

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

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## Abstract

We merge classical kinetic theories for viscous dispersions of rigid rods, extended to semi-flexibility [3], 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 conformation 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.

## 1 Introduction

Nanocomposites are materials that are created by introducing nanoparticulates (**filler**) into a macroscopic sample material (**matrix**).

• **Filler**: semiflexible nematic nanorods (modeled by ellipse)

• **Matrix**: flexible polymer (modeled by bead-spring chain)

Recent research has proposed continuum models of nanorods and nanoclays based on the GENERIC formalism. 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 [1]. This theory extended the work of:

• Forest and Wang on blends of polymers and rodlike Liquid crystals [2]

• Semenov and Khokolov on semiflexible liquid crystal polymers [3]

## 2 Governing equations

• Probability density per unite volume of nanorods (pdf):  $f(\mathbf{x}, \mathbf{m}, t)$  at  $(\mathbf{x}, t)$  with the orientation axis  $\mathbf{m}$

• Number Density of nanorods:  $\Phi(\mathbf{x}, t) = \int_{\|\mathbf{m}\|=1} f(\mathbf{m}, \mathbf{x}, t) d\mathbf{m}$

• Number density function of polymer:  $\Theta(\mathbf{x}, \mathbf{q}, t)$  at  $(\mathbf{x}, t)$  with the chain conformation  $\mathbf{q}$  (the end-to-end vector of a bead-spring model)

• volume fraction of polymer:  $\phi(\mathbf{x}, t) = \int_{\mathbb{R}^3} \Theta(\mathbf{x}, \mathbf{q}, t) d\mathbf{q}$

### Continuity equation

$$\frac{d}{dt}\rho + \rho \nabla \cdot \mathbf{v} = 0. \quad (1)$$

### Balance of linear momentum

$$\rho \dot{\mathbf{v}} = \nabla \cdot (-p\mathbf{I} + \boldsymbol{\tau}) + \rho \mathbf{g}, \quad (2)$$

where  $p$  is the static pressure, and  $\mathbf{g}$  is the external force per unit mass.

### Smoluchowski kinetic equations

$$\begin{cases} \frac{df}{dt} = \mathcal{R} \cdot \left( \frac{D_{\mathbf{m}}(\mathbf{m})}{k_B T} f \mathcal{R} \mu \right) - \mathcal{R} \cdot (\mathbf{m} \times \dot{\mathbf{m}} f), \\ \dot{\mathbf{m}} = \Omega \cdot \mathbf{m} + a[\mathbf{D} \cdot \mathbf{m} - \mathbf{D} : \mathbf{m}\mathbf{m}], \\ \frac{d\Theta}{dt} = -\frac{\partial}{\partial \mathbf{q}} \cdot ((\mathbf{K} - (1 - a_0)\mathbf{D}) \cdot \mathbf{q}\Theta) + \frac{\partial}{\partial \mathbf{q}} \cdot \mathbf{H} \cdot \left( \frac{\partial}{\partial \mathbf{q}} \mu \Theta \right), \end{cases} \quad (3)$$

### Stress constitutive equation

$$\begin{aligned} \boldsymbol{\tau} = & 2\eta_v \mathbf{D} + 2k_B T \zeta (1 - \phi) \mathbf{D} : \langle \mathbf{m}\mathbf{m}\mathbf{m}\mathbf{m} \rangle + \zeta_2 k_B T (1 - \phi) (\mathbf{D} : \langle \mathbf{m}\mathbf{m} \rangle + \langle \mathbf{m}\mathbf{m} \rangle \cdot \mathbf{D}) + \\ & \frac{ac(1-\phi)}{2} [\langle \mathcal{R}(\mu_{nr}) \mathbf{m} \rangle + \langle \mathbf{m} \mathcal{R}(\mu_{nr}) \rangle] + \frac{c(1-\phi)}{2} [\langle \mathcal{R}(\mu_{nr}) \mathbf{m} \rangle - \langle \mathbf{m} \mathcal{R}(\mu_{nr}) \rangle] \\ & + 2a_0 \gamma k_B T \phi (\xi + \alpha_2 c (1 - \phi)) \ll \mathbf{q}\mathbf{q} \gg + \gamma c \phi (1 - \phi) k_B T [(\alpha_1 - \alpha_2) a_0 \langle \mathbf{m}\mathbf{m} \rangle \cdot \ll \mathbf{q}\mathbf{q} \gg + \\ & \ll \mathbf{q}\mathbf{q} \gg \cdot \langle \mathbf{m}\mathbf{m} \rangle + \langle \mathbf{m}\mathbf{m} \rangle \cdot \ll \mathbf{q}\mathbf{q} \gg - \ll \mathbf{q}\mathbf{q} \gg \cdot \langle \mathbf{m}\mathbf{m} \rangle]. \end{aligned} \quad (4)$$

