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Perspective: Outstanding theoretical questions in polymer-nanoparticle hybrids

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This topical review discusses the theoretical progress made in the field of polymer nanocomposites, i.e., hybrid materials created by mixing (typically inorganic) nanoparticles (NPs) with organic polymers. It primarily focuses on the outstanding issues in this field and is structured around five separate topics: (i) the synthesis of functionalized nanoparticles; (ii) their phase behavior when mixed with a homopolymer matrix and their assembly into well-defined superstructures; (iii) the role of processing on the structures realized by these hybrid materials and the role of the mobilities of the different constituents; (iv) the role of external fields (electric, magnetic) in the active assembly of the NPs; and (v) the engineering properties that result and the factors that control them. While the most is known about topic (ii), we believe that significant progress needs to be made in the other four topics before the practical promise offered by these materials can be realized. This review delineates the most pressing issues on these topics and poses specific questions that we believe need to be addressed in the immediate future. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4990501]

I. INTRODUCTION

The behavior of mixtures of nanoparticles (NPs) and polymers, termed polymer nanocomposites (PNCs), has been of ongoing interest because these hybrids offer unexpected improvements in properties, well-above that predicted by traditional rules of mixtures. For instance, orders of magnitude enhancements in mechanical strength and conductivity have been reported at extremely low NP loadings. Such studies have recently been expanded to consider more complicated situations involving polymer blends and block copolymers, where multifunctionality, e.g., novel electric, magnetic, and optical properties, has been reported.[1–6]

While there have been significant advances, a number of barriers still confront the full practical realization of such materials. Primary among these, and probably the most widely studied topic in this area, is the ability to control the structure and dispersion state of the polymer-NP mixtures (e.g., Fig. 1).[7–40] The difficulty that arises here is that most (inorganic) NPs are hydrophilic, while polymers are typically hydrophobic. While functional groups can be introduced on the polymer chains to aid in this miscibility, a more popular and generalizable strategy is to functionalize the NP with either small ligand molecules or larger polymeric grafts. In addition to aiding in the miscibility of the mixture,[28,32,34,41–49] interestingly, in some instances, the polymer grafting strategy has been shown to convert the NPs into a new class of amphiphiles. This new functionality allows them to self-assemble into a variety of superstructures reflecting their hydrophilic/hydrophobic balance.[50–68] Other methods to facilitate miscibility are to use processing (e.g., use of solvents, extrusion) to drive these systems into long-lived metastable states with favorable properties[38,69–71] or to push them into far-from quiescent,

but still equilibrium, states under the action of electric/magnetic fields.[72–74]

While many of the theoretical developments are discussed below, we only offer a limited, personal perspective of what is necessarily a very broad field. In particular, we focus our discussion around five questions that need to be answered theoretically:

(i) *Phase diagrams*: The theoretical/simulation works of Schweizer,[46,75–79] Striolo,[60,80–83] Roan,[84,85] Pakula,[86,87] Jayaraman,[24,37,88–95] de Pablo,[96–102] Panagiotopoulos,[50,56,103–105] Grest,[34,42,71,106–114] Riggleman,[97,115–118] Binder,[119–124] Egorov,[81,119–121,125] Theodorou,[126–130] Müller-Plathe,[131–133] Starr and Douglas,[40,54,61,134–138] and Ganesan[22,26,139,140] have opened this field to a broad range of practitioners. However, the full phase diagram even of a canonical mixture of spherical NPs and polymer chains needs to be enunciated. Connecting with associated experiments requires rational and systematic means to study the influence of specific interactions and to account for variations of NP shape and size.

(ii) *Self-assembly of polymer grafted NP*: The role of polydispersity in both particle size distributions as well as the grafting characteristics has to be critically enunciated in the case of polymer grafted NP. Explicitly, how do NP core size distributions, distributions in the number of grafts, and in the isotropy of the grafting process affect their self-assembly behavior?

(iii) *Solvent effects*: What is the role of the casting solvent on the NP dispersion state, and in particular what is its effect on the bound layer that is thought to play a central role in miscibility and therefore end-use properties?
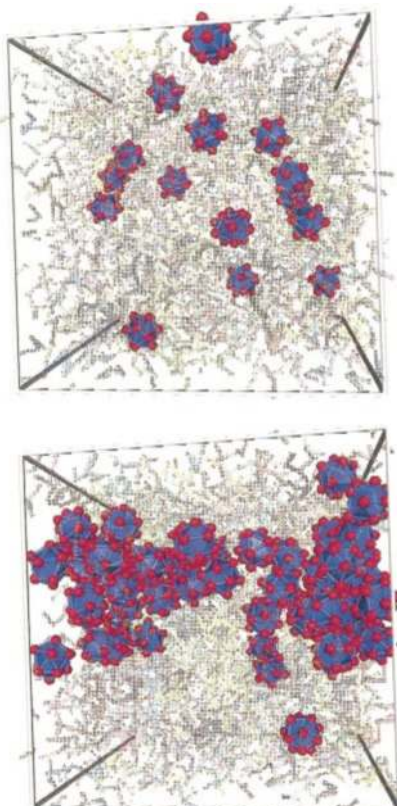
FIG. 1. Clustering of NPs in a polymer melt with increased loading. Reproduced with permission from Starr *et al.*, J. Chem. Phys. **119**(3), 1777–1788 (2003). Copyright 2003 AIP Publishing LLC.

(iv) *External field effects*: How does processing (e.g., extrusion) affect the NP dispersion state? Can we produce morphology-processing maps to help guide experiments? How do potential fields, e.g., magnetic, electric, and chemical fields, modify the dispersion and assembly behavior of the NPs?

(v) *Properties*: While the focus on topics above has been on the structure of the hybrids, their most important consequence is in the properties' space. A critical issue is that the addition of NPs typically improves some properties while worsening others. Thus, while the addition of well-dispersed NP increases the Young's modulus of a glassy polymer, it frequently decreases its toughness. Are there rational means to simultaneously improve all properties, or failing that, are there ways to optimize the NP dispersion state that represents the best compromise? Is this dependent on the specific properties considered or can general rules of thumb be formulated?

Below we describe developments that have already been made in these issues. Subsequently, we focus on critical unanswered questions that need to be addressed.

