

A 2-D Kinetic Theory for Flows of Monodomain Polymer-Rod Nanocomposites

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Abstract. We merge classical kinetic theories [M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, 1986] for viscous dispersions of rigid rods, extended to semi-flexibility [A. R. Khokhlov and A. N. Semenov, *Macromolecules*, 17 (1984), pp. 2678-2685], and for Rouse flexible chains to model the hydrodynamics of polymer nano-rod composites (PNCs). A mean-field potential for the polymer-rod interface provides the key coupling between the two phases. We restrict this first study to two-dimensional conformational space. We solve the coupled set of Smoluchowski equations for three benchmark experiments. First we explore how rod semi-flexibility and the polymer-rod interface alter the Onsager equilibrium phase diagram. Then we determine monodomain phase behavior of PNCs for imposed simple elongation and shear, respectively. These results inform the effects that each phase has on the other as parametric strengths of the interactions are varied in the context of the most basic rheological experiments.

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1 Introduction

Polymer-nanoparticle composites are made from blends of flexible polymers and various anisotropic nanoparticles, including nano-clay platelets and graphene sheets, carbon

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nanotubes, nanowires, and metals. They have shown promising, extraordinary properties in chemical, electrical, environmental, and thermal transport as well as ultrahigh mechanical strength. We refer to various review articles [9,18,21–24,27] on the promising diverse applications of polymer nanocomposites.

Given the promising applications of blends of flexible polymers and nanoparticles, a thorough understanding of their phase behavior, dynamics, morphology development and mesoscopic structure evolution, and the full spectrum of rheological behavior in processing conditions, becomes important. Yet theoretical studies of these aspects of polymer blends are sparse. Liu and Fredrickson developed a mean field thermodynamic theory to study phase separation kinetics focusing on low frequency and long wave behavior [16]. Muratov and E proposed a kinetic theory for the incompressible mixture of flexible polymers and rodlike liquid crystalline polymers [8, 19], in which they investigated the phase separation kinetics employing a gradient expansion of the density function of the rodlike liquid crystalline polymer and identified various transitions leading to phase separation including a micro-phase separation transition. In both of these theories, the detailed conformational dynamics of the flexible polymers and the semiflexibility of the rods are ignored. There is now overwhelming evidence that the polymer phase is modified due to surface chemistry with the rod phase, and the local rod-polymer interactions are critical elements of a predictive theory. This paper takes into account the local conformational dynamics of the blend of the flexible polymer and the semiflexible nanorod in a hydrodynamic theory in a 2-D configurational space setting.

Two recent research papers have proposed continuum models of nanorods and nanoclays based on the GENERIC formalism [10,20]. The models yield a reasonable qualitative agreement with experimental data. To explore more detailed microscopic information and their role in mesoscopic material properties, our aim is to develop a kinetic theory for flowing polymer nanoparticle dispersion systematically accounting for the conformational dynamics of the flexible polymer, the polymer nano-particle interactions and semiflexibility of the nano-particles [12]. This theory extends work of the authors on blends of polymers and rodlike liquid crystals [14], and of Semenov and Khoklov on semiflexible liquid crystal polymers [15].

In the blend system, we introduce a statistical weight for the flexible polymer matrix $\Theta(\mathbf{x}, \{\mathbf{R}_i\}, t)$, where \mathbf{x} is the location of the material point, t is time, and $\{\mathbf{R}_i\} = (\mathbf{R}_1, \dots, \mathbf{R}_n)$ describes the conformation of the flexible polymer chain modeled as a bead-spring chain [1, 3]. We assume

$$\Theta = \phi \theta(\mathbf{x}, \{\mathbf{R}_i\}, t), \quad (1.1)$$

where θ is a probability density function for the conformation of the bead-spring chain and ϕ is the volume fraction of the polymer per unit volume at the macroscopic level. The time evolution of θ is governed by the Rouse dynamics while ϕ is a constant in the monodomain case considered here. Since the added conformational dynamics is local, it does not affect the macroscopic incompressibility constraint. It does however add a detailed conformational contribution of the flexible polymer to the elastic stress as well as to