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Valeriy V. Ginzburg  
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# Theory and Modeling of Polymer Nanocomposites

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Editors

# Theory and Modeling of Polymer Nanocomposites

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# Preface

Polymer nanocomposites (PNCs) are multiphase, multicomponent materials in which one or more components come in the form of particulates with the size less than 100 nm in at least one spatial dimension. The particulates (dispersed phase or fillers) can be metal, ceramic, carbon, or even polymer nanocrystals; they could have spherical, cylindrical, platelet, or other shapes; they can possess various chemical, mechanical, optical, or electrical properties. The polymer matrix, in turn, can be thermoplastic or thermoset; the polymer can be partially crystalline, rubbery, or glassy. One example of a PNC is cross-linked styrene-butadiene rubber with nanoscopic silica or carbon black filler particles, along with other additives, included in varying amounts to create car tires with good traction and acceptable rolling resistance and wear properties. Another example is a typical paint, where sub-100-nm pigments can be added to a liquid formulation, which then undergoes the processes of drying and film formation to create a nanocomposite coating seen on the walls of our houses and on the bodies of our vehicles. In these and other cases where PNCs have already found significant use, including in consumer products such as shoe soles, packaging, and membranes, even minor adjustments to the formulation to improve the material properties can have significant practical implications. It is thus important to develop the Formulation→Structure→Property→Performance roadmap, in which both experimental and theoretical/modeling studies are utilized.

Nanocomposite modeling has made significant progress in recent decades, and many excellent reviews highlighting various specific topics have been published in recent years. Yet, with some notable exceptions (such as “Modeling and Prediction of Polymer Nanocomposite Properties,” edited by Vikas Mittal, Wiley, 2012), there have been very few books surveying multiple theoretical methods and analyzing multiple topics under the same cover. Indeed, in order to successfully develop, say, a nanocomposite gas separation membrane, one needs to consider the question of the nanoparticle design (length and density of grafted ligands), their dispersion in the polymer matrix, the processability of the material, and lastly, the gas permeability and selectivity. This design requires multiscale, multiphysics, interdisciplinary modeling that does not come naturally even to the best researchers.

In putting this book together, we hope to stimulate such efforts and highlight some successful examples.

The structure of the book can be described as follows. The first three chapters describe molecular or mesoscale approaches to predict the structure, dispersion, and nanoscale morphologies of nanocomposite materials, given the nanoparticle shape and loading and, in some cases, the length and density of grafted ligands. The next two chapters discuss the dynamics of nanocomposites, concentrating specifically on the behavior of polymer chains at and near the particle surfaces. The remaining six chapters deal with the prediction of mechanical, transport, electrical, and optical properties of nanocomposites, and the implications for product design. We now proceed to describe each chapter more specifically.

In Chap. 1, Arthi Jayaraman discusses the use of the polymer reference interaction site model (PRISM) theory, which is generally applied at the coarse-grained level and includes monomer-scale packing effects along with overall chain and nanoparticle statistical behavior. PRISM requires information about the polymer conformations as an input, and this can be either assumed or calculated self-consistently from molecular simulations as is briefly discussed. A recently developed open-source code pyPRISM is described that allows for easy use of these methods.

In Chap. 2, Valeriy V. Ginzburg describes the application of density functional theory (DFT) to PNCs, which is also generally applied at the coarse-grained level. This approach, based on classical statistical mechanical functionals that calculate the free energy from the density profile, has been particularly useful for describing monomer and nanoparticle packing in confinement or near surfaces. The chapter first details several examples of standard DFT methods, including calculations of the polymer-mediated interactions between polymer-grafted spherical, rod, and plate-shaped particles. The combination of DFT with self-consistent field theory (SCFT) is then discussed. As is made clear by several examples, this is especially attractive to describe nanoparticle behavior in systems with long-range microphase separation such as in block copolymers (where SCFT has found widespread application for systems without nanoparticles).

In Chap. 3, Robert A. Riggleman and co-workers review their newly developed coarse-grained method of simulating nanocomposite morphologies, polymer nanocomposite field theory (PNC-FT). Based on the state-of-the-art polymer field theory, PNC-FT incorporates the nanoparticles via the excluded volume interactions (“cavity functions”) and enables the evaluation of the free energy of various nanoscale structures. The authors discuss the application of their modeling approach to predict the distribution of “hairy” nanospheres in drying polymer films; calculate the effective interactions between nanoparticles with multicomponent ligands; and evaluate the interaction between nanorods in a cylinder-forming block copolymer film. Similar to SCFT-DFT, PNC-FT is now widely used to predict nanocomposite equilibrium structures and morphologies.

In Chap. 4, Argyrios V. Karatrantos and Nigel Clarke describe the dynamics of polymers near the nanofiller surfaces, and specifically the impact of the nanoparticle size and the particle–polymer interaction on the relaxation time, the self-diffusion

coefficient, and the glass transition temperature. They utilize coarse-grained molecular dynamics (CG-MD) to show that the mobility of the polymer chains near a strongly attracting particle surface is severely depressed compared to the bulk polymer; near a weakly attracting or repulsive surface, on the other hand, the mobility seems to be slightly enhanced. Overall, CG-MD provides a very useful insight into the interfacial dynamics of PNCs.