II. SYNTHESIS OF NANOPARTICLES

Most of the theoretical works and simulations on the miscibility and the self-assembly of NPs make the idealized assumptions of perfect nanoparticle shape (e.g., spheres) and monodisperse size.[40,76–79,135] Further, in the case of NPs

grafted with polymer chains, it is frequently assumed that the number of grafts is specified (i.e., there is no polydispersity in this quantity), and that their grafting sites are uniformly positioned on the NP surface and their lengths are uniform (i.e., monodisperse). Such idealized assumptions, which are rarely representative of experiments, can critically control the emergent behavior. Even in the case of uniform grafting sites, the conformational fluctuations of the small number of polymer chains ensure that the NPs are frequently anisotropically covered by the polymer corona.[141] This fact has been shown to strongly impact the self-assembled NP structures that form. Below, we outline some outstanding issues in this regard.

A. Modeling variations in NP size

While we believe that it would be useful to systematically understand how synthesis protocols affect the NP size (and size distribution), at this stage it is sufficient to understand the consequences of such size distributions on phase behavior (see Sec. III). A highly desirable development would be if progress can be achieved in this step.[24,55]

B. Bound polymer layers and their dependence of particle size and shape

When bare NPs are mixed with a polymer melt, good dispersion typically results when the polymer-NP interaction is favorable. In these cases, some of the polymer chains adsorb onto the NP surface and form an essentially irreversibly "bound" layer. It is experimentally known that the bound layer thickness is dependent on the (spherical) NP diameter, increasing from ≈ 1 nm for a NP diameter of ~10 nm to 4-5 nm for flat surfaces.[142] However, there is currently no theoretical understanding of the bound layer thickness, its temporal stability, and the effect of NP shape. The consequences of the bound layer on nanocomposite mechanical properties and how these are affected by both equilibrium (e.g., interactions) and non-equilibrium (casting solvent, rate of evaporation, temperature) factors also remain open. Developing such an understanding is of central importance to understanding a common route to facilitating NP/polymer miscibility and improving properties.

C. Grafted nanoparticles

We now focus on polymer grafted NPs, which is a topic of much current research.[22,24,26,33,37,42,50,88,90,95,109,119–122,125,143–150] Ganesan *et al.*[22] have shown that the morphologies adopted by grafted NPs in a selective solvent are sensitively determined by the ratio of the NP core size to the native size of the polymeric grafts. Recent work by Jayaraman,[88,89,92] which is in good agreement with experiments, illustrates that the polydispersity of graft lengths can play a critical role in the miscibility of NPs in a polymer matrix with the same chemistry as the brush.

In this context, studies by Bozorgui *et al.*,[141] Lane and Grest,[110] and Chakravarty *et al.*[151] clearly show that polymer chains do not "uniformly" cover the NP, even in the hypothetical limit where the graft points are randomly distributed on the surface (Fig. 2). Additionally, Bockstaller *et al.*[152] found experimentally that the distribution of the number of grafted chains on the NPs follows a modified Poisson distribution
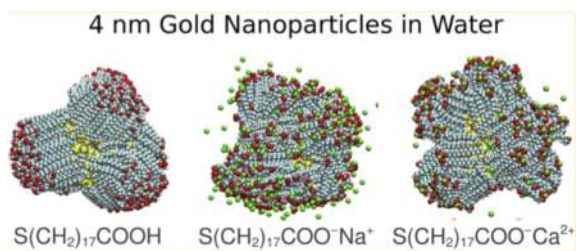
FIG. 2. Change in ligand conformation with different end group functionalization. Reproduced with permission from J. M. D. Lane and G. S. Grest, Phys. Rev. Lett. **104**, 235501 (2010). Copyright 2010 American Physical Society.

(Fig. 3). These results elegantly illustrate that "non-idealities" in the grafting process, e.g., variations in the number of chains across the NPs and fluctuations in the polymer coverage of the surface, are routine features of these systems. Given the fact that the "morphological" diagrams that describe the self-assembly of these polymer-grafted NPs are intimately controlled by the grafting density (or the number of grafted chains per NP) and thus the polymer coverage of the NPs, such non-idealities could have profound effects on the self-assembled structures that are formed by these NPs. However, the precise effect and how it can be manipulated to obtain desired structures, and hence properties, are currently poorly understood.

The above results raise several additional questions that need to be addressed theoretically. Even given that the grafting sites are randomly placed on the NP surface, do "grafting from" protocols (i.e., growing chains from the surface) and "grafting to" methods yield identical polymer surface coverages of the NPs? Preliminary experiments have revealed that these two protocols yield distinctly differing surface coverages, and hence such systems may be expected to yield significantly different self-assembly and miscibility behavior.[39,153] What these differences are caused by (i.e., variations in grafting density achieved and differences in chain conformations and how they affect polymer coverage of the NP surface), where these effects are maximized, and their consequences on self-assembly remain as the outstanding questions. If indeed these differences are found to have major differences in system
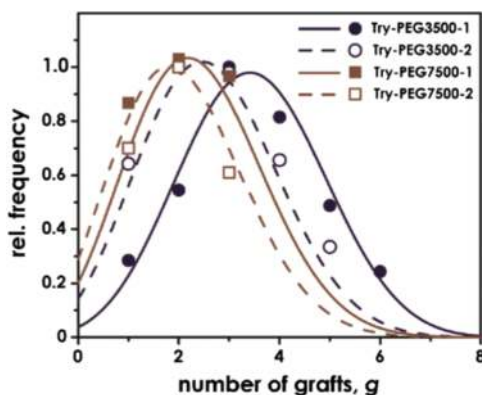
behavior, then they suggest that the synthesis protocol (solvent quality, interaction of the monomers/chains with the NP in addition to "grafting to" vs. "grafting from") has to be studied critically to understand the basic character of this PNC building block.

III. PHASE BEHAVIOR IN POLYMER-NANOPARTICLE MIXTURES

In contrast to the traditional "colloid" limit, where $R \gg R_g$ (R is the particle diameter and R_g is the chain radius of gyration), polymer-NP mixtures correspond to the nanoparticle limit where $R_g \geq R$.[16,46,76–79] In the latter case, both R_g/R and the NP curvature are expected to be significant in influencing interactions and phase behavior. More importantly, the range of effective inter-NP interactions are such that dilute NP concentrations may suffice for the NPs to "see" each other and interact (through polymers).[46,139] Consequently, new physics, driven by multibody polymer-mediated interactions, are expected.[154]

Most of the early equilibrium theoretical studies of polymer-NP mixtures relied upon pair interactions,[155,156] either obtained while accounting accurately for NP curvature effects or approximately through a Derjaguin approach with the results for flat surfaces.[157,158] Such approaches integrate out the polymer degrees of freedom and the resulting interactions truncated at the level of two-body interactions. An advantage of this approach is that a wide variety of polymer-NP interactions can be modeled and their influence on the interparticle interactions be explicitly characterized.[157,159]

