyzing the receptive fields. The knowledge learned in model pruning also guides the determination of the pre-trained layers to be transferred in developing structure-property predictive models. In summary, the proposed approach provides an end-to-end – i.e. image-to-image for reconstruction or image-to-property for property prediction – and off-the-shelf solution which generalizes well and requires minimum prior knowledge of material systems.

Despite the advantages demonstrated in this work, the present approach has some potential limitations. For instance, while the Gram-matrix matching ensures the statistical equivalence in stochastic microstructure reconstructions, it is not guaranteed to be applicable in deterministic microstructures such as periodic crystallographic structures. The reconstruction of these deterministic microstructures may be handled by adding customized loss function terms to the proposed approach. In addition, the adoption of pre-trained ImageNet deep convolutional network
implicitly constraints the application of the proposed approach on 2D microstructures. 3D microstructure reconstruction tasks may be solved by extending the proposed transfer learning strategy using existing 3D convolutional network models [218]. From the perspective of deep learning, advanced deep learning models such as ResNet [72] may further improve the results.
Chapter 6 A Deep Adversarial Learning Methodology for Designing Microstructural Material Systems

6.1 Introduction

To date, Computational Materials Design (CMD) has revolutionarily changed the way advanced materials are developed [1, 5, 13, 219-222]. In the plethora of successes in CMD [60, 64, 88, 177, 223-225], microstructure sensitive design [226] has shown its significance in driving the rapid discovery and manufacturing of new materials. In designing material microstructures, the appropriate design representation of microstructures determines its ultimate success. A common practice of selecting microstructural design variables is to choose key microstructure characteristics from existing microstructure characterization and reconstruction techniques (MCR). A comprehensive review of existing MCR techniques is provided by Bostanaband et al. [34]. Together with some recent works using deep learning, the existing techniques are classified into the following categories:

1. Correlation function-based methods [227]
2. Physical descriptor-based methods [15]
3. Gaussian Random Field (GRF)-based methods [228]
4. Markovian Random Field (MRF)-based methods [36]
5. Deep Belief Network-based methods [37]
6. Spectral Density Function (SDF)-based methods [64], and
7. Transfer Learning-based methods [38, 203]

However, not all existing MCR techniques are applicable for materials design. Two major limitations exist: 1) Some MCR methods (methods 3, 4, 5 and 7) are not applicable for material...
microstructural design, because no parameters are available to serve as design variables for generating new microstructure designs. 2) While methods 1, 2 and 6 are applicable for material microstructural design, their efficacy is limited by the potential information loss (i.e. loss of either dispersive or geometrical characteristics) in microstructure representation and/or dimensionality reduction. In microstructure representations, some approximations such as taking radial averages in method 1 & 6 or approximating cluster shapes with ellipses in method 2 could result in the loss of microstructural characteristics. Dimension reduction is often needed in microstructure optimization due to the high-dimensional representation of microstructures. A common practice is to conduct a transformation of microstructure representations (e.g. using Principal Component Analysis (PCA)) and remove some insignificant dimensions. Information loss would also occur in the removal process. For instance, Paulson et al.[229] use spatial correlation function as the microstructure representation, and conduct a PCA transformation. It is shown in their work that removing some principal components could lead to a significant reduction in explained structural variance. Another example is the use of descriptor-based approach. After obtaining the full list of descriptors, a supervised learning-based feature selection step is often used to remove the lower-ranked descriptors [17], wherein some geometric or higher-order dispersive information is lost. It should be noted that the aforementioned dimensionality reduction techniques do not guarantee the capability of generating new microstructural designs using the reduced dimension. For example, while the principal components learned by PCA are capable of identifying new dimensions that are not linearly correlated, it is not clear how to generate a new microstructure by sampling in the learned principal dimensions.

Compared to the existing MCR techniques, generative models are promising alternatives to address the problems in materials design. Instead of identifying characteristics from
microstructures, generative models emphasize the ability of using a low-dimensional latent variables $Z$ to generate high-dimensional data $X$ through a generative mapping $G: Z \rightarrow X$ to approximate the real data probability density $P_{data}(x)$. In other words, the evaluation criteria for generative models is whether it is capable of producing very realistic samples, which are indistinguishable from real samples. The latent variables learned in the generative model can therefore serve as design variables for microstructural design. In addition, generative models are especially powerful for materials design because the approach is model-based and it can rapidly generate new microstructures by changing the values of latent variables, while existing MCR approaches often need tedious optimization for microstructure reconstructions (e.g. Simulated Annealing is used in correlation function-based reconstruction).

In the realm of deep learning, Variational Auto-Encoder (VAE) [230] and Generative Adversarial Networks (GAN) [81] are two major categories of generative models. It is well recognized that VAE suffers from the issue of “maximum likelihood training paradigm” when combined with a conditional independence assumption on the output given the latent variables, and they tend to distribute probability mass diffusely over the data space and generate blurry samples [231]. Despite these theoretical disadvantages, both Cang et al. [232] and Guo et al. [233] developed VAE-based models for representing sandstone material microstructures and topology optimization respectively. However, their generative capability is bottlenecked at images of size 40x40, and it is impossible to scale up because fully-connected layers are involved in their network architecture.

In contrast to VAE, GAN is a better choice to bypass these problems. Different from VAE, GAN identifies the latent variables of data by training a generator-discriminator model pair in adversarial manner. In [234, 235], GAN is used for reconstructing different types of
microstructures, but their applications in computational materials design are unexplored. In this work, as illustrated in Figure 6-1, we apply a fully scalable GAN-based approach to determine the latent variables of a set of microstructures once its dimensionality is pre-specified. The latent variables are then treated as design variables in microstructure optimization. Thereafter, the material property for the latent variables is obtained by propagating the latent variables through the generator in GAN, followed by physical simulations of structure-property or structure-performance relations. Considering that physical simulations are usually computationally costly, we also want to minimize the number of property evaluations. Therefore, we pursue a response surface model-based GP-Hedge Bayesian optimization framework to optimize microstructure with desired material property/performance.