## 3 Numerical method: collocation method

We numerically solve the nonlinear system of equations given above. Given the nonlinear terms in the Smoluchowski equation, it is advantageous to use the collocation method to discretize the pde [4]. We discretize the interval  $[0, \pi]$  into  $n$  equal intervals with grid points:  $\theta_j = \frac{1}{2}(jh + \pi)$ ,  $h = \frac{2\pi}{n}$ ,  $j = -n/2, \dots, n/2$ , and approximate the function using the interpolant

$$f_a = \sum_{j=-n/2}^{n/2-1} f_j S_n(2(\theta - \theta_j)), \quad (5)$$

where  $f_j = f(\theta_j)$  and  $S_n(x) = \frac{\sin \frac{n\pi x}{2}}{n \tan \frac{\pi x}{2}}$  defined in  $(-\pi, \pi)$  is the Sinc function which is an approximate  $\delta$  function with the property  $S_n(0) = 1$ . Then,

$$f_a(\theta_j) = f_j, j = -n/2, \dots, n/2.$$

Thus, the Smoluchowski equation could be fully discretized at each grid point  $\theta_j$ .

## 4 Numerical results

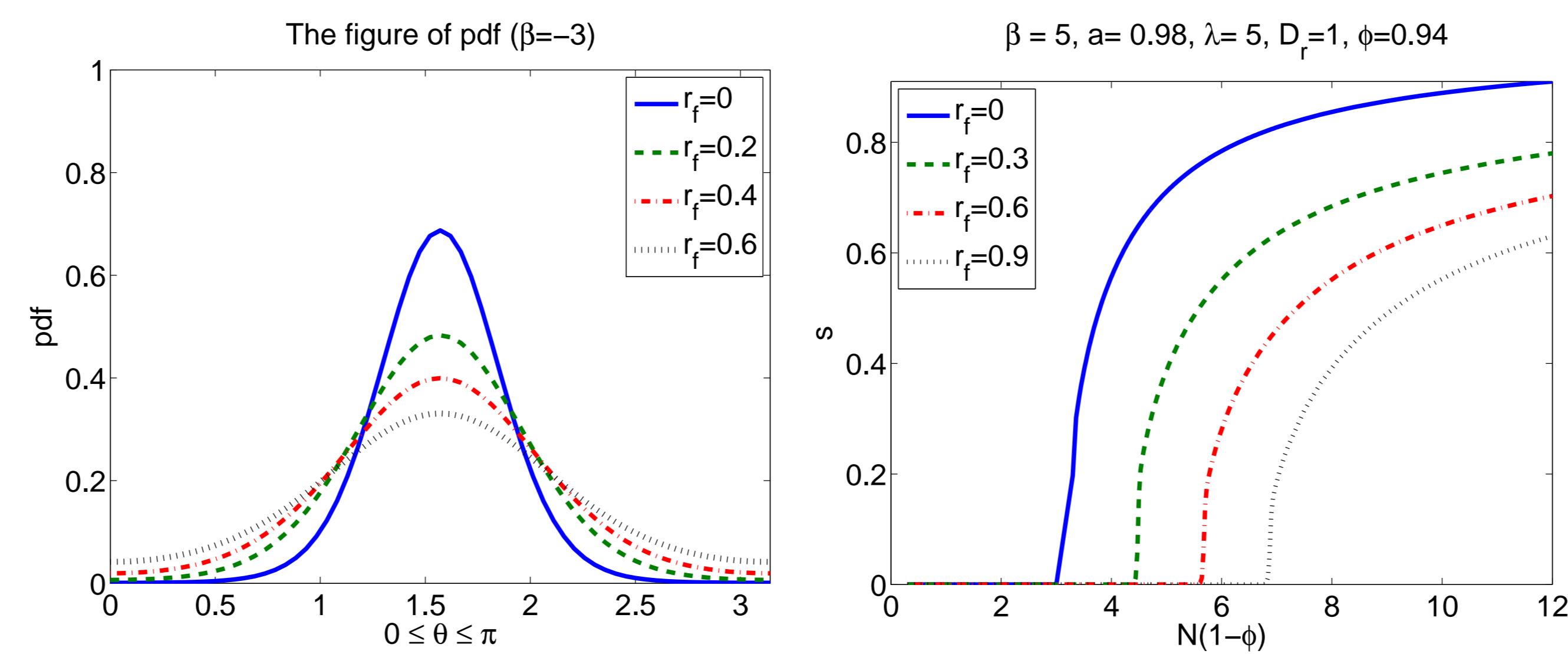
• Nanorod:  $N$ - concentration,  $r_f$ -nanorod semiflexibility,  $\mathbf{Q}$ - orientation tensor