Motivated by the importance of multibody interactions, a number of more recent hybrid theory/simulation approaches have characterized the equilibrium features of polymer-NP mixtures while accounting for both the polymer and particle degrees of freedom. For instance, Fredrickson and co-workers[160,161] implemented a hybrid particle/polymer self-consistent field theory (SCFT) framework in which the solution of the equilibrium characteristics of the polymers is obtained for a specified configuration of the particles. This was followed by NP moves based on the forces they experience (Brownian dynamics) or the energy of the system (Monte Carlo). Such hybrid methods[162] were used to address the structural features of particle assemblies within self-assembled block copolymer matrices for spherical[2] and rod-like nanoparticles.[3] Recently, Riggleman and co-workers have generalized this framework to enable field theoretic simulations that avoid the mean-field approximation for the same family of models.[116,117] Balazs[64,163–167] and Frischknecht[29,33,168,169] have pursued similar, field-theory/density functional theory approaches to study the organization of NPs in both homo- and block copolymers. In this context, Schweizer and co-workers[16,44,46,55,76,170] have pioneered the use of integral equation PRISM-based approaches to study the structure, effective forces, and thermodynamics in polymer NP mixtures in conditions ranging from dilute polymer solutions to the melt state. We particularly highlight the work by Zukoski and Schweizer which shows excellent agreement between theory and experimentally determined structure factors in the case of polymer solutions containing NPs.[171]

FIG. 3. The points represent the frequency of NP with a certain number of grafted ligands. Lines are theory based on a Poisson distribution.[157] Reprinted with permission from Hakem *et al.*, J. Am. Chem. Soc. **132**(46), 16593–16598 (2010). Copyright 2010 American Chemical Society.

Computer simulations with explicit representation of NP and polymer degrees of freedom (in contrast to the hybrid approach discussed above) have also been used. For instance, de Pablo *et al.* have developed a number of MC techniques to study the structure and properties of polymer nanoparticle mixtures.[96–98] Bolhuis, Louis, Hansen, and co-workers[172–175] have developed a "soft-particle" approach to studying polymer-NP mixtures in which the polymers are coarse-grained to a soft particle which possesses a single degree of freedom.

From the above discussion, it is evident that considerable progress has been achieved in the development of theoretical approaches to characterize the structure and morphology of multiparticle-multicomponent polymer mixtures. Despite such advances, significant gaps remain in our understanding, and the following represents some of the areas where we believe that further efforts are warranted.

A. A comprehensive phase diagram for the simplest polymer-nanoparticle model

Despite considerable interest, the equilibrium phase diagram of the simplest model system of spherical NPs (exhibiting only steric excluded volume interactions) dispersed in a solution of flexible (threadlike) polymers remains outstanding. While studies have considered certain parametric ranges,[50,76,78,103–105,172–179] there is still a lack of clarity on the phase behavior (including particle crystallization[103,177,178]) expected for arbitrary ratios of NP to polymer size and correlation lengths, and particle and polymer concentrations. While such a model system does not always mimic experiments, it serves as a useful baseline to compare the behavior of more complex experimental systems.

The primary challenge is that the theories and simulations developed for polymer and particle systems have followed somewhat distinct paths. Indeed, in the context of polymer physics, coarse-grained models involving simple interaction forces have played an important role in understanding equilibrium and dynamical properties.[180–182] In contrast, particulate systems have primarily been concerned with the phase behavior resulting from the steric exclusion presented by the particle cores.[183–185] Marrying these distinct approaches pursued by the polymer and particulate community has been an outstanding hurdle. For instance, while the SCFT based approaches for multiparticle-polymer systems capture the polymer physics aspects adequately, typically, the steric exclusion of the polymers is not captured at a fine detail, thereby rendering such methods limited in their utility for high particle concentrations. In contrast, while density functional theory is well-suited for particle phase behavior, incorporating polymer physics at arbitrary solution concentrations has been challenging.[165] While computer simulations are capable of bridging these gaps, the resolution needed for disparately sized polymers and particles, and the inherent difficulties of simulating dense systems and/or equilibrating particle degrees of freedom, has stymied progress.

Naturally, once methods have been developed for a relatively simple system, it will be essential to characterize the phase diagrams for more complex systems with chemical heterogeneity (e.g., polymer blends and copolymers). While there have been numerous applications of the various polymer field theories to examine the distribution of nanoparticles in block copolymers, the miscibility of particles in block copolymers has rarely been studied. Experimentally, it has been shown that attractive interactions are generally necessary to reach high nanoparticle loadings, and the attractions can arise from either direct polymer/particle interactions (see Fig. 4)[186] or those mediated through a small-molecule additive.

B. Influence of complex interaction features on the phase behavior of polymer-NP mixtures

As discussed above, the simplest model system, while useful, is not expected to readily mimic experiment. Indeed, depending on the chemistry of the polymer and particles, short-ranged van der Waals forces, directional hydrogen bonding attractions, and long-ranged electrostatic interactions may manifest. An outstanding question is the manner in which such interactions impact the NP/polymer phase diagram.[76,77] In contrast to the model in Sec. III A, which is expected to exhibit solid-gas and liquid-gas like phase transitions, the presence of other interactions should lead to richer phase behavior involving equilibrium self-assembled morphologies. For instance, recent experiments and theories have suggested the formation of equilibrium cluster phases in systems possessing long-range electrostatic interactions in conjunction with the polymer-mediated depletion attraction.[187] While some studies have made progress in the incorporation of such interactions,[188,189] the behavior expected in a vast parameter space of particle/polymer sizes and concentrations remains to be clarified.
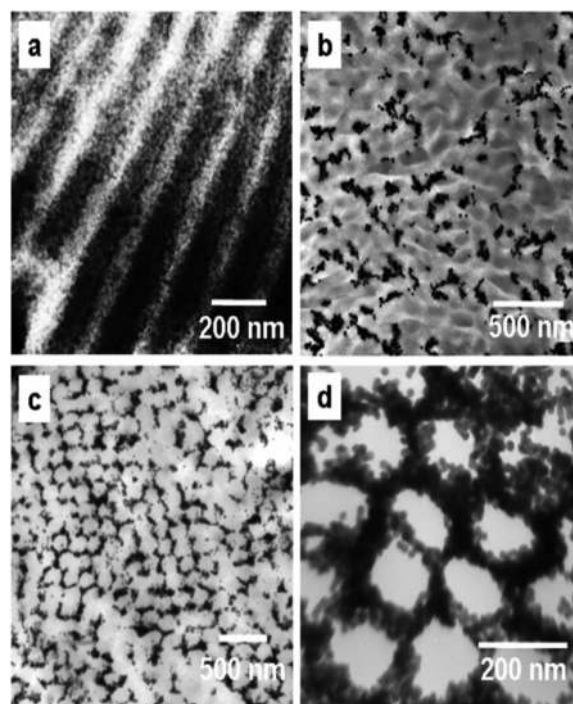

FIG. 4. Nanoparticles grafted with poly(hydroxystyrene) dispersed in bottle block copolymers of poly(styrene) and poly(ethylene oxide). Particle loadings are (a) 0 %$_{vol}$, (b) 5.5 %$_{vol}$, (c) 12 %$_{vol}$, and (d) 25 %$_{vol}$. Reprinted with permission from Song *et al.*, J. Am. Chem. Soc. **137**(11), 3771–3774 (2015). Copyright 2015 American Chemical Society.

