RX15-2

1. **Research Title:** Computational Study of Polymer Grafted Nanoparticle Systems
2. **Individual Sponsor:** List the AFRL research topic sponsor's contact information

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3. **Academic Area/Field and Education Level**

Materials Science & Engineering, Chemical Engineering, Chemistry, Physics, Mechanical Engineering (MS or Ph.D. level)

4. **Objectives:** Simulate and characterize systems of polymers grafted to nanoparticles, i.e. hairy nanoparticles (HNP), to determine the effect of HNP design on self-assembly, structure and entanglement of "neat" (i.e. solvent free) materials. This will include: (1) examining the effect of graft density and chain length on the crystal structure of the various HNPs; (2) the impact of core shape, (i.e comparing rods, plates and spheres); and (3) determining the effect of adding free polymer on the overall polymer morphology. Understanding these will enable finding the optimal grafting density, chain length, core shape, and filler to maximize toughness while maintaining high inorganic content.
5. **Description:** Conventional nanocomposites, where free polymer is added to inorganic nanoparticles, are used in a range of applications, including dielectrics for pulsed power, optical coatings, and multifunctional structures. Ongoing experimental activities have found that high inorganic loading without agglomeration can be achieved by instead using HNPs, which eliminates morphology features that underlie numerous failure processes commonly limiting traditional nanocomposite application, scalability, and reliability. However, little is understood about the polymer morphology and its effect on the mechanical properties in these systems, especially for high molecular weight chains at low grafting densities. Theoretical work on these systems is limited by assumptions of uniform polymer density and current simulations are limited to either using short chains with many NPs, or including only a single NP. In order to guide further development of these materials, simulations are needed that include many nanoparticles and long chains. Specifically, these will examine the crystal structure and mechanical properties and include chains with more than 1000 monomers. This requires that new methods be developed and employed to construct equilibrated structures and calculate their structural and mechanical properties. In addition to graft density and chain length, addition of free chains or solvents can have significant impact on structure and subsequent performance. For example, Nealey and de Pablo have recently demonstrated that (1) chains grafted around corners stretch to accommodate the underlying chemical pattern and (2) the entropic penalty of chain stretching can be relieved by adding much shorter free chains. This results in a heterogeneous distribution of free chains that mimics the heterogeneous chain stretching forced by the underlying pattern (i.e. corners). Similarly, in the HNP system where chains are grafted to a curved surface, adding free polymer will influence the polymer distribution around the nanoparticles, altering the proportion of polymer that is between the NPs versus in the interstitial spaces. Understanding this effect will allow the further

optimization of HNP properties. Once these basic properties are understood and validated experimentally for a model system, e.g. polystyrene grafted to silica, various polymers and nanoparticle materials can be explored to investigate the effect of the polymer-nanoparticle interactions.

6. **Research Classification/Restrictions:** This research is unrestricted, and results will be in the public domain.
7. **Eligible Research Institutions:** Indicate to what organizations this topic should be provided

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