• Polymer:  $\mathbf{U}$ : structure tensor,  $\beta$ : nanorod polymer surface interaction

### 4.1 Equilibria

All equilibria of the nanorod Smoluchowski equation and the polymer Smoluchowski equation are invariant under a planar rotation. The dual orientation of the nanorod ensemble and the polymer matrix are measured by the scalar order parameter  $s$  of the nanorod and the scalar order parameter  $s_u$  of the polymer matrix, respectively,

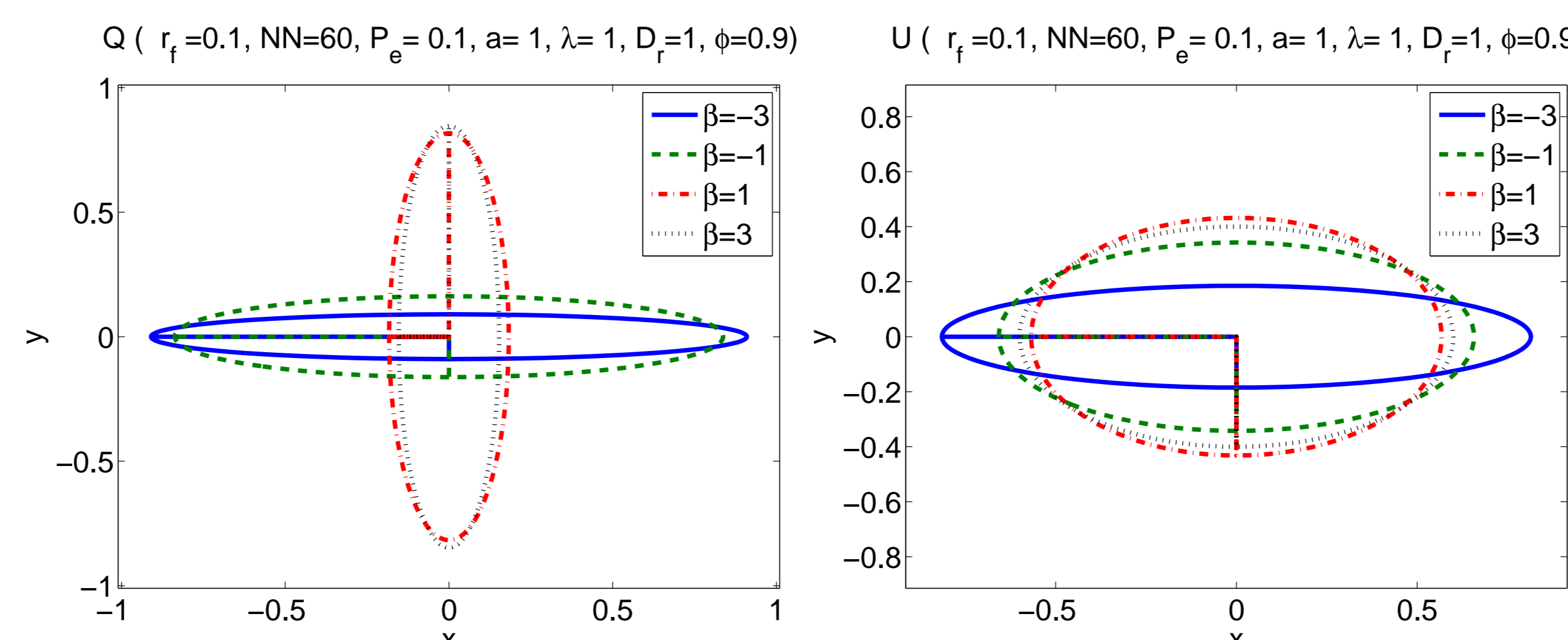
$$s = \sqrt{2(\mathbf{Q} - \mathbf{I}/2) : (\mathbf{Q} - \mathbf{I}/2)}, s_u = \sqrt{2(