C. Influence of particle shape anisotropy and polymer rigidity

Understandably, most theories and simulations of polymer-NP mixtures have concerned themselves with spherical particles and flexible polymer chains. However, many of the recent synthetic developments have focused on nonspherical particles such as nanorods and nanocubes.[190,191] An interesting feature of such systems is the possibility for liquid crystalline phases to arise even at low NP volume fractions.[192] Similarly, many polymeric systems, especially in biological contexts, exhibit a degree of rigidity which render them semiflexible. While some preliminary studies have considered the influence of particle anisotropies and/or polymer semiflexibilities on the interactions and phase behavior,[193–196] such explorations have been very limited relative to the vast parameter space such systems presents (even in the context of the model interactions). Herein, we believe that a significant opportunity lies for theory and simulations to shed light on the phase/self-assembly behavior and identify potentially interesting parametric regions to achieve morphologies which may not be otherwise attainable.

IV. DYNAMICS IN POLYMER NANOCOMPOSITES

Despite the significant progress that has been made in recent years, there are numerous outstanding fundamental questions about system dynamics, e.g., chain diffusion, NP diffusion, and their consequences on viscosity. This is a difficult problem because the factors that determine chain level dynamics, i.e., the NP size, the tube diameter, and the polymer R_g, are frequently on the same scale. Meanwhile on the segmental scale, the dynamics near the NP surfaces are also strongly perturbed. Separating these effects can be challenging.

It is well-known from studies in the context of polymer thin films that interfaces perturb the glass transition temperature, T_g,[197–201] and several simulation studies have shown that the segmental dynamics near NP surfaces are also distinct from the bulk.[202–204] The general trend that has emerged is that the polymer dynamics typically slows down if the NP-polymer interaction is attractive (T_g increases) and speeds up if this interaction is strongly repulsive (T_g decreases).[200,203,205–214] The consequences of these changes on properties and their effects on dynamics and the NP dispersion are poorly understood. For instance, is it possible to design a system that enhances the segmental dynamics near the particle surface where the NPs remain well-dispersed?

If the dynamics are perturbed by the NP surface,[215] is it fair to model the effect of the NP surface on chain level dynamics as a locally increased friction coefficient,[202,216,217] or are the effects of local perturbations in the chain dynamics more akin to modifying the entanglement network of the polymer?[97,106,107,218–221] Furthermore, since in the tube model the diffusivity is proportional to the ratio of the molecular weight between entanglements to the monomer friction coefficient, $D \sim N_E/\zeta$, these effects will likely only be meaningfully distinguished through their temperature dependence. In turn, NP dynamics as they move through an entangled polymer melt is also an area of active interest.[107,222–225] For systems where there is no specific interaction between the NPs and the matrix,

theory predicts that NP diffusion will be controlled by a constraint release mechanism, which opens up the network locally, enabling NP motion.[223,226]

Although simulations have provided a microscopic picture of the distribution of entanglements around grafted spherical NPs, many basic questions remain. For example, how do the entanglement distributions change as the grafted layer transitions from a state that is wet by the matrix to a dry brush, and how does this subsequently affect the diffusion of grafted NPs? Can the dynamics of entangled grafted NPs be modeled similarly to star polymers diffusing through a linear polymer matrix? How do we predict phenomena observed in recent experiments where the dynamics on short time scales is slowed, leading to a decrease in the viscosity despite an apparent enhancement of the tube escape process?

Through the use of primitive-path algorithms, which straighten the polymer chains (without allowing them to cross) to identify entanglement locations, Toepperwein *et al.* have shown that the effective entanglement density increases when the nanorods are left in place during the primitive path reduction of the polymer conformations.[97,115] Interestingly, if the nanorods were removed prior to the primitive path reduction, the entanglement density was very similar to that of the pure polymer, suggesting the possibility that the nanorods simply add a set of independent entanglements to the polymer melt without significantly perturbing the density of polymer-polymer entanglements.[107] This suggests the possibility that the nanorods could provide an independent set of topological constraints, potentially with their own local friction due to strong adsorption and constraint release time. Similar results have been found for spherical NPs in polymer melts.[106,227] These simulations, combined with recent experiments showing that the diffusion coefficient of polymers in the presence
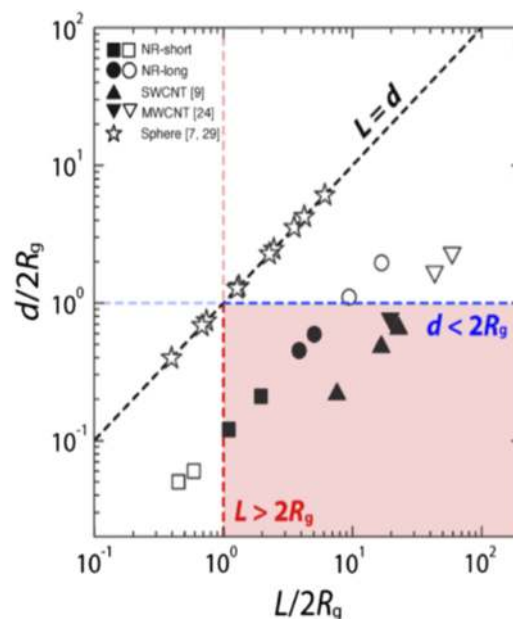

FIG. 5. Map indicating nanoparticle geometry where the polymer diffusion exhibits a minimum as a function of nanoparticle concentration (filled symbols) and where the polymer mobility monotonically decreases (open symbols). Reprinted with permission from Choi *et al.*, ACS Macro Lett. **3**(9), 886–891 (2014). Copyright 2014 American Chemical Society.

of nanorods can exhibit non-monotonic changes with nanorod concentration (see Fig. 5), suggest that there is still much to understand about the dynamics of polymer nanocomposites.