In Chap. 5, Jack F. Douglas, Francis W. Starr, and co-workers attack a very similar problem using a combination of CG-MD and analytical scaling theories. They specifically investigate the relationship between the glass transition temperature shift in nanocomposite materials and the density changes induced by the addition of nanoparticles. The authors discuss the relationship between the mobility gradient scale and the density gradient scale, and also comment on the similarities and differences between nanocomposites and thin films in terms of their glass transition and glassy dynamics.

In Chap. 6, Alexey V. Lyulin and co-workers describe the use of multiscale modeling to predict the transport properties of polyelectrolyte membranes (PEMs). Such membranes are used in fuel cells and batteries. The authors discuss how the addition of nanoparticles (such as graphene oxide or silicon dioxide) can influence the proton conductivity through the membrane by impacting the phase separation between the water-rich and polymer-rich domains, as well as the diffusion coefficient and mobility of water near the particle surfaces. Several relevant simulation techniques, from *ab initio* simulations of electronic structure to classical atomistic molecular dynamics to coarse-grained dynamic density functional theory (DDFT), are employed in this multiscale modeling study.

In Chap. 7, Nitin K. Hansoge and Sinan Keten describe the use of multiscale modeling to predict mechanical properties of matrix-free (or “one-component nanocomposites”) assemblies of “hairy nanoparticles.” They start by discussing the “energy renormalization” procedure to go from atomistic to coarse-grained molecular dynamics. Using CG-MD, they calculate the morphology of the nanocomposite (i.e., the crystalline structure of the rigid nanoparticle cores separated by the soft ligands). They then used CG-MD to calculate mechanical properties (Young’s modulus and toughness) and generate Ashby plots and Pareto fronts to come up with the optimal designs to balance the two properties. Finally, an approach is described whereby the conformational degrees of freedom for the ligands can be integrated out, allowing for computationally inexpensive mesoscale models involving only the particle cores interacting via effective pairwise potential of mean force (PMF).

In Chap. 8, Pavan K. Valavala and Gregory M. Odegard review various approaches to predict mechanical properties of composites and nanocomposites. They start by differentiating between discrete-medium (like MD) and continuous-medium models, and provide an extensive overview of the latter. Within the continuous-medium framework, the authors distinguish between analytical micromechanical theories and computational finite element analysis (FEA), both of which are based on linear elasticity and enable the prediction of linear elastic moduli (Young’s modulus and shear modulus for the case of isotropic



materials). Multiscale modeling is also discussed for those cases where a number of disparate length scales is involved.

In Chap. 9, Valeriy V. Ginzburg and Jian Yang describe theoretical and modeling approaches to the prediction of thermal conductivity (critically important in many applications, including electronics and transportation). Similar to the previous chapter, the authors discuss the use of analytical micromechanical models and FEA. The role of interfacial thermal resistance—often leading to thermal conductivity being significantly lower than expected—is also reviewed.

In Chap. 10, Michael J. A. Hore discusses ways to predict optical and electrical properties of PNCs. Calculating those properties requires solving Maxwell's equations in complex media, at either very high frequencies (optical) or low frequencies (electrical). Optical properties of interest include scattering and absorption cross section, UV–Vis spectra, and plasmonic resonances. As the author shows, the calculation techniques here range from analytical theories (Rayleigh and Mie scattering) to more computationally expensive finite difference, time domain (FDTD) simulations. For the case of electrical properties (static electrical conductivity), the author emphasizes the importance of percolation (infinite clusters of conducting bonds) and simple methods to predict it (resistor network models). The dependence of electrical conductivity on the conducting filler loading, shape, and alignment is also discussed.

Finally, in Chap. 11, Craig Burkhart, L. Catherine Brinson, and co-workers describe the application of both first-principles and data-driven approaches to the design of nanocomposite materials for automotive tires. The material considered is carbon-black (CB)-filled styrene-butadiene rubber (SBR). The authors discuss the importance of experimental characterization (microscopy) to precisely determine the morphology of the CB network in the SBR matrix; once this morphology is determined, it can serve as input into FEA simulations analyzing the viscoelastic behavior of the material. The predicted linear viscoelastic (LVE) response can be then compared to the “optimal” response known to the industry. Given the complexity of the process, one also looks to simplify the search for best compositions by employing machine learning (ML) tools, and the authors highlight their roadmap in this quest.

In summary, PNC material designers seeking to take advantage of many potential options for polymer and nanoparticles, including their chemical types and amounts, length/size, and architecture (e.g., whether and to what extent chains are cross-linked or grafted to the nanoparticle surface), can turn to modeling approaches to understand how PNC component properties lead to desirable overall material behavior. While the chapters of this book, in order, are meant to present a coherent picture of the range of current PNC modeling techniques from small to large scales and from structure to dynamics to specific material properties, each chapter is written to be independent and readable by itself. We hope the reader will take away an understanding of which modeling methods can be effective and how

they can be used, depending on the system and properties of interest, to closely connect synthetically controllable polymer and particle variables to the resulting overall PNC structure and/or dynamics, and allow for rational design of future materials.