Figure 6-1 The flowchart of the proposed deep adversarial learning methodology

The proposed deep adversarial learning methodology provides an end-to-end solution that offers a low-dimensional and non-linear embedding of microstructures for material microstructural design. Compared with the existing methods which cannot fully capture microstructural characteristics (e.g. two-point correlation function in method 1 and physical descriptors in method 2), the proposed method does not make any geometrical or dispersive approximations and thus there is no information loss. In addition, the non-linear embedding of microstructures in the proposed method avoids the removal of insignificant dimensions of microstructure representations (e.g. physical descriptors in method 2 and principal components in method 1) so that more
microstructural information is preserved. Moreover, the proposed method is also beneficial for materials design because the dimensionality of latent variables can be pre-specified as needed. Meanwhile, since the GAN is implemented by deep neural networks with large model capacity, it is able to capture very complex microstructural characteristics. In addition to the contribution of the proposed approach to materials design, we also demonstrate that the proposed approach is advantageous in: 1) *scalability*: the proposed approach is capable of converting microstructures into reasonable and computationally affordable low-dimensional representations as needed, and the generator in proposed model is scalable to produce arbitrary sized microstructures; 2) *transferability*: the discriminator in the proposed approach could be reused to serve as a pre-trained model to facilitate the development of structure-property predictive models. To the best of the authors’ knowledge, this work is the first that applies adversarial learning in computational design of materials microstructure.

In the remainder of this chapter, we break our presentation of the deep adversarial learning design methodology into five sections. In the first part (Section 6.2 – Design Representation), we present the technical fundamentals of the deep adversarial learning approach, and show how the latent variables of microstructures are learned using the proposed approach. The latent variables are then treated as design variables in the latter sections. In the second part (Section 6.3 – Design Evaluation), we demonstrate how material properties are evaluated from design variables using the proposed model. This demonstration is then followed by Section 6.4 – Design Synthesis, in which Gaussian Process metamodelling is used to create a surrogate response surface between the latent variables and the objective property/performance, and a GP-Hedge Bayesian optimization is applied to optimize the microstructure to achieve the target material property. After that, we elaborate two additional features of the proposed methodology -- scalability which provides
flexibility in taking arbitrary sized input/output, and transferability which makes it possible to utilize the trained weights to build a more accurate structure-property predictive model (Section 6.5). Last but not the least, we draw conclusions and discuss potential directions to further extend this proposed methodology.

6.2 Microstructural Design Representation using Deep Adversarial Learning

In the proposed methodology, the deep adversarial learning approach, specifically Generative Adversarial Network (GAN), is first used to identify a set of latent variables as microstructure design variables based on microstructure images collected for the same material system. In this section, the fundamentals of GAN are first introduced. It is then followed by a presentation of the proposed network architecture and designated loss function. Finally we specify some training details of the proposed deep adversarial learning model.

6.2.1 Fundamentals of Generative Adversarial Network (GAN)

Generative Adversarial Network is a type of deep generative neural network first proposed by Goodfellow et al.[81]. Originated from game theory, the training process of GAN is essentially a two-player competitive game. Specifically, GAN trains a generator network \( G(z; \theta^G) \) that produces samples \( x_G \) from latent variables \( z \) to approximate real samples \( x_{data} \), and a discriminator network \( D(x) \) that distinguishes the generated samples from the real samples. This competitive game would eventually lead to a Nash Equilibrium [236] between the generator \( G \) and the discriminator \( D \). A more vivid analogy of GAN is given by Goodfellow et al. [81]: in this adversary scenario, the generator can be thought of a group of counterfeiters who tries to produce fake currency, while the discriminator is analogous to a team of police, trying to detect the
counterfeit currency from the real money. Competitions in this adversary game would keep pushing both sides to the equilibrium in which the counterfeits are indistinguishable. When the generator is capable of producing realistic samples at the equilibrium, the latent variables $z$ would be naturally taken as the “code” of the data. In the context of proposed generative microstructural design framework, the “code” will serve as the design variables to create new microstructure designs.

Figure 6-2 The architecture of the proposed generative adversarial network

An illustration of GAN is shown in Figure 6-2. The latent variable space is denoted as $Z$ while the microstructure data space is represented by $X$. On the left hand side, to learn the generator distribution $p_g$ that approximates the data distribution, a prior distribution of the latent variables is defined by $Z \sim P_z(z)$. $z$ is then propagated through a deep neural network to create a differentiable mapping $G(z; \theta^{(G)})$ from the latent variable space $Z$ to microstructure data space $X$. On the right hand side, we also define a discriminator network that takes $x$, either generated or real microstructures, and produces a scalar label that indicates if $x$ is from real data. In other words, we train discriminator $D$ to maximize the probability of assigning the correct label to both real (label=1) and generated samples (label=0), while we train generator ($G$) to maximize the number
of occurrences that the labels are incorrectly assigned by $D$. Essentially, $D$ and $G$ plays a two-player minimax game, which can be expressed as the following equation:

$$\min_G \max_D V(D, G) = \mathbb{E}_{x \sim \text{data}(x)} [\log D(x)] + \mathbb{E}_{z \sim p_z(x)} [\log (1 - D(G(z)))]$$ (6.1)

6.2.2 Network architecture

In this work, the architecture of deep convolutional generative adversarial network in [237] is adopted except that we use convolutional layers to replace the fully-connected layers in both generator and discriminator for the sake of scalability (this will be introduced in section 5). The generator and the discriminator have the same number of layers, and the number of the convolutional filters are aligned symmetrically in the generator and the discriminator. In the generator, the last de-convolutional layer is associated with a tanh activation function to produce images with bounded pixel values, while the other de-convolutional layers are attached with batch normalization operations [238] and Rectified Linear Unit (ReLU) activations [239]. In the discriminator, the last convolutional layer has a sigmoid activation function appended to produce probabilities between 0 and 1, while the other convolutional layers are all associated with batch normalization operations [238] and leaky Rectified Linear Unit (Leaky ReLU) activations [240].

Figure 6-2 is a simple demonstration of the proposed architecture with 5 layers in both generator and discriminator. It should be noted that, arbitrary number of layers could be applied in the proposed architecture, as long as the symmetry is kept.

6.2.3 Loss function

While the optimality of GAN model is Nash equilibrium theoretically, in practice, the global optimality or sufficiently good local optimality is not guaranteed [241]. A common example
of failure is the model collapse, in which the generator converges to a state that consistently produces identical samples. Therefore, in order to produce morphologically and statistically equivalent microstructures from the generator, we carefully design the loss function which can be generalized to different applications (Section 6.2.3) and training parameters (Section 6.2.4). Specifically, the total loss consists of three major components: 1) **adversarial loss (aka. GAN loss)** that combinatorially evaluates the performance of generator and discriminator, 2) **Style transfer loss** that imposes morphological constraints to the generated microstructures, and 3) **Model collapse** that prevents the training from collapsing.

**GAN adversarial Loss:** The GAN adversarial loss is essentially the optimization objective in the vanilla version of GAN (Eqn. (6.2)) expressed as

$$L_{GAN} = \mathbb{E}_{x \sim p_{data}(x)}[\log D(x)] + \mathbb{E}_{z \sim p_{z}(z)}[\log (1 - D(G(z)))]$$  \hspace{1cm} (6.2)

Note again that, in the min-max training $\min_{G} \max_{D} L_{GAN}$ essentially wants the generator $G$ to minimize this loss and let $D$ maximizes it. In practice, we follow [241] to alter the loss of $\min(\log(1 - D))$ to $\max(\log(D))$ when optimizing $G$.

**Style Transfer Loss:** This loss essentially imposes morphology constraints to the generated samples. The style transfer loss, namely Gram-matrix loss, is originated from a work by Gatys et al. [206] for the purpose of texture synthesis. In the field of material science, Cang et al. [232] included the style transfer loss into the total loss function as a penalty term when training a Variational Auto-Encoder network. In our early work, Li et al. [38] takes the style transfer loss as an optimization objective and uses its gradients with respect to each entry in the microstructure image to reconstruct statistically equivalent microstructures. They also discover an interesting intrinsic relationship between the layers included in the calculation of style transfer loss and the reconstructed microstructure: higher level convolutional layers could be dropped to reduce the
computational cost while preserving the reconstruction accuracy. Recognizing this intrinsic relationship, in this work, we only retain the first four lowest convolutional layers in the VGG-16 model [242] and compute their Gram-matrix as the style representations. The style transfer loss [206] can be expressed as

\[ L_{\text{style}} = \sum_{l} \sum_{i,j} \frac{1}{4N_l^2M_l^2} (G^l_{ij} - A^l_{ij})^2 \quad (l = 1,2,3,4) \tag{6.3} \]

which measures the distance between style representations of generated images and real images.

In Eqn. (6.3), \( N_l \) and \( M_l \) are number of feature maps and size of each feature map (i.e. height x width) of the \( l \)-th convolutional layer. \( G^l \) and \( A^l \) are the Gram-matrix of generated images and real images, respectively. The formula of Gram-matrix is

\[ G^l_{ij} = \sum_k F^l_{ik} F^l_{jk} \tag{6.4} \]

which calculates the inner product between the \( i \)-th and \( j \)-th vectorized feature maps of the \( l \)-th convolutional layer.

**Model Collapse Loss**: Model collapse is a common problem of training a GAN model where the generated samples are clustered in only one or few modes of \( p_{\text{data}}(x) \). Thus, model collapse loss [243]

\[ L_{\text{collapse}} = \frac{1}{n(n-1)} \sum_{l} \sum_{j \neq l} \left( SS_j^T S_j \right)^2 \tag{6.5} \]

is introduced to prevent the training from getting into collapse mode. In this equation, \( n \) denotes the number of samples in a batch and \( S \) represents a batch of sample representations from outputs.
of the first four convolutional layers of VGG-16 model [242]. In other words, $S$ is the concatenated vectorized feature maps of the first four convolutional layers of VGG-16 model.

**The total loss**: The total loss is a weighted combination of the three aforementioned losses.

$$L(G, D) = L_{GAN} + \alpha L_{style} + \beta L_{collapse}$$  \hspace{1cm} (6.6)

$\alpha$ and $\beta$ are the moderating weights that prevent the style transfer loss and model collapse loss from diminishing to zero or overwhelming the GAN adversarial loss. The composition of loss functions and the information flow in the proposed neural network architecture is depicted in **Figure 6-3**.

**Figure 6-3** The composition of loss function and information flow in the proposed architecture.

6.2.4 Numerical Validation of Latent Variables

We apply the proposed deep adversarial learning approach to determine the latent variables for a dataset of material microstructures.
**Training data:** To train the proposed GAN model, a dataset of material microstructure images that covers a variety of microstructural dispersions are required. In addition, it is also required that all the training microstructure images share the same size. In this work, to validate the proposed approach, 5,000 synthetic microstructure images of size $128\times128$ are created using Gaussian Random Field (GRF) method [35]. In order to reasonably cover the vast space of compositional and dispersive patterns that correspond to different processing conditions for the same material system, three parameters (mean, standard deviation and volume fraction) are carefully controlled in the GRF model to produce microstructures with different dispersive status but sharing similar underlying characteristics of morphology. Figure 6-4 row 1 demonstrates some examples of the training microstructures. 5,000 of these samples are used for training the GAN model. While 5,000 seems to be an unrealistic number in material data gathering, we note that multiple images can be cropped from one microstructure image in practice. For example, for $1,000\times1,000$ sized microstructure images, thousands of $128\times128$ samples can be cropped with partial overlapping of the samples.
Figure 6-4 Examples of original (training) microstructures and microstructures produced by the generator.

**Network architecture specifications and training parameters:** One advantage of the proposed methodology is the flexibility in assigning the dimension of latent variables. The generator network is essentially a mapping between latent variables and microstructure images, so the neural network architecture depends on both the dimensionality of latent variables pre-specified and the size of microstructure images. Typically, lower dimensionality is desired for latent variables from the microstructural design perspective, because smaller number of design variables helps to reduce the computational cost in microstructure optimization. However, smaller dimensionality of latent variables will increase the depth of neural network or increase the stride parameter in the convolutional layers, which makes the training of GAN more difficult. Therefore, a trade-off between the latent variables’ dimensionality and the training difficulty needs to be considered. After several experiments, it is discovered that the 5-layer architecture with stride $2\times2$ as illustrated in Figure 6-2 is practically easy to stabilize and converge while providing sufficiently low dimensionality for the latent variables. The $2\times2$ stride configuration essentially results in a scaling factor of 2 on each dimension in each layer, thus 5 stacked layers would scale down the microstructures by a factor of 32 (i.e. $2^5$) on each dimension. For the aforementioned dataset, the
128×128 images are converted to a 4×4 latent variable tensor, which is flattened to a 16-dimensional latent variable vector $z$.

In addition to the dimensionality of $z$, a bounded latent variable space is defined by setting each entry of $z$ to be independent and uniformly distributed between -1 and 1. For generator network, four (de-convolutional)-batch normalization-ReLU layers are appended to $z$ sequentially, which is then followed by a (de-convolutional)-tanh layer to produce 128×128×1 sized microstructure images. In contrast, the discriminator network is composed by four sequentially connected convolution-batch normalization-leaky ReLU layers. A convolutional-sigmoid layer is appended to the end of the discriminator network to produce a scalar valued between 0 and 1 to represent the probability of classifying if the image given to the discriminator is from real microstructure dataset (instead of artificially generated ones). A detailed specification of the dimensionality in each layer is illustrated in Table 6-1. Note that to achieve the specified dimensionality, in both de-convolutional and convolutional layers, the filter size is set as 4×4 and strides are all 2×2 (The only exception is that we use 8×8 filter with stride 1×1 between discriminator layer 4 and 5).

Table 6-1 The dimensionality of each layers in the proposed network architecture (bs. is the abbreviation of batch size)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random Tensor $z$</td>
<td>$bs.\times 4\times 4 \times 1$</td>
</tr>
<tr>
<td>Generator Layer 1</td>
<td>$bs.\times 8\times 8 \times 128$</td>
</tr>
<tr>
<td>Generator Layer 2</td>
<td>$bs.\times 16\times 16 \times 64$</td>
</tr>
<tr>
<td>Generator Layer 3</td>
<td>$bs.\times 32\times 32 \times 32$</td>
</tr>
<tr>
<td>Generator Layer 4</td>
<td>$bs.\times 64\times 64 \times 16$</td>
</tr>
<tr>
<td>Image X</td>
<td>$bs.\times 128\times 128 \times 1$</td>
</tr>
<tr>
<td>Discriminator Layer 1</td>
<td>$bs.\times 64\times 64 \times 16$</td>
</tr>
<tr>
<td>Discriminator Layer 2</td>
<td>$bs.\times 32\times 32 \times 32$</td>
</tr>
<tr>
<td>Discriminator Layer 3</td>
<td>$bs.\times 16\times 16 \times 64$</td>
</tr>
<tr>
<td>Discriminator Layer 4</td>
<td>$bs.\times 8\times 8 \times 128$</td>
</tr>
</tbody>
</table>
Discriminator Layer 5
\[ \begin{array}{c|c}
\text{bs.} & 1 \times 1 \times 1 \\
\end{array} \]

The \( \alpha \) and \( \beta \) parameters discussed in Section 6.2.3 are set as 0.03 and 0.03 for optimal balance between the three components of losses, respectively. Adam optimizer [209] is applied in training by setting the learning rate as 0.0005, \( \beta_1 \) value as 0.5 and \( \beta_2 \) value as 0.99. In the alternating training of the generator \( G \) and the discriminator \( D \), it is found that it is optimal to set the ratio of network optimization for discriminator and generator to 3:1 (i.e. update discriminator three times and then update generator once) to achieve stability and convergence.

Some other significant training parameters include: number of epochs -- 15,000; batch size -- 30 and the \( \alpha \) parameter in leaky ReLU -- 0.2.

**Validation of the latent variables** The validity of the latent variables and the amount of information loss are evaluated by comparing the original microstructure set and a set of microstructures produced by randomly sampling latent variables \( z \) and propagating through the generator network. Specifically, we compare the two-point correlation functions [34, 227] and lineal-path correlation functions [62] of the 5,000 original microstructures and 5,000 generated ones produced by the generative model trained in GAN. Figure 6-4 shows that the generator in GAN is capable of producing visually similar microstructures as the original image data used for training. Figure 6-5 shows the two-point and lineal-path correlation functions of original microstructures and microstructures generated by the proposed generator. Figure 6-5 (a) & (b) show that the mean correlation functions of the 5,000 training samples matches those of the 5,000 generated ones. In addition, the two-point correlation functions’ envelop of the generated samples overlaps with all possible regions that the original data covers and its slightly broadened envelop suggests that the proposed model might be capable of extrapolating the range of microstructures.
(by exploring more possibilities of the microstructures) while retaining the morphological characteristics of the collected samples.

![Image](image_url)

Figure 6-5 Comparison of two-point correlation functions and lineal-path correlation functions of original microstructures and microstructures generated by proposed generator

### 6.3 Microstructure Design Evaluation

In the context of materials design, design evaluation is the process of evaluating the material properties of interest for a generated microstructure controlled by the design variables. In the proposed methodology, it includes two steps: 1) Latent variables (design variables) to microstructures: the GAN generator learned in the deep adversarial learning is used to propagate the values of latent variables to obtain microstructure images. 2) Microstructure to material property: For a generated microstructure, physics-based simulation is used to obtain the corresponding material property or structure performance. For the case study in this work, the Rigorous Coupled Wave Analysis (RCWA) [64] is used to simulate the optical absorption performance of the given microstructure. RCWA is a Fourier-domain-based algorithm that can solve the scattering problems for both periodic and aperiodic structures. Detailed mathematical formulations of RCWA could be found in [244, 245].
6.4 Microstructure Design Synthesis

Each entry of the latent variables vector $z$ identified by GAN is independent and bounded in $[-1, 1]$. They serve as the microstructure design variables in design synthesis which is accomplished through simulation-based optimization. Since the structure-property or structure-performance evaluation is often computationally expensive, a Bayesian optimization approach is applied to search for the optimal microstructure with desired material behavior through sequential adaptive sampling. The design optimization problem is formulated as

$$z = \arg\min_z - f(G(z))$$
$$s.t. \quad z_i \in [-1, 1]$$

(6.7)

where $G(\cdot)$ is the generator mapping in GAN, and $f(\cdot)$ is the physical simulation. After obtaining the optimal value of $z$, the optimal microstructure can be generated rapidly by generator $G(z)$.

In the remaining part of this section, we illustrate the use of response surface-based Bayesian optimization through a materials design case study. The 2D metamaterial structures being explored have similar morphological characteristics as the ones used in Section 2 (Figure 6-4), but a smaller size of 96x96 pixels. The design objective is to obtain the microstructure that maximizes the optical absorption simulated by RCWA, a desirable performance in applications such as solar cell design. The learned model in Section 6.2 is applied in this case study, and the dimensionality scaling factor is still $\times 32$ in each dimension. In other words, the 96x96 microstructure images would be represented by 3x3 dimensional tensor (i.e. 9-dimensional vector).
6.4.1 Exploration of Design Variable Space using Design of Experiments (DoE)

To create the response surface model between the design variables and the objective material property, a set of design of experiments (DOE) are sampled. In this work, Latin Hyper-cube Sampling (LHS) [211] is applied to sample 250 points in the 9-dimensional space. Then the material optical performance for these designs, denoted as $y$, is obtained by following the design evaluation process described in Section 6.3. The dataset of 250 samples $(z, y)$ are used to create the initial response surface model for Bayesian optimization.

6.4.2 Gaussian Process Metamodeling and GP-Hedge Bayesian Optimization

After the initial sampling using LHS, metamodel-based Bayesian optimization is conducted to iteratively explore the potentially optimal design point. Compared to stochastic optimization approaches such as Genetic Algorithm (GA) and Simulated Annealing (SA), Bayesian optimization is a much more efficient global optimization technique as it encourages both exploration and exploitation in the optimization search process. In each optimization iteration, we fit a metamodel (aka. surrogate model or response surface model) using Gaussian Process metamodeling [246] to statistically approximate the relationship between design variables and the design performance. The dataset $(z, y)$ is expanded by one more sampling point in each iteration using the GP-Hedge criteria [247]. Figure 6-6 illustrates how Gaussian Process metamodeling and the GP-Hedge optimization strategy are integrated in this work.
Gaussian Process model [246], also known as Kriging model, is a statistical model that interpolates the observations and supplies uncertainty for the metamodel prediction at each estimation point. In essence, Gaussian Process models the data points \( \{ \mathbf{X}, \mathbf{y} \} \) and the estimations \( \{ \mathbf{X}', \mathbf{y}' \} \) using

\[
\begin{bmatrix} \mathbf{y} \\ \mathbf{y}' \end{bmatrix} \sim \mathcal{N} \left( 0, \begin{bmatrix} \text{Cov}(\mathbf{X}, \mathbf{X}) & \text{Cov}(\mathbf{X}, \mathbf{X}') \\ \text{Cov}(\mathbf{X}', \mathbf{X}) & \text{Cov}(\mathbf{X}', \mathbf{X}') \end{bmatrix} \right)
\]

(6.8)

where \( \text{Cov}(\mathbf{A}, \mathbf{B}) \) represents that covariance matrix between \( \mathbf{A} \) and \( \mathbf{B} \), defined by \( \text{Cov}(\mathbf{A}, \mathbf{B}) = \mathbb{E}(\mathbf{A}\mathbf{B}^T) - \mathbb{E}(\mathbf{A})\mathbb{E}(\mathbf{B}^T) \). Conditioning on the data \( D = \{ \mathbf{X}, \mathbf{y} \} \), the posterior \( P(\mathbf{y}'|\mathbf{X}, \mathbf{X}', \mathbf{y}) \) yields a Gaussian distribution in which,

\[
\begin{align*}
\mu &= \text{Cov}(\mathbf{X}, \mathbf{X}')\text{Cov}(\mathbf{X}, \mathbf{X}')^{-1}\mathbf{y} \\
\Sigma &= \text{Cov}(\mathbf{X}', \mathbf{X}') - \text{Cov}(\mathbf{X}, \mathbf{X}')\text{Cov}(\mathbf{X}, \mathbf{X}')^{-1}\text{Cov}(\mathbf{X}', \mathbf{X})
\end{align*}
\]

(6.9)

Gaussian Process metamodeling essentially gives a surrogate model that quantifies the statistical mean estimations and uncertainties at the unexplored design points. By using the mean
estimations and the uncertainties, a smaller set of design points that could potentially improve the performance can be identified. In this case, expensive design evaluations only need to be conducted on these candidate design points, thereby eliminating redundant design evaluations. As a consequence, the overall computational cost of the design process is reduced tremendously.

In each iteration of the Bayesian optimization, the Gaussian Process metamodel is applied to determine the next sampling point. Typical criterion (aka. acquisition functions) to locate the next sampling point include expected improvement (EI) [248], probability of improvement (PI) [249] and lower confidence bound (LCB) [250]. These criterion are different in how the trade-off is made between exploration (picking samples at locations with large uncertainty) and exploitation (choosing samples at locations close to the optimum based on the mean prediction). In this work, we apply the GP-Hedge mechanism to probabilistically choose one of the above three acquisition functions at every optimization iteration. The general procedure of GP-Hedge Bayesian optimization is illustrated in Algorithm 1.

<table>
<thead>
<tr>
<th>Algorithm 1 GP-Hedge Bayesian Optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: Select parameter $\eta \in \mathbb{R}^+$</td>
</tr>
<tr>
<td>2: Set the gains for acquisition function $i$, $g^i_0 = 0$ for $i = 1, 2, ..., N$</td>
</tr>
<tr>
<td>3: $t = 0$</td>
</tr>
<tr>
<td>4: while stopping criteria is not met do</td>
</tr>
<tr>
<td>5: $t = t + 1$</td>
</tr>
<tr>
<td>6: Each acquisition function propose a point $x_t^i$</td>
</tr>
<tr>
<td>7: Set $x_t = x_t^i$ with softmax probability $p_t^i = \exp(\eta g^i_{t-1}) / \sum_{i=1}^{K} \exp(\eta g^i_{t-1})$</td>
</tr>
<tr>
<td>8: Obtain the objective function value $y_t = f(x_t)$</td>
</tr>
<tr>
<td>9: Augment data $D_{1:t} = {D_{1:t-1}, (x_t, y_t)}$</td>
</tr>
<tr>
<td>10: Receive rewards $r_t^i = \mu(x_t^i)$ from the updated GP</td>
</tr>
<tr>
<td>11: Update gains $g_t^i = g_{t-1}^i + r_t^i$</td>
</tr>
<tr>
<td>12: end while</td>
</tr>
</tbody>
</table>

This GP-Hedge Bayesian optimization process is applied to our design case study beginning with the metamodel created using the 250 initial LHS samples, followed by 120 iterations of
optimization. Throughout the optimization process, the values of the latent (design) variables are constrained between [-1, 1] to retain the morphological characteristics learned from the sample images.

Figure 6-7 The microstructure optimization history and microstructure designs indicated at a few iterations

Figure 6-8 The comparison of the optical absorption property between 1) 30 randomly sampled microstructures from training dataset, 2) 30 microstructures generated by the trained generator, and 3) optimal design
Figure 6-7 shows the optimization history with microstructure design solution indicated at a few iterations. A few observations can be made: 1) Design performance is improved significantly at the very beginning of the Bayesian optimization, while the improvement becomes less as the number of iterations increases. 2) Design performance is not necessarily improved in the new iteration. This is reasonable because the new sampling point is chosen for both exploration and exploitation using the criterion that combines both the mean estimation and the uncertainty in the metamodel.

Figure 6-8 illustrates the comparison between the optical performance of three datasets: a) 30 randomly sampled microstructures from training set, b) 30 microstructures generated by randomly sampling latent variables $z$ and propagating through the trained generator, and c) the optimized microstructure. It should be noted that in order to make a fair comparison, we randomly sampled 30 microstructures from training set in each trial for dataset a), and repeated this trial 10 times. It is observed that the results of randomly sampled microstructures have the lowest optical performance and the largest variance. It is found that the mean optical performance of the microstructures produced by the GAN generator (0.6827) is 4.8% ($0.6827/0.6509-1$) greater than that of the randomly sampled microstructures (0.6509), while the optimized microstructure's performance (0.7630) exceeds the mean performance of randomly sampled microstructures by 17.2% ($0.7630/0.6509-1$). It should be noted that the theoretical upper bound of the evaluated optical absorption property is 1.0, so the design solution provided by the proposed approach is reasonably good. These results verify the effectiveness of the proposed design optimization framework.
6.5 Scalability and Transferability

In the previous sections, we have discussed the process of applying the proposed deep adversarial learning model for identifying latent variables of microstructures and conducting microstructural materials design. With the proposed methodology, the dimensionality of latent (design) variables can be prescribed and the information loss is negligible even for complex microstructural geometries. In addition to these advantages, in this section a few additional useful features of the proposed deep adversarial learning model are elaborated.

6.5.1 Scalability of the generator

Benefited from the exclusion of fully-connected layers in the network architecture, the scalability of the generator provides the proposed GAN model the flexibility of taking arbitrary sized inputs (latent variables) and outputs (microstructures). This is a signature of the proposed model because confining the input dimensionality could lead to a low dimensional microstructural design space, and varying the output size can consequentially produce different sized microstructures to serve different analytical purposes (e.g. analysis in Statistical Volume Elements (SVEs) vs. Representative Volume Elements (RVEs)).

Specifically, the scalability is useful in two ways: a) **Flexibility in setting the dimensionality of latent variables.** In the proposed network architecture, adding each additional convolutional layer increases the scaling factor between the generated image and the latent variables by a factor of 4 (×2 on each dimension). Therefore, in the aforementioned design case in Section 4, when the 9216-dimensional (96×96) microstructure is to be converted into 9-dimensional (3×3) latent variables, five network layers are stacked (i.e. \( \frac{96}{3} = 32 = 2^5 \)). In theory, stacking more neural network layers in the proposed model can enlarge the scaling factor, and the accuracy would be
retained as long as the training is well handled. However, adding more layers inevitably increase the difficulty of training the GAN. In other words, while low dimensionality of the latent variables often leads to less microstructure design optimization cost because of less design variables, it increases the GAN training cost because of higher model complexity. Hence a key consideration in choosing the number of latent variables is the trade-off between the optimization cost and the GAN training cost. When the computational resource for design optimization is limited (e.g. physics-based simulations are extremely expensive), it would be better to keep a lower dimensionality of the latent variables though more training time for GANs is needed. In contrast, if the design optimization is not limited by the computational resource, a reasonably higher dimensionality of the latent variables is acceptable so that the burden on training GANs can be reduced. 

b) Generating arbitrary sized microstructures. While the deep learning network is trained by setting the dimension of $z$ as $bs.\times 4\times 4\times 1$, one may modify the dimensionality of latent variables $z$ to control the size of the generated images without retraining the model. Figure 6-9 illustrates the generated images with different sizes using different dimensional settings of $z$. It demonstrates that the proposed generator is capable of generating arbitrary sized microstructures for the material system of interest. An alternative way of controlling the size of microstructures is to include/remove convolutional layers. For instance, 256×256 images could be generated by adding one more layer in both generator and discriminator before training and keep the size of $z$ as $bs.\times 4\times 4\times 1$. However, the deeper the neural network is, the harder the training process would be. Moreover, retraining is required if model's architecture is changed. Hence changing the dimensionality of $z$ is often preferred for this reason.
Figure 6-9 An illustration of microstructures of different sizes generated by the scalable generator

6.5.2 Transferability of the discriminator

In addition to the aforementioned materials design contributions of the proposed approach, we also discover an additional utility of the discriminator in improving structure-property predictions via transfer learning. While the generative capability is usually emphasized [76, 81], the utilization of discriminator is more or less ignored. However, totally discarding the discriminator is wasteful as there is always significant “knowledge” about the data (in the context of this work, microstructures) learned by the discriminator. In this work, we propose to leverage the knowledge learned from the discriminator into the development of machine learning-based structure-property predictions via transfer learning. In training deep networks, Stochastic Gradient Descent (SGD) based algorithms are the typical choices. Since SGD converges to local minimum, its optimized value is very sensitive to the initialization of the network. With transfer learning, instead of
randomly selecting a starting point for the weights of the structure-property predictive network, the weights are initialized using ones obtained in the GAN discriminator trained on the microstructure dataset in Section 6.2, by analogy to [215].

In the context of this work, the discriminator is essentially a binary classifier trained together with the generator to distinguish generated microstructure from real ones. Our objective is to utilize the trained weights in this classifier and transfer them into a structure-property regression model. It should be noted that, in training and testing this regression model, we use additional 250 samples (microstructures and their corresponding properties) exclusive from the 5,000 samples used for training the GAN, and we randomly split them into 200/50 sets for training/testing. There are three primary steps in building the regression model:

1) **Transferring partial architecture and weights:** We borrow the first four convolutional layers of the trained discriminator (their architecture and the corresponding weights) as the basic building blocks.

2) **Appending full-connected layers at the end:** The output of the 4th convolutional layer is flattened and two fully-connected layers of 2048 and 1024 neurons with ReLU activation are appended. Dropout normalization (p=0.5) is applied after each fully connected layer. A fully-connected layer of 1 neuron is added at the end to produce the scalar output of the regressor. The weights of all these additional layers are initialized randomly.

3) **Fine-tuning weights using Adam:** Adam optimizer is applied to fine-tune the weights in some of the layers. As it is well recognized that the early convolutional layers (Convolutional layers 1-3 of the discriminator) usually contains general Gabor-like filters, we freeze these layers’ weights from Adam optimization. The other layers are subject to the Adam optimization (learning rate=0.0005, $\beta_2=0.5$, $\beta_3=0.99$) for 4,000 epochs with batch size of 50.
To demonstrate the advantage of applying this transfer learning strategy for building the structure-property model, we also conduct another training process with exactly the same network architecture but initializing all weights randomly (instead of using pre-trained weights) as a control group. This control group is named “training from scratch” in the remainder of this section. We compute the mean-squared-errors (MSE) and the mean-absolute-errors (MAE) on the 50 reserved testing data with 30 repetitive trials, as shown in Figure 6-10 and Figure 6-11. From these results, it is found that, compared to training from scratch, transfer learning strategy can facilitate the development of structure-property predictive model by improving its accuracy and stability. This finding is consistent with our intuition that prior knowledge learned by the discriminator network could help in building a more accurate predictive model.
Figure 6-10 The comparison of the mean-squared-errors (MSE) for training from scratch and transfer learning

Figure 6-11 The comparison of the mean-absolute-errors (MAE) for training from scratch and transfer learning

6.6 Summary

In this chapter, we proposed a deep adversarial learning methodology for microstructural material design. In the proposed methodology, the dimensionality of latent variables for microstructures are prescribed first. Then a GAN consisting of a generator and a discriminator is trained on a dataset of microstructures being studied. The latent variables are then taken as design
variables in a Bayesian optimization framework to obtain the microstructure with desired material property. Gaussian Process metamodeling is used at each optimization iteration to update the relationship between the design variables and the microstructure performance, and GP-Hedge criterion is used for proposing the next candidate sampling point. The proposed methodology features several contributions: First, the proposed methodology provides an end-to-end solution for microstructural design, which reduces information loss and preserves more microstructural characteristics. Second, this work is to extend the use of GAN to be a part of the design loop. The GP-Hedge Bayesian optimization incorporates Gaussian Process metamodeling to reduce the number of design evaluations and thus decreases the computational cost while improving the design performance. Third, a customized loss function with the proper moderating parameters is presented for generating new microstructural design with similar characteristics. Finally, the deep learning network architecture and the training parameters obtained in this work could be re-used as a starting point for other applications of deep learning in materials science (e.g. transfer learning).

While this work demonstrates the benefits of the proposed methodology, a few technical details can be further examined in future work. First, this work could make a boarder impact on other material microstructures such as ones with very sharp features (e.g. pointy edges), crystalline structures or grain boundary maps, multiphase or continuous phase microstructures. Next, the processing or manufacturing constraints are not considered in the design optimization. In order to take the processing conditions as design variables, the processing-structure-property (PSP) linkage needs to be established. Similar to our earlier work [64, 177, 251], we will study the relationship between latent variables and such processing or manufacturing parameters, including appropriate constraints in the optimization process. Attempts would be also made to associate physical
meanings to the learned latent variables so that materials scientists could explicitly control some characteristics of the optimized microstructure. In addition, the choice of dimensionality of latent variables can be guided through detailed numerical studies to better understand the impact of low dimensionality on network training. Special attention needs to be paid towards the network theory and practice for stabilizing the training process. Other potential directions for improving network modeling include but are not limited to utilizing Wasserstein GAN [241] for solving model collapse problem, introducing ResNet structure [72] for higher learning capability, or investigating visual attention mechanism [252] for better interpretation of the model.
Chapter 7 Contributions and Future Works

7.1 Summary of the contributions

The goal of this dissertation is to develop computational methods, algorithms and design methodologies to accelerate the developments of advanced materials systems with superior material properties. The overall contribution of this dissertation is the completion of the processing-structure-property paradigm using descriptor-based approach by introducing two energy-mediated processing descriptors and presenting a new gradient interphase representation which is also implemented in Finite Element Analysis. The other contributions of this dissertation are the developments of transfer learning-based microstructure reconstruction approach and a deep adversarial learning based design methodology for designing microstructural material systems. It is noteworthy that, to the best knowledge of the author, this is the first work that utilizes deep adversarial learning in the context of designing advanced materials.

Regarding to each individual research tasks presented in Chapter 1, the major contributions of this dissertations are:

1) The development of quantitative processing-structure relationship for polymer nanocomposites: In Chapter 3, a quantitative processing-structure relationship is developed for polymer nanocomposites. This part of the dissertation focuses on the most popular polymer composite processing technique, single screw extrusion and appropriately represent the great number of processing parameters with two energy-mediated processing descriptors. The first processing descriptor is the processing energy. While there are a lot of existing works that simulate the flow in the extruder, a fast-track mathematical approach is taken to bypass the computationally costly simulations to obtain the approximate energy consumption in processing the polymer
nanocomposites through extrusion. The second processing descriptor is inherited from one of our earlier works, namely interface energy descriptor. This descriptor is defined as the adhesive work between the fillers vs. that between filler and matrix and it determines the infiltration of the melt matrix into the particle agglomerates. For quantifying the microstructure characteristics, physical descriptor-based microstructure characterization method is utilized to first obtain the set of physical descriptors to represent the microstructure images. The processing descriptors and the microstructure descriptors are then correlated together to establish a predictive model for each combination of constituents. Finally, a general model with a polymer matrix specific term is then proposed to combine all the previous findings together.

The learned processing-structure relationship extends the former study of structure-property relationship by Xu et al. [16] in which only structure-property relationship is considered. By integrating this work and Xu et al. [16], the processing-structure-property paradigm using descriptor-based approach is completed. In addition, this work also illustrates how the processing energy could contribute to the microstructure dispersion and thus provides a useful guidance for further exploration of processing conditions to produce the optimal microstructures.

2)Finite Element Analysis of gradient interphase for polymer nanocomposites. In Chapter 4, a new gradient interphase representation is presented in the light of the recently available AFM experimental observations. The proposed interphase representation contains two parts, single-body interphase gradient and multi-body interphase compound effect. Single-body interphase gradient illustrates the spatial distribution of local interphase properties created by one single filler aggregate, while compound effect describes the interactions between interphases from different filler aggregates. The functional forms of these two parts of the interphase representations are learned via data mining on the AFM experimental data, and they are applied in the
implementation of the corresponding Finite Element model. Numerical studies illustrate the effects of the interphase representations and the advantages of the proposed interphase representation is shown by comparing with existing uniform interphase modeling approaches.

The contribution of this part of the dissertation is that, it breaks the current barrier that only effective interphase property is considered in modeling the structure-property relationship of polymer nanocomposites. With the available AFM experimental measurements of the local interphase property, this work is the first to quantitatively represent these measurements via functional forms. While this work only focuses on modeling the viscoelastic property of polymer nanocomposite, it could be potentially extended to investigate other intriguing material properties such as dielectric property.

3) A transfer learning-based approach for microstructure reconstruction and structure-property prediction: In Chapter 5, a transfer learning based approach for microstructure reconstruction and structure-property prediction is presented. Different from existing microstructure reconstruction methods which are mostly material system-specific, the proposed approach is applicable for a wide range of material systems with distinct microstructure dispersions. The proposed approach integrates an encoding stage, which converts one-layer phase image into 3-layer representation, a gradient-based microstructure optimization stage, in which reconstructed microstructures are synthesized, and a decoding stage, in which 3-layer reconstructed microstructures are converted back to phase labelled images. By conducting a comprehensive comparison of the reconstruction approaches on a variety of material system, the generality and the accuracy of the proposed approach is demonstrated. In addition, noticing that the transferred network is computationally costly, a model pruning process is conducted to make it computationally cheaper. At the meantime, interpretations about the relationship between the
network hierarchy and microstructure dispersions are learned from the perspective of reconstruction accuracy and receptive fields. The knowledge learned from this model pruning is then leveraged to determine the architecture and initialization conditions in establishing a structure-property prediction model via transfer learning.

This part of the dissertation provides a general off-the-shelf and end-to-end solution for microstructure reconstruction for a wide range of materials systems. Compared to the existing MCR approaches, the presented approach is unprecedentedly capable of capturing the complex microstructure characteristics for very different material systems. Without requiring a huge amount of prior knowledge about the material microstructure, the presented approach could be directly utilized by material scientists and thus would accelerate the process of exploring a new advanced material system. In addition, the interpretations of the network hierarchy would be potentially beneficial for other deep learning-based MCR developments by providing a guidance of model reduction.

4). **Microstructural materials design via deep adversarial learning:** In Chapter 6, a deep adversarial learning based methodology for designing microstructural material systems is presented. In this part of the dissertation, the design representation is first learned via a deep adversarial learning approach, namely Generative Adversarial Network (GAN). This design presentation method is of great advantages because the dimensionality of the representation could be pre-specified while minimizing the information loss of the microstructure characteristics. After learning the design representation, the design evaluation is realized by integration the generator network from GAN and Gaussian Processing metamodeling, which effectively reduce the number of physics-based simulations. At last, the design synthesis is achieved by GP-Hedge Bayesian optimization to explore the optimal microstructure with the desired material property. A numerical
A case study on optical material system is utilized to demonstrate the validity of the proposed design methodology.

This part of the dissertation provides an end-to-end solution that offers a low-dimensional and non-linear embedding of microstructures for material microstructural design. With the presented methodology, the dimensionality of microstructure representation could be prescribed as desired and the presented methodology could effectively quantifying and designing microstructural materials with complex dispersive and geometric characteristics. To the best knowledge of the author, the presented work is the first one that utilizes deep adversarial models in designing microstructural materials. The configuration of the network architecture and training parameters could be also utilized in developing more advanced deep neural networks for other applications in materials science.

7.2 Recommendations of future works

The following research directions are recommended to extend the works presented in this dissertation:

1) Further exploration of processing-structure relationships using larger datasets from materials databases

The quantitative relationship of the processing-structure linkages in this work is developed based on a small database of in-house experimental data. With the limited data, only the effects of screw speed on processing energy descriptor and the effects of surface modification on surface energy descriptor are investigated. Currently, materials databases that are publicly accessible have been established. Examples of these databases are NanoMine, Materials Projects and PolyInfo.
The processing-structure relationship could be further explored if the huge amount of data in these databases could be utilized. It should be also noted that, in order to utilize these data, efforts on developing reasonable and universal data schema and making the data fully-accessible to the public via user-friendly Application Programming Interface (API) have to be accomplished.

2). Extension of the interphase representation on other material properties of polymer nanocomposites

In this dissertation, the proposed gradient interphase representation is utilized to solve the inverse problem of inferring the spatial distribution of viscoelastic properties in polymer nanocomposites. However, due to the limited availability of AFM experimental data, the compound effect is learned on composites with two filler aggregates and then it is generalized for the case of multiple fillers. It is expected that, the availability of a great amount of AFM measurements on composites with different microstructure geometries would lead to a more in-depth understanding of the compound effect and would probably result in more precise mathematical forms of the interphase representations. The improved interphase representation would be utilized not only in solving the inverse property inference problem, but also contribute to the prediction of local properties of polymer nanocomposites.

Moreover, viscoelasticity is the primary focus in the analysis in this dissertation. This is primarily because all the insights drawn in this dissertation are based on AFM technique. Experimental techniques such as EFM which measures other aspects of interphase properties are rapidly being developed. Once these interphase local properties are available, the interphase representation for describing other material properties could be developed by analogy to the study presented in this dissertation.
In addition, limited by the computational cost, the implementation of the proposed interphase representation is limited to 2D Finite Element simulations. It would be very helpful if this representation could be implemented and numerically studied in 3D.

3). **Transfer learning-based microstructure reconstruction for deterministic microstructural material systems**

While it has been shown that the proposed transfer learning-based microstructure reconstruction approach is capable of reconstructing stochastic microstructural material systems, its capability in reconstructing deterministic or periodic microstructures is limited. Noticing that Spectral Density Function (SDF) applied discrete Fourier Transformation to describe the periodic patterns within the microstructures, integrating SDF of the original microstructure into the loss function of the reconstruction would be very helpful to improve the approach for handling deterministic microstructural material systems.

4). **Investigating advanced network architecture and computational method for microstructure reconstruction**

In the proposed transfer learning-based microstructure reconstruction approach, a 19-layer deep convolutional network, namely VGG-19 network is adopted. The inclusion of this 10-layer convolutional network inevitable introduce significant computational costs, even after the model pruning. So far, there have been a lot of advanced deep convolutional network architectures such as inception net [71] or ResNet [72] being utilized to reduce the computational cost. It would be very intriguing to study if these advanced networks could also be utilized for microstructure reconstruction via transfer learning.
In addition, in recent years, Google Research proposes that deep attention model [252] could effectively reduce the computational cost while providing comparably similar performance as regular deep convolutional network. The investigation of deep attention model would be beneficial in developing a computationally cheaper model for microstructure reconstruction.

5). Investigating the effects of training data in the deep adversarial learning design methodology

The proposed deep adversarial learning design methodology utilizes a generative adversarial network trained on 5,000 synthetic images. It would be of great interest to study the effects of training data in the following settings:

a). Less data: it would be very interesting to numerically investigate how the model would perform if the GAN is trained on less data (e.g. 500 images).

b). Data with limited variation: the 5,000 synthetic data in the presented work covers a wide range of microstructure dispersion and it is shown that the design methodology could identify a new microstructure that has better optical property than any of the training data. It would be also interesting to test the model with a data set of microstructure with limited dispersive variations.

c). Transferability of the GAN: Despite the success in the presented work, GAN is generally hard to train. It would be helpful to numerically investigate if transfer learning could be utilized in training GAN. The success of this study could potentially reduce the training time of GAN when dealing with a new material system.

6). Learning physically meaningful latent variables via GAN
In material design, it is always desired that the design variables could be physically meaningful and correlated to some processing parameters. However, the latent variables learned in the proposed deep adversarial learning do not associate well with physical meanings. Therefore, it is of great interest to improve the GAN settings to learn physically meaningful latent variables.

In computer vision field, a variation of GAN, maximum-information GAN (a.k.a. info-GAN) has been developed to extract meaningful latent dimensions from images. Some examples are learning the width of the stoke from MNIST hand-written digits or learning facial characteristics (eyebrows, eye colors or the existence of sunglasses) from database of celebrity faces. In info-GAN, a special loss function, mutual information, is added to the loss function. In the context of microstructural design, it would be very interesting and rewarding to improve the presented GAN work with the new settings in info-GAN. The identified physically meaningful latent variables could be further correlated to processing parameters and make the designed microstructure manufacturable.
REFERENCE


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BOOK CHAPTER

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INVITED TALKS

[1] Li, X., Zhang, Y., Brinson L.C. and Chen W., A Deep Convolutional Network-based Approach for Microstructure Characterization and Reconstruction, MRS 2017 Spring Conference and Exhibition


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