V. KINETICS OF NANOPARTICLE DISPERSION AND ASSEMBLY

It is an experimental reality that the NP dispersion state, and hence properties, is often sensitive to the casting solvent.[228–230] For example, it is known that the relative preference of the solvent for the NP surface *vs.* the preference of the polymer for the NP surface can play a critical role. Thus, silica-P2VP mixtures cast from tetrahydrofuran (THF) yield well-dispersed NPs, whereas processing from a pyridine solution results in agglomerated NPs. Durning *et al.*[28] found that silica was well-mixed with poly(methylacrylate), but that the introduction of small quantities of ethyl acetate caused NP agglomeration. Similarly, it is well-known from the work of Mackay *et al.*[12] that the rapid precipitation technique typically yields well-dispersed NP states, regardless of the chemistry of the NPs and the polymers.

A. Role of solvent evaporation

To our knowledge, the only work that has examined the effect of solvent evaporation on the NP dispersion state in a homopolymer matrix is the computer simulations of Grest and coworkers.[71] A simple film construct is used, and solvent is allowed to evaporate through the top of the film (Fig. 6). When the interaction between the NPs and polymer is weak, the NPs are uniformly distributed in the film, while the NPs tend to concentrate at the air interface when NP/polymer interactions are strongly favorable. Separately, Riggleman and co-workers showed that tuning the solvent evaporation rate relative to the particle diffusion rate can allow control over the NP distribution through a thin film.[231]

These first studies opened up a number of questions that need to be answered. What is the relative role of the interactions between the solvent-NP-polymers and what is the interplay of these effects when the solvent evaporates? Can this behavior be understood purely on the basis of a depletion attraction between a pair of NPs in the case of non-adsorbing polymers *vs.* good dispersion arising from the formation of a bound layer when NP/polymer interactions are more favorable than the NP/solvent interactions? What is the structure of the bound layer and how is it affected by the interplay between evaporation and adsorption kinetics? How does NP diffusion affect the dispersion state that results? What is the character of chain
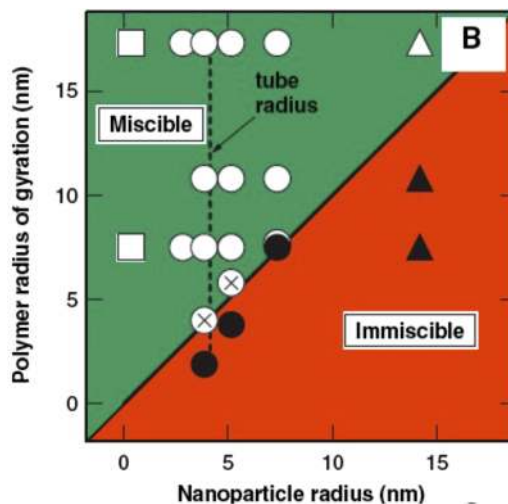

FIG. 7. Role of NP and polymer size on miscibility. Reproduced with permission from Mackay *et al.*, Science **311**(5768), 1740–1743 (2006). Copyright 2006 American Association for the Advancement of Science.

entanglements, especially those between the bound polymer layer and the bulk polymer? Similarly, what are the interactions between two bound layers? How does this affect the properties that result?

In a similar spirit, still unresolved are the experiments of Mackay and co-workers,[12] who showed that adding a non-solvent, which caused the precipitation of the nanocomposite, could be used to control the NP dispersion state. These workers found that the dispersion state is purely controlled by the relative sizes of the NPs and the polymer chains, with enthalpic interactions apparently playing no role (Fig. 7). Why do enthalpic interactions play apparently no role? Why are the relative sizes of the NP and the polymer determining miscibility, and can we explain data in Fig. 7?

B. Nanoparticle assemblies driven by solvents

While much focus has been placed on NP miscibility with polymer melts, a particularly interesting aspect is NP organization and self-assembly caused by the casting solvent, e.g., the presence of selective or immiscible solvents. A striking example was presented by Park and co-workers where a block copolymer [poly(acrylic acid)-*b*-poly(styrene), PAA-b-PS] and iron oxide NPs were initially dispersed in a series of solvents, slowly titrated with water, and then the resulting self-assembled structures were collected, dispersed, and characterized in water (Fig. 8).[232] Depending on the initial casting solvent, stable core-shell structures, micelles, or particle-loaded
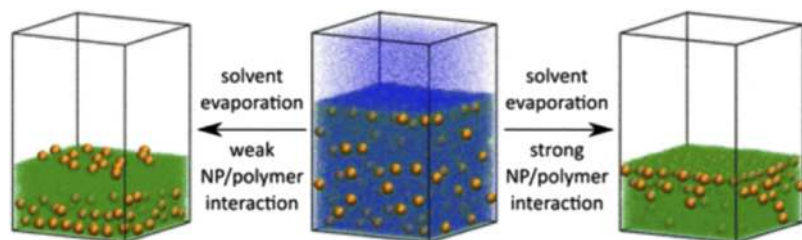

FIG. 6. Role of solvent evaporation on the NP dispersion state. Reprinted with permission from S. F. Cheng and G. S. Grest, ACS Macro Lett. **5**(6), 694–698 (2016). Copyright 2016 American Chemical Society.
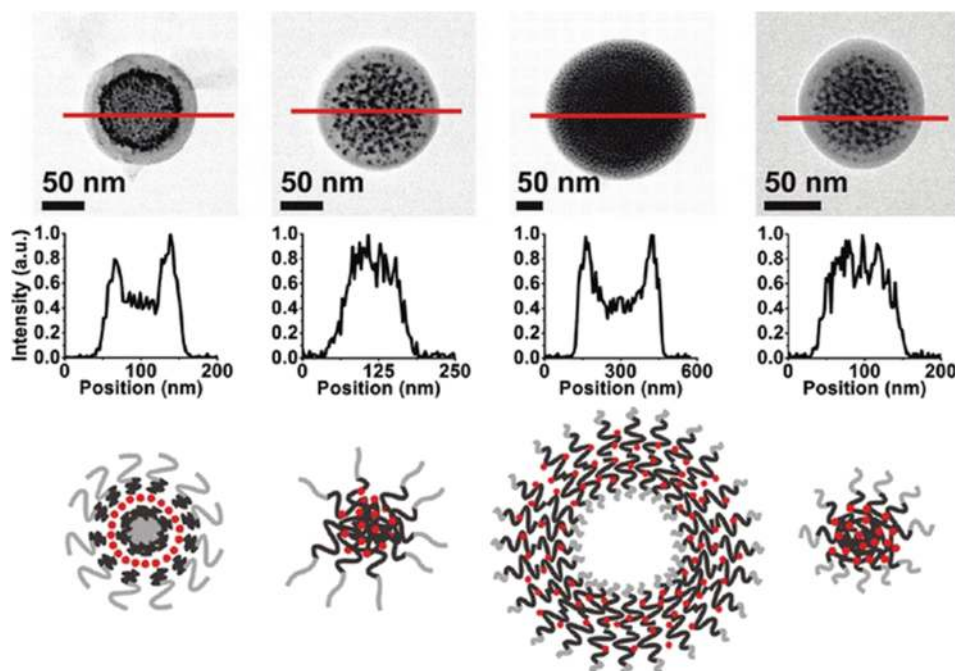
FIG. 8. Images and distribution of iron-oxide NPs in block copolymer assemblies in water after assembling in (left) DMF/THF (96.8% dimethylformamide (DMF)), (middle) THF, and (right) dioxine/THF (96.8% dioxane). Reprinted with permission from Hickey *et al.*, J. Am. Chem. Soc. **133**(5), 1517–1525 (2011). Copyright 2011 American Chemical Society.