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# Chapter 1

## Polymer Reference Interaction Site Model (PRISM) Theory and Molecular Simulation Studies of Polymer Nanocomposites



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**Abstract** This chapter is focused on Polymer Reference Interaction Site Model (PRISM) theory and its use along with molecular simulation techniques for studying polymer nanocomposites (PNCs). In the first section of this chapter, we summarize key experimental and computational studies on PNCs from the literature to show the reader the types of fundamental questions that these studies have tackled. These are the types of questions that one could also use PRISM theory to answer. Then, we describe the basics of PRISM theory with relevant equations and show how PRISM theory is linked to molecular simulations to obtain meaningful results pertaining to PNC structure and thermodynamics. We also bring to the readers' attention the open-source package, *pyPRISM*, developed for both expert and novice computational researchers to easily incorporate PRISM theory into their PNC studies. We then discuss briefly past, present, and potential new directions of PNC studies using PRISM theory and conclude the chapter highlighting some of the limitations of PRISM theory.

### 1.1 Introduction

Polymer nanocomposites (PNCs) are a specific class of macromolecular soft materials that have garnered significant attention in the past two to three decades from researchers around the world. This is evident from the many review articles and perspectives on this topic [1–17]. As the name suggests, a polymer nanocomposite is a mixture of the polymer (matrix) as the majority component and nanoscale additives (fillers) as the minority component. The chemical and physical nature of the fillers and matrix and their relative composition in the PNC is selected based on the eventual

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application of the PNC. There is a broad range of applications where PNCs have been used, such as in automobile parts (e.g., car bumpers, tires) [18], aerospace industry (e.g., components of thermal resistance aircraft body parts) [19], in separations (e.g., membranes for gas transport and absorption) [20], in electronics (e.g., organic/hybrid solar cells) [21], and in biomaterials (e.g., tissue mimics, drug delivery vehicles) [22]. To achieve the desired function or macroscopic property of the PNC needed for these applications, one has to select the components of the PNCs based on their individual properties (e.g., biocompatible matrix and filler when used in biomedical applications, electron donating/accepting matrix and filler in organic/hybrid electronics) as well as on how they interact and spatially organize within the PNC (i.e., structure/morphology). Additionally, the ease during processing (e.g., response to shear, temperature) of the PNC, a critical feature for large-scale manufacturing, is another variable to consider during the material selection process. The non-trivial relationship between the structure/morphology, dynamics, and thermodynamics for a selected filler and matrix at a specific composition within PNCs has motivated exciting research aimed at unraveling the complex interplay between PNC design and its macroscopic behavior. In particular, computational tools (e.g., coarse-grained models, theory, and simulation) have become valuable tools in this quest to both predict PNC behavior for a variety of PNC design parameters as well as to explain less understood experimental observations in PNCs.

This chapter specifically focuses on how Polymer Reference Interaction Site Model (PRISM) theory and molecular simulation methods have been used to tackle questions about PNC *structure and thermodynamics*. To help the reader appreciate the value of these tools, we first review in Sect. 1.2 relevant past experimental, computational, and theoretical work on PNC structure and thermodynamics to describe the types of fundamental questions that researchers working with PNCs tackle and that PRISM theory can be used for. Then, in Sect. 1.3, the details of PRISM theory, the open-source package for readers wishing to use this method, and complementary molecular simulation methods used along with PRISM theory are discussed. In Sects. 1.4 and 1.5, the past, present, and potential new directions for PRISM theory-based studies of PNCs are described along with the key limitations of PRISM theory.

## 1.2 Relevant Past Experimental and Computational Studies on PNCs

Past studies focused on PNCs (see references in review articles [1–13, 15, 17]) have shown that any experimental or computational tool that is used to study PNC structure and morphology should be able to tackle/probe all relevant length scales including the size of the monomer, the polymer chain, the nanoscale (bare or unmodified) particle or filler, and if phase separated, size of the domains of fillers and matrix chains. As the nanoscale dimension of the fillers decreases (e.g., curvature of spherical nanoparticle

increases), the total interfacial area between filler and matrix in the PNC increases, which in turn affects the polymer chain conformation (e.g., radius of gyration) as compared to its (zero-filler or neat polymer) melt-state ideal chain conformation. The chain conformation also alters the *effective* filler-matrix interaction. If one sets aside the polymer and filler chemistry and the resulting enthalpic driving forces from consideration for a moment, they will realize that the effective filler-matrix interaction is purely a function of the entropic driving forces determined by the filler shape and size, the matrix polymer molecular weight and architecture, and their relative volume fractions in the PNC. The effective filler-matrix or filler-filler interactions dictate whether the filler and the polymer matrix remain mixed (i.e., dispersed filler morphology) or demixed (i.e., aggregated filler morphology) within the PNC. If one also takes into consideration the actual chemistries of the (unmodified) filler and matrix polymer(s), the enthalpic driving forces arising from the filler-filler, matrix-matrix, and filler-matrix (direct) interactions will cooperate/compete with entropic driving forces to alter/retain the chain conformations and the effective filler-matrix interactions that lead to dispersed/aggregated filler morphologies.