polymersomes were observed in water. Clearly, the initial solvent plays a dominant role on the final structure, but there is no means to anticipate these structures without performing experiments. Can theory or simulations be developed to gain an understanding of these issues? Doing so would likely require the development of mesoscale simulation techniques that can efficiently deal with phase separation kinetics in the presence of nanoparticles, and it may be necessary to capture local composition-dependent dynamics in any microphases that form.

Another germane example is the formation of Pickering emulsions, i.e., the non-equilibrium placement of NPs at the interface between immiscible liquids.[233–239] It is now well-known that NPs partition to the dividing surface between immiscible liquids. It is thought that this phenomenon is inherently non-equilibrium in nature and that the NP structures that form are driven by factors such as the energy that is input into the system. Can we find ways to model this process? Would non-equilibrium transport modeling be of relevance?

VI. FIELD-DRIVEN SYSTEMS

We now focus on the assembly of NPs in the presence of external fields such as flow, electric, or magnetic fields.[10,240–244] Looking ahead, there is also considerable interest in using other fields, such as optical traps, to assemble NPs. There are really two classes of problems. First are conservative systems such as those in the presence of a potential field, e.g., an electric field or an elongational flow field, where we can use a system Hamiltonian to probe phenomena. The other interesting situation involves non-potential flows such as shear where dissipation in inherent. We believe that potential flows can be used to direct equilibrium assembly of NPs, but the latter emphasizes far from equilibrium processes (e.g., large amplitude oscillatory shear) that can drive the systems

into completely new states. We see this area as being ripe for developments in the near future.

A. Nanoparticle dispersion due to flow

Unidirectional flow (e.g., extrusion) is thought to assist in improving NP dispersion into the polymer matrix.[245] While this methodology is pervasive, to our knowledge, there has not been a systematic means of modeling the role of shear fields on NP dispersion; an important exception is the recent work of Kalra *et al.* who showed that nanoparticle aggregation is reduced in the presence of flow.[246] Questions that persist are as follows: can we predict morphology as a function of shear rate for NPs of different shapes (spheres, cylinders, and rods) and sizes?[247] Is there a universal dependence of dispersion on flow fields? Do the NPs form assemblies such as strings/sheets in flow, as seen in the case of larger colloids, and under what conditions do they form?[248,249]

A related question is how oscillatory shear (especially large amplitude oscillatory shear, LAOS) affects NP assemblies. Experimental work in this area suggests that LAOS does not help in ordering the NPs but rather breaks up existing structures into smaller entities and aligns them into the shear direction.[250] Does shear ever help improve NP organization? What are the underpinning issues here and how do we begin to model them? Such questions remain open at this time and represent an area of tremendous interest at the intersection of fundamental understanding and applications.

B. Effect of magnetic/electric fields

The role of external electric, magnetic, and optical fields on the organization of NPs has only found limited interest especially in the case of polymer nanocomposites. Take, for example, the case of magnetic fields. Much work has focused
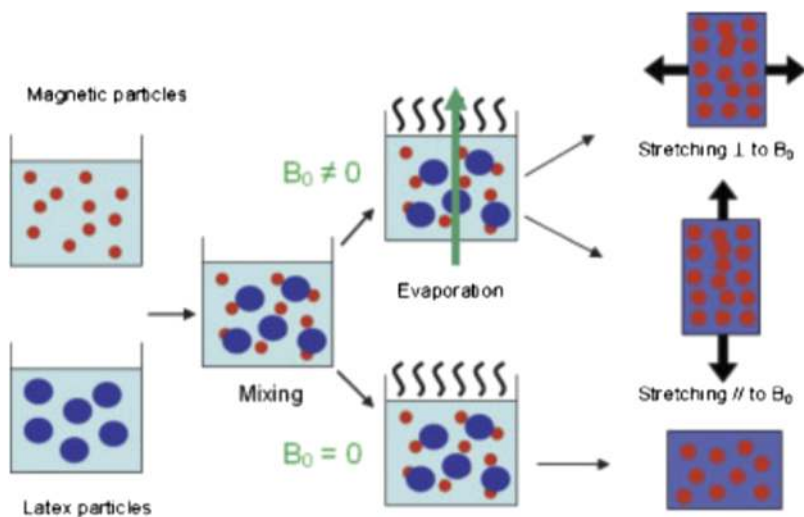
FIG. 9. Schematic role of magnetic fields. Reproduced with permission from Jestin *et al.*, Adv. Mater. **20**(13), 2533–2540 (2008). Copyright 2008 John Wiley & Sons.

on the interactions between NPs and the structures that form in solution.[251–256] However, to our knowledge, only a few works have considered the corresponding phenomena when magnetic NPs are placed in a polymer matrix in an external field.[25,257–259] Jestin *et al.*, for example, incorporated iron oxide NPs in a polymer matrix in the presence of solvent (Fig. 9). Drying this solution under the action of a magnetic field yielded an ordered array of NPs. The properties of the resulting composite also acquired a directional nature. Control experiments in the absence of a field resulted in no such orientation effects. Similarly, placing the field after the drying of the solvent yielded no measureable NP ordering.

Electric fields are also known to order NPs into structures, e.g., Fig. 10.[260–263] Bishop and his coworkers, for example, considered conducting NPs in an insulating liquid in a DC field.

The contact electrification of a single NP leads it to execute oscillatory motion between the two plates. The same phenomenon leads a collection of NPs to be ordered into strings and further into sheets and other more complicated structures (Fig. 10).

The underpinning questions here are the same for both of these topics. What is the role of the field in ordering NPs and does the presence of the solvent simply facilitate the ordering by lowering viscosity? How does the field interact with the factors controlling quiescent NP assembly (in the absence of field) and modify this assembly process? What is the role of the NP size and is there a threshold size/field beyond which structures form? Are strings/sheets the only structure that form, or can we use grafted NPs (especially in the low grafting limit) to obtain other structures? What is the effect of these assemblies on properties?

VII. (ENGINEERING) PROPERTIES

The ultimate goal of the study of NP assembly in polymer matrices is the effects these self-assembled states have on engineering properties. The specific properties of interest, of course, depend on the application and can range from mechanical reinforcement, flame retardancy, gas transport, charge transport, electrical transport or conductivity, and optical properties which are relevant to the creation of photonic crystals, and in optical transparency. Each of these areas is by itself vast, and the confronting issues are unique to the properties themselves. Here, we focus on sampling of such properties and identify some salient questions that remain outstanding at this time.

A. Mechanical properties

The mechanical behavior of PNCs is sensitively determined by whether the polymer is liquid-like or solid-like before it is blended with the NPs. When the polymer is liquid-like in the unblended state, the addition of NPs makes it behave increasingly like a solid. These effects, which are primarily probed through rheology, are of continuing interest in this field.[19,27,40,136,202,216,264–270]
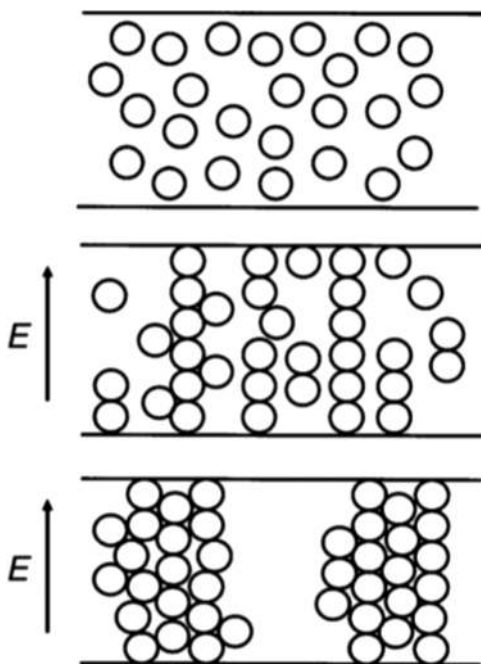

FIG. 10. Electric field alignment of NPs. Reproduced with permission from K. Tanaka and R. Akiyama, Polym. J. **41**(12), 1019–1026 (2009). Copyright 2009 Nature Publishing Group.

We summarize one result, from the work of Baeza *et al.*,[271] that highlights our current understanding. Rheological measurements on favorably interacting mixtures of spherical silica NPs and poly(2-vinylpyridine) show that system dynamics are polymer-like but with increased friction for low silica loadings. However, it turns network-like when the mean face-to-face separation between NPs becomes smaller than the entanglement tube diameter. Gel-like dynamics with a William-Landel-Ferry temperature dependence then result. This dependence turns particle dominated, i.e., Arrhenius-like, when the silica loading increases to ∼31 vol. %, i.e., when the average nearest distance between NP faces becomes comparable to the polymer's Kuhn length. These results demonstrate that the flow properties of nanocomposites are complex and can be tuned via changes in filler loading, i.e., the character of polymer bridges which "tie" NPs together into a network.[139,140,216] The questions that remain here are as follows: What is the role of the attractive interactions between the NP and the polymer on the mechanical properties? Can we rationalize the experimental findings discussed above? If so, does it substantiate the picture of Long *et al.*[199,207,272–274] who postulated that mechanical reinforcement only results when a glassy layer forms at the NP surface? How do these results help explain the findings of Wang and co-workers[275] who suggested that reinforcement is purely a particle effect or the work of Sternstein[276–278] who argues that it is mainly a polymer bridging effect?[216,217] How do these results apply to non-linear rheology, specifically the Payne effect,[279] which has remained of on going interest? How are these results modified when we deal with grafted NPs?[264]

We now move to the glassy state, where there is very little systematic experimental work. Maillard *et al.*[280] found that the Young's modulus, the yield strain, and the strain-to-failure can all be tuned by varying the polymer grafted NP dispersion state in polymer glasses. To our knowledge, the only systematic theoretical work in this area is by Riggleman, de Pablo, and Douglas,[97] who have looked at the entanglement network in these situations and how it is modified under the action of extension. Similarly, Meng *et al.* have looked at the crazing of glassy PNCs with polymer-grafted NPs.[281] These workers have also looked at the distribution of mechanical stresses in the material. While these are informative, there is currently no understanding of the role of NP dispersion on the mechanical properties that result. This is an open topic that remains to be resolved.

B. Barrier properties in polymer nanocomposites

While polymeric materials find extensive use in gas separations, there is often a performance trade-off between permeability and selectivity which defines an empirical upper bound on their performance.[8,282–288] In this regard, incorporation of inorganic NPs such as porous zeolites, carbon molecular sieves, and nonporous silica has been pursued to improve the performance of gas separation membranes.[8,282,286] Initial reports focused on the use of highly anisotropic fillers to "block" the transport of penetrants and gas molecules.[289] More recently, however, a number of groups have reported that the addition of inorganic non-porous particles can alter the polymer chain packing in glassy, high-free-volume polymers

and concomitantly increase the free volume and lead to a significant enhancement in permeability and vapor/gas selectivity.[8] Interestingly, such results are often in contradiction with the Maxwell model prediction of a reduction in permeability on the addition of nonporous fillers to a polymer matrix.[290–292] While such observations have raised intense interest in the application of polymer nanocomposites for modifying the barrier properties, a number of outstanding questions still remain.[293,294]

1. Role of filler-polymer and filler-gas interactions

While it is generally believed that the polymer-filler interactions should not be too favorable (which would lead to a densification of the polymer similar to bound layers discussed earlier), the exact extent to which polymer filler interactions influence the free volume characteristics is still unknown. Of even more fundamental nature is the question, what is the distribution of free volumes around particles and surfaces? Does the free volume distribution follow the local density of the polymer matrix? While the above questions relate to the polymer-NP interactions and its influence on free volume, the fillers may have additional influence on gas solubilities and selectivities through its direct interactions with the components of the gas mixture. Very little is known about these competing influences.

2. Role of filler dispersion state

Even in circumstances where the free volume distributions are influenced by the added filler, it is unclear whether a well-dispersed particle state can significantly enhance gas transport properties. This brings up another outstanding issue, viz., what is the influence of the particle dispersion state on the overall gas transport properties? Is there a need to create a percolated network of pathways for gas transport?[292] How does one tune the polymer-filler interactions to address the dual (and sometimes) competing requirements for the free volume modulations and the mechanical properties that result?

3. Role of fillers on physical aging

Another property of significant interest is the impact of fillers on physical aging of glassy membranes.[213,295,296] While long range surface effects have been observed in the context of glass transition temperatures, surprisingly, even longer range effects (of the order of many microns) have been observed in the context of physical aging phenomena.[297–301] As such, the origins of such phenomena, the role of pre-existent stresses, and the influence of polymer-surface interactions remain to be clarified. When such observations are combined with the presence of multiple interfaces in polymer NP mixtures, these effects can be expected to be significantly amplified. Indeed, recent experiments have shown that despite the general similarity between the segmental dynamics of the nanocomposites and that of pure polymer, the former systems display markedly accelerated physical aging in comparison to the pure polymer.[302,303] An outstanding challenge is in being able to develop models which can address such effects and clarify their impact on gas transport and mechanical properties.

C. Conductivity of polymer nanocomposites

Polymer NPs mixtures have been extensively explored for their conducting properties. Below, we briefly discuss the findings and unresolved questions in two broad areas in this context.

1. Polymer nanocomposites for enhanced electrical conductivity

A number of experiments have highlighted the potential of anisotropic carbon based fillers, e.g., nanotubes and graphene, to improve the conductivity of polymer matrices. Indeed, several orders of magnitude enhancement in electrical conductivity have been demonstrated even at a very small loading of fillers. In most instances, composites containing conducting fillers in insulating polymers become electrically conductive when the filler content exceeds the percolation threshold which results in the formation of a three-dimensional conductive network of the fillers within the matrix.[304–306] However, it is expected that the percolation thresholds are themselves influenced by the dispersion and alignment of the fillers in the polymer matrix.[307] Interestingly, in some studies,[304,308] a slight aggregation of the fillers was found to lower the percolation threshold by increasing the local interactions between nanotubes. Such observations raise the following questions: What is the influence of polymer particle interactions on the percolation threshold of anisotropic fillers? Is there an optimal degree of favorable polymer-particle interaction to facilitate low percolation thresholds without a loss of electrical conductivity arising from the bound polymer layers?

Related to the above issue, the influence of chemical functionalization on the conductivity is still unresolved.[309–311] On the one hand, chemical functionalization could disrupt the conductivity mechanism and thereby have a deleterious effect. However, experiments have shown that functionalization can sometimes improve electrical properties.[312] In such cases, it has been suggested that the improved NP dispersion dominates behavior. However, it can be expected that there would be an optimal dispersion state in determining such competing characteristics (and in turn upon the percolation thresholds).[194] The physics of such competing interactions are unresolved. Similarly, the alignment of the nanotubes in the polymer matrix is expected to reduce the number of contacts and the electrical conductivity. However, some experiments[313–315] have demonstrated that intermediate levels of nanotube alignment may sometimes possess higher conductivities than isotropic orientations. Such observations motivate the question: What is the interplay of polymer-particle interactions and the filler aspect ratio on the degree of orientational alignment, and in turn, the percolation threshold?

2. Ionic conductivity of polymer nanocomposites

PNCs have also recently been proposed for advanced rechargeable batteries. The addition of ceramic nanoparticles to solid polymer electrolytes was shown, in certain circumstances, to increase conductivity.[316,317] Such observations were initially rationalized by suggesting that NPs suppress or dramatically slow down the crystallization of the polymer matrix to promote local chain mobility.[318,319] However,

other experiments found conductivity enhancements in composite polymer electrolytes which can occur even at temperatures above the polymer melting point. These facts suggest that the physical mechanism underlying conductivity enhancements cannot be attributed solely to the suppression of crystallization. Further, in a number of cases, lowering of conductivity has been observed upon the addition of NPs.[320–324]

While some atomistic simulations have examined the mechanism of ion transport in PNCs and pointed the importance of features such as polymer segmental motion, NP interaction with ions and the polymer segments, and changes in polymer conformations induced by nanoparticles, a number of important features are still unaccounted.[325–333] Specifically, due to the detailed and atomistic nature of such simulations, the influence of filler structure and its impact on ionic conductivity has still not been clarified. Moreover, much of the studies (with some exceptions[325,333]) have been concerned with systems of specified chemistries, and hence there is still a lack of general principles underlying the ionic conductivity and their mechanisms in polymer nanocomposites. For instance, in almost all such computational studies, enhancements in conductivities have been accompanied by a decrease in the mechanical properties of the electrolyte.[333] An outstanding question is whether simultaneous enhancements in conductivity and mechanical strengths can ever be achieved, say by the adoption of anisotropic fillers (such as been noted in the context of electrical conductivity). Finally, a critical missing component of the simulations is the absence of accounting for the crystallization of the polymer electrolytes and the role played by nanoparticle fillers. Indeed, the crystalline and noncrystalline phases of the electrolyte possess drastically different conductivity characteristics.[334] Hence, if the fillers influence the relative volume fractions of such phases, profound effects (not captured by any of the present simulations) can result.

In the above discussion, we chose to mainly highlight the unresolved, open questions in the context of material properties, without making any claims or suggestions regarding the appropriate advance needed in simulation methodologies. In some cases, the development needed would be as simple as incorporating the appropriate physics within existing simulation methodologies, whereas, in many other cases, appropriate methodologies which can tackle the length and time scale challenges are needed. Unfortunately, since the methodologies pertaining to this section are in early stages of development, and moreover, very distinct for different properties, we refrain from making broad generalizations.

VIII. CONCLUSIONS

We have discussed the theoretical progress made in the field of polymer nanocomposites, but we have primarily focused on the outstanding issues in this topic. Building off published work, we believe that significant progress has been made in delineating the phase behavior of PNC, and the assembly of NPs into well-defined superstructures. Even here there is a lack of understanding for the simplest case of hard nanoparticles mixed with thread-like polymers across a

broad range of parameter space. Similarly, there are outstanding issues in the synthesis of functionalized nanoparticles and understanding the role of processing on the states realized by these hybrid materials. The dynamics of the systems, including the mobilities of the different constituents, also remain poorly understood, even though there have been broad-based efforts on these topics to date. We also see that future work must necessarily focus the role of external fields (electric, magnetic) on the active assembly of the NPs. Finally, the consequences of these assembly states on the engineering properties that result and the factors that control them remain as the ultimate challenge to the practical applications of these hybrids.

ACKNOWLEDGMENTS

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