To go beyond the (limited) design space of PNCs with *unmodified* or *bare* additives and incorporate additional tuning parameters that can alter the energetic and entropic driving forces for the PNC morphology and dynamics, one can functionalize the filler surfaces. The many advances in synthetic schemes in the past two decades have paved the way for controllably engineering functionalized/grafted/tethered nanoparticles at the molecular level with a variety of ligand—surfactants, polymers, proteins, and nucleic acids—at a desired grafting density, dispersity, and with desired chemistries. PNCs comprised of polymer-grafted nanoparticles (PGNs) have garnered much interest within the PNC community, both from computational and experimental researchers. References in review articles [10–13, 15–17] have established the link between the molecular design of PGNs and the macroscale structure of PGNs within a polymer matrix for linear (architecture) graft and matrix polymers. At high grafting density or the brush-limit, if the chemistry of the graft and matrix polymer is the same or similar, the system is driven purely by entropic driving forces. Much focus has been placed on tailoring the PGNs such that the resulting entropic driving forces favor mixing of PGNs and matrix chains. The extent to which the matrix chains mix with and penetrate the grafted layer is termed extent of ‘wetting.’ As wetting increases, the matrix chains and PGNs mix, and the extent of filler dispersion within the PNC increases. The key design rules for tuning entropic driving forces to favor wetting are: (a) use matrix polymers of a smaller molecular weight than that of the graft polymer, with the curvature of the filler particle and the value of grafting density dictating how much smaller the matrix chains need to be compared to the graft chain to achieve wetting; (b) include a high dispersity in molecular masses of the graft polymers so as to include few long graft polymers and many short polymers within the grafted layer; and (c) if grafting density and particle size are fixed, choose graft and matrix polymer chemistries that are less flexible and have higher persistence lengths. If the matrix and graft polymer chemistries are dissimilar, then the Flory-Huggins  $\chi$  parameter between the matrix and graft polymer chemistry together with the other factors that govern the entropic driving forces dictate whether the PGNs and the

matrix will demix or mix at a given temperature. Using a negative  $\chi$  graft–matrix pair, one can improve grafted layer wetting and push the limits of PGN volume fraction that exhibit PNC dispersion. Recent studies [23–25] have shown that the first-order dispersion to aggregation transition is not synonymous with the wetting to dewetting transition; the latter occurs continuously as the PNC transitions from dispersed to aggregated states. For linear graft and matrix polymers, at low grafting density, the filler surface may not be completely shielded by the grafted chains from the matrix chains and then the energetic driving forces based on the direct filler-graft, filler-filler, and filler-matrix interactions along with the entropic driving forces decide the extent of mixing/demixing of the PGNs and the matrix.

Moving away from a traditional definition of PNCs that has a matrix and a filler component mixed together, one could also consider a melt of PGNs in the absence of a matrix making an effectively one-component PNC. These systems are termed ‘matrix-free PGNs’ and have been receiving attention in the past few years (see for example studies in references [20, 26–29]). One advantage of using these matrix-free PGNs is the ease of processing without dealing with the hassles of creating a homogeneously mixed PNC. Second advantage is the regularity of particle spacing in a polymer melt accomplished through the grafted polymer segments extending from the nanoparticle core. This regularity in interparticle spacing can be exploited in applications like optics, photonics, separation of small molecules, etc. In the absence of *free* matrix chains, at high grafting density, the grafted chains create a dense region around the core extended outward. Depending on the molecular weight of the grafted chains and the grafting density, one could observe interpenetration between grafted chains on adjacent particles or isolated ‘soft’-grafted particles arranged in an array. Instead of melts, if one created a dense solution of matrix-free PGNs, one can create porous polymer material that can be used for separations [20, 29, 30]. In a recent study conducted on a *dried* matrix-free PGN solution, upon exposure to a solvent, a combination of small angle x-ray and neutron scattering results showed that the small molecule solvent uniformly distributes around the nanoparticle surface [29]. Going beyond homopolymers as grafts, one could also use block copolymer grafts in such matrix-free PGN melts/dense solutions to achieve matrix-free PNCs with nanoparticles at precise periodicities within microphase-separated block copolymer domains. For example, in a recent experimental study done on poly(styrene-block-(n-butyl acrylate))-grafted silica nanoparticles, the authors found that at higher grafting density, there was better microphase separation of the block copolymers and more uniform filler (core) dispersion in the covalently linked matrix polymer than at lower grafting density with similar polymer chain length and composition [31].

In thin films of PGNs with and without matrix, additional factors including the competing PGN interaction with the free surface, substrate and matrix will affect structure and dynamics. Kim and Green [32], for instance, showed the three regimes of structural organization—PGNs phase separating from the matrix and residing at the free surface and bottom substrate (unstable film is regime I and stable film is regime II) or PGNs being miscible within the film (regime III). They also find that the phase separation in regime I is analogous to thin film of polymer blends (specifically micelles in homopolymers) while the phase separation in regime II is like that seen

in hard spheres in an athermal homopolymer melt. Going beyond homogeneous surfaces, recent experiments on topographically patterned substrate [33] show that the segregation of PGNs can be achieved by varying the relative confinement entropy of grafted versus matrix chains. In studies of matrix-free PGNs adsorbed on a surface, it has been found that increasing the monomer–surface adsorption strength leads to extended polymer chain conformations and adsorption on the surface and adoption of a ‘canopy’ shape. The grafted chains from neighboring ‘canopies’ can interpenetrate at low-moderate graft density and low surface attraction strength. In contrast, at high graft density and/or high surface attraction strengths, the spacing between particles increases and interparticle entanglements reduce. Self-assembly within monolayers of PGNs on surfaces as a function of core–core and core–polymer interactions has also been shown using simulations [34]. These simulations show the relative values of these interactions where one can observe dispersed PGNs, single PGN wide strings of PGNs, stripes of PGNs with width equal to two or three PGNs and clusters of PGNs.

PRISM theory has played an important role in some of the above studies. Before describing these studies in Sect. 1.4, it is useful to first go into the basics of PRISM theory, how it links to simulations and ways one could conduct PRISM theory calculations, in the next section.

## 1.3 PRISM Theory

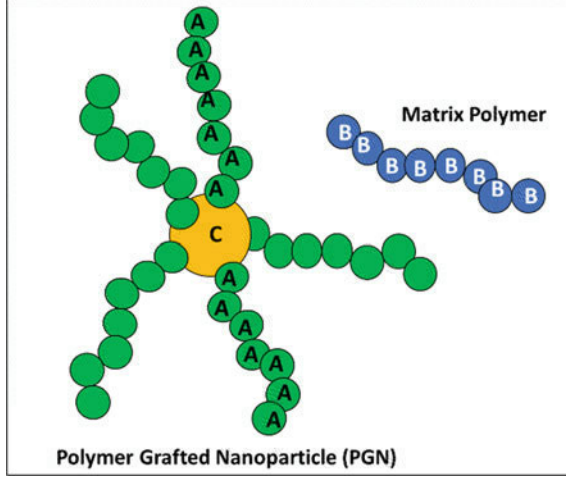
### 1.3.1 Basics

PRISM theory was developed by Schweizer and Curro [35, 36] from the Reference Interaction Site Model (RISM) theory [37–40] to study chain molecules (i.e., polymers). Its formalism is similar to the Ornstein–Zernike integral equation [40, 41] with the total site–site intermolecular pair correlation function,  $h_{ij}(r)$ , being related to the intermolecular direct correlation function,  $c_{ij}(r)$ , and intramolecular pair correlation function,  $\omega_{ij}(r)$ . In Fourier space, PRISM theory takes on the form:

$$\widehat{H}(k) = \widehat{\Omega}(k)\widehat{C}(k)\left[\widehat{\Omega}(k) + \widehat{H}(k)\right] \quad (1.1)$$

where each term is a matrix of size  $N \times N$  for a system that can be modeled with  $N$  types of interaction sites. For example, in a PNC comprised of homopolymer matrix chains of chemistry A with bare nanoscale fillers of chemistry B, if all repeat units along each matrix chain can be treated as equivalent sites of type A and each nanofiller treated as a single site or collection of sites of type B,  $N$  would be equal to 2. If the PNC has PGNs, then the graft polymer site (A), matrix polymer site (B) and particle site (C) make it a 3-site system (see Fig. 1.1), and thus, the matrices would be  $3 \times 3$ . In that 3-site system, the components of the matrices in (1.1) will be:





**Fig. 1.1** Schematic of a polymer-grafted nanoparticle (PGN) and a matrix polymer chain, and the definition of the three possible types of sites A, B, and C. The reader should note that in this figure, for the grafted chains, the tethered end segment, the intermediate segments and the free end segment are treated equally with the same type of site (type A). Similarly, for the matrix chain, the free ends and intermediate segments are treating equally (with type B site). In principle, this could be relaxed by using different types of sites representing various parts of the chains. As the number of sites used to represent/model, the system increases so does the size of the matrices in (1.2a–c) and the corresponding numerical complexity for solving the PRISM equations

$$\widehat{H}(k) = \begin{bmatrix} \rho_{AA}^{pair} \widehat{h}_{AA}(k) & \rho_{AB}^{pair} \widehat{h}_{AB}(k) & \rho_{AC}^{pair} \widehat{h}_{AC}(k) \\ \rho_{BA}^{pair} \widehat{h}_{BA}(k) & \rho_{BB}^{pair} \widehat{h}_{BB}(k) & \rho_{BC}^{pair} \widehat{h}_{BC}(k) \\ \rho_{CA}^{pair} \widehat{h}_{CA}(k) & \rho_{CB}^{pair} \widehat{h}_{CB}(k) & \rho_{CC}^{pair} \widehat{h}_{CC}(k) \end{bmatrix} \quad (1.2a)$$

in which  $\rho_{\alpha\beta}^{pair} = \rho_{\alpha}\rho_{\beta}$  and  $\rho_{\alpha}$  and  $\rho_{\beta}$  correspond to the site number densities of site types  $\alpha$  and  $\beta$ ,

$$\widehat{\Omega}(k) = \begin{bmatrix} \rho_{AA}^{site} \widehat{\omega}_{AA}(k) & \rho_{AB}^{site} \widehat{\omega}_{AB}(k) & \rho_{AC}^{site} \widehat{\omega}_{AC}(k) \\ \rho_{BA}^{site} \widehat{\omega}_{BA}(k) & \rho_{BB}^{site} \widehat{\omega}_{BB}(k) & \rho_{BC}^{site} \widehat{\omega}_{BC}(k) \\ \rho_{CA}^{site} \widehat{\omega}_{CA}(k) & \rho_{CB}^{site} \widehat{\omega}_{CB}(k) & \rho_{CC}^{site} \widehat{\omega}_{CC}(k) \end{bmatrix} \quad (1.2b)$$

where  $\rho_{\alpha\beta}^{site} = (\rho_{\alpha} + \rho_{\beta})$  if  $\alpha \neq \beta$  otherwise  $\rho_{\alpha\beta}^{site} = \rho_{\alpha}$ , and

$$\widehat{C}(k) = \begin{bmatrix} \widehat{c}_{AA}(k) & \widehat{c}_{AB}(k) & \widehat{c}_{AC}(k) \\ \widehat{c}_{BA}(k) & \widehat{c}_{BB}(k) & \widehat{c}_{BC}(k) \\ \widehat{c}_{CA}(k) & \widehat{c}_{CB}(k) & \widehat{c}_{CC}(k) \end{bmatrix} \quad (1.2c)$$

where  $c_{\alpha\beta} = c_{\beta\alpha}$ . The design parameters of the PNC, for example, the filler composition (or volume fraction of filler), grafting density, and graft and/or matrix molecular masses (i.e., chain lengths of the polymer) dictate the  $\rho_i$  of the sites of type  $i$ .

The matrix elements of  $\widehat{\Omega}(k)$  are the intramolecular pair correlation functions in inverse space (or wave vector  $k$ ) between sites  $i$  and  $j$  within a certain molecule; these are known and given as an input to the (1.1). For some systems, these functions can be derived analytically (e.g., ideal chain conformations in a polymer melt). The analytical expression for a Gaussian chain conformation is

$$\widehat{\omega}_{\alpha\beta}(k) = \frac{1 - f^2 - \frac{2f}{n} + \frac{2f^{n+1}}{n}}{(1 - f)^2} \quad (1.3)$$

where  $f$  is defined as  $f = \exp(-k^2\sigma^2/6)$ ,  $n$  is the number of monomers in the Gaussian chain, and  $\sigma$  is the characteristic distance unit [42]. Similarly, (1.3) can be used to model a freely jointed chain (FJC) with  $f = \sin(kl)/kl$ , where  $l$  is the bond length between sites along the chain [42]. For PGNs, analytic expressions for the particle–graft and graft–graft  $\widehat{\omega}_{\alpha\beta}(k)$  have been derived when the number of grafted chains on the surface is small [43–46]. The scattering community has also derived many analytical forms of  $\widehat{\omega}_{\alpha\beta}(k)$  as ‘form factors’ for fitting the scattering data of commonly studied polymer systems. However, in many cases, analytical expressions for  $\widehat{\omega}_{\alpha\beta}(k)$  for the PNC of interest does not exist. Rather than deriving a new analytical expression, one can simulate the PNC and sample configurations of the molecule of interest to calculate the  $\widehat{\omega}_{\alpha\beta}(k)$  (see description in Sect. 1.3.2.1).

The matrix elements of  $\widehat{H}(k)$  and  $\widehat{C}(k)$  are usually unknown and are to be solved for. Given two unknown matrices and one PRISM equation (1.1), we need one more independent equation to solve for the two unknowns. This additional equation is called the closure relation. Closure relations connect the real-space direct pair correlation functions  $c_{ij}(r)$ , total intermolecular pair correlation function  $h_{ij}(r)$ , and pair-wise interaction potentials,  $U_{ij}(r)$ . Since the closures include pair-wise interaction potentials,  $U_{ij}(r)$ , it is through these closures that the chemical details of the PNC are specified. Examples of closures include Percus–Yevick (PY), Hypernetted Chain (HNC), Mean-Spherical Approximation (MSA), Martynov–Sarkisov (MS), and Laria–Wu–Chandler (LWC) [47, 48]. The choice of the type of closure used to solve (1.1) is critical as this choice dictates how realistic or correct the PRISM theory predictions are. We discuss this again in the limitations of this method (Sect. 1.5). Therefore, the right closure must be found or developed for the system being studied. For PNCs, based on agreement between PRISM theory and molecular simulations, for mixtures of nanoparticles and homopolymers, many studies [43–46, 49–54] have used the PY closure for polymer–polymer pair and polymer–particle pair, and the HNC closure for particle–particle pair. If  $\sigma_{ij}$  is the distance of closest approach between sites  $i$  and  $j$ , (e.g.,  $\sigma_{ij} = d$  for monomer–monomer pairs and  $\sigma_{ij} = (D + d)/2$  for particle–monomer pairs, where  $d$  is the size of the monomer site and  $D$  is the size of the particle) the impenetrability condition applies inside the hard core.

$$g_{ij}(r) = 0 \quad r < \sigma_{ij} \quad (1.4a)$$

Outside the hard core, the PY approximation for  $ij$  pair of sites is written as

$$c_{ij}(r) = (1 - e^{\beta U_{ij}(r)})g_{ij}(r) \quad r > \sigma_{ij} \quad (1.4b)$$

and the HNC closure, often used for the particle–particle pair (hence the subscript CC based on type of sites as shown in Fig. 1.1), is described as

$$c_{CC}(r) = h_{CC}(r) - \ln g_{CC}(r) - \beta U_{CC}(r) \quad r > D \quad (1.4c)$$

Past studies by Schweizer and Yethiraj have suggested that molecular closures [47, 55, 56] could prove more accurate for systems with strongly segregating polymers or monomer species (e.g., strongly segregating copolymer matrix polymer or copolymers grafts, or strongly segregating graft and matrix homopolymers). For this statement to be confirmed for the PNC system at hand, one needs to conduct systematic comparisons of results from PRISM theory using atomic and molecular closures against results from experiments and/or molecules simulation results.

After the closures have been selected, one can solve the above system of coupled nonlinear integral (PRISM theory) equation and closure(s). Analytical solutions only exist for atomic systems while numerical solutions are found for complex polymer systems. In principle, one could select any method from existing numerical methods used commonly to solve integral equations [57, 58]. Recent studies have employed the KINSOL algorithm [59] with the line search optimization strategy which minimizes the objective function along an optimum descent direction. KINSOL exhibits convergence for complex nonlinear integral equations easier and faster as compared to the Picard technique, which has also been used in some PRISM theory studies [7, 58]. Irrespective of the numerical algorithm one chooses to use, upon solving the PRISM equation and closure(s), one will obtain the total intermolecular pair correlation functions,  $h_{ij}(r)$ , which can be related to the  $g_{ij}(r)$  ( $=h_{ij}(r) + 1$ ) and the partial collective structure factors,  $S_{ij}(k)$ . The partial structure factors are the elements of the  $\hat{S}(k)$  matrix which are related to the direct pair correlation functions and total pair correlation functions as

$$\hat{S}(k) = \hat{C}(k) + \hat{H}(k) \quad (1.5a)$$

These pair-wise structure factors can be compared to the corresponding pair correlation functions from simulations or scattering results from experiments. By obtaining the  $g_{ij}(r)$ , one can calculate other properties of interest as well. For example, the potential of mean force (PMF) between particles,  $W_{CC}(r)$ , can be calculated, from the particle–particle pair correlation function as follows.

$$W_{CC}(r) = -kT \ln g_{CC}(r) \quad (1.5b)$$

Similarly, the second virial coefficient can be calculated from  $g_{cc}(r)$  for PNCs at infinitely dilute concentrations. The pair-wise structure factors and the intermolecular direct correlation function together also provide an estimate of the induced solvation potential that one component (e.g., PGN) feels because of the other component (e.g., matrix chains); this is described in Sect. 1.3.2.2.

For some PNC design parameters, (e.g., stronger attractive interaction strengths, large site size ratios,  $D/d$ , etc.), the numerical method selected may not yield any solutions. This could be an issue with numerical convergence due to a poor initial guess [57] or due to deviations from liquid-like behavior due to (micro/macro) phase separation within the system. This is discussed further in the limitations described in Sect. 1.5.

### 1.3.2 Linking to Molecular Simulation

PRISM theory calculations can be complemented by molecular simulations in multiple ways and this section describes some of these synergies.

#### 1.3.2.1 Providing Realistic Intramolecular Pair Correlation Function (i.e., Shapes of Molecules)

In many past PRISM theory studies of PNCs (e.g., bare fillers in homopolymer matrix or lightly grafted PGNs in homopolymer matrix) [43–46, 49–54] the intramolecular pair correlation,  $\Omega_{ij}$ , was calculated by assuming *ideal* conformations of the matrix chains. But, assuming ideal chain conformations for the polymer could be far from reality in some systems. For example, the chains on a densely grafted PGN or a copolymer-grafted particle have been shown to adopt non-ideal conformations, and therefore, using ideal conformations for the grafted chains is not valid. Similarly, the grafted chains in chemically dissimilar graft–matrix systems could adopt extended (collapsed) configurations to initiate (deter) formation of energetically favorable (unfavorable) contacts with matrix chains. For such cases where an off-the-shelf analytical expression of the intramolecular pair correlation,  $\Omega_{ij}$ , is not available or existing analytical intramolecular pair correlation functions are not valid, molecular simulations serve as a valuable tool for providing realistic intramolecular pair correlation,  $\Omega_{ij}$ . For example, one can use molecular dynamics simulations or Monte Carlo (MC) simulation techniques (e.g., see review articles on simulations of polymers and PNCs [60–64]) to sample a single homopolymer-grafted nanoparticle in a polymer matrix. These simulations provide the ensemble average graft monomer–graft monomer, graft monomer–particle, matrix monomer–matrix monomer intramolecular pair correlation functions. These correlation functions are calculated using the Debye scattering relation [65, 66]

$$\widehat{\omega}_{\alpha\beta}(k) = \left\langle \frac{1}{N^{\text{total}}} \sum_i^{N_\alpha} \sum_j^{N_\beta} \frac{\sin(k \cdot r_{ij})}{k \cdot r_{ij}} \right\rangle \quad (1.6)$$

in which  $\alpha$  and  $\beta$  represent site types,  $N_\alpha$  is the total number of sites of type  $\alpha$  in each molecule,  $N_\beta$  is the total number of sites of type  $\beta$  in each molecule,  $N^{\text{total}} = (N_\alpha + N_\beta)$  if  $\alpha \neq \beta$  otherwise  $N^{\text{total}} = N_\alpha$ ,  $r_{ij}$  is the distance between sites  $i$  and  $j$ , and the angle brackets represent ensemble averaging over uncorrelated snapshots in a simulation trajectory.

In some cases, to reduce the computational intensity of having to simulate the PGN(s) in a melt-like matrix, one could simulate separately a single matrix polymer chain in vacuum and a single PGN in vacuum to obtain the pair-wise intramolecular correlations. However, these vacuum simulations do not capture the effects of the matrix chains on the grafted polymer configurations or vice versa, and thus, are approximate intramolecular pair correlations.

### 1.3.2.2 Self-consistent PRISM Theory-Simulation Loop

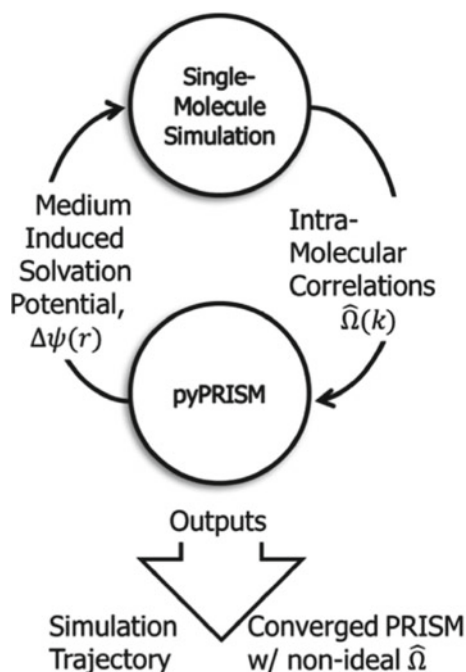
PRISM theory and molecular simulations can also be linked together in a self-consistent loop where the intramolecular pair correlation functions (e.g., chain conformations) that are input to PRISM theory are provided by simulations of a single PGN in an external medium-induced solvation potential that is obtained from PRISM theory. The interdependence of the chain conformations and the medium-induced solvation potential gives rise to the self-consistent loop (Fig. 1.2). The steps involved in this self-consistent loop are described next.

First, the pair-wise decomposed medium-induced solvation potential,  $\Delta\psi_{ij}(r)$ , is obtained from the PRISM theory output. This pair-wise function describes the interaction between any two sites  $i$  and  $j$  as mediated by all the other sites in the system. The form of the solvation potential depends on the approximation used in its derivation [67–72]. The PY and HNC forms of the solvation potential are as follows:

$$\Delta\psi_{ij}^{PY}(r) = -k_B T \ln[1 + c_{ik}(r) * s_{kk'}(r) * c_{k'j}(r)] \quad (1.7a)$$

$$\Delta\psi_{ij}^{HNC}(r) = -k_B T c_{ik}(r) * s_{kk'}(r) * c_{k'j}(r) \quad (1.7b)$$

where ‘\*’ in (1.7a) and (1.7b) denote a convolution integral in spatial coordinates and  $k_B$  is the Boltzmann constant and  $T$  is the temperature. The terms on the right-hand side of (1.7a) and (1.7b) are the real-space pair-wise direct pair correlation function and real-space analog of the structure factors. The solvation potential,  $\Delta\psi_{ij}(r)$ , is then input to a molecular simulation of a single PGN and/or a single matrix chain. In the simulation, the total interaction potential between sites  $i$  and  $j$  separated by a distance  $r$ ,  $U_{ij}^{\text{tot}}(r)$  is defined as the sum of  $U_{ij}(r)$  and the solvation potential,  $\Delta\psi_{ij}(r)$ , obtained from the preceding PRISM step. To ensure the sites in the PRISM theory



**Fig. 1.2** Flowchart of self-consistent PRISM—molecular simulation approach. ‘pyPRISM’ is the open-source package which the reader could use to conduct this calculation. This package is described in Sect. 1.3.3. This figure is reprinted with permission from [58] (2018) American Chemical Society

and molecular simulations represent the same thing, it is best to keep the model chosen to represent the PGN and the matrix polymer to be the same in both PRISM theory and molecular simulations.

Next, the PRISM theory calculation and molecular simulation steps are repeated one after the other. In PNCs with PGNs, one could either alternately simulate a single PGN or a single matrix chain with the newest set of pair-wise solvation potentials from PRISM calculations or simultaneously simulate the single PGN and a single matrix chain (in parallel) with the same set of solvation potentials calculated from the previous PRISM step. Irrespective of the simulation method, the intramolecular structure factors between site pairs are sampled from uncorrelated configurations and the ensemble average of the intramolecular structure factors is calculated to serve as the new input for the following iteration of PRISM theory calculations.

The self-consistent PRISM theory—molecular simulation loop iterations are continued until convergence is achieved. One convergence criterion is the sum of squared errors (*SSE*) of  $\Delta\psi_{ij}(r)$  between iterations  $n$  and  $n + 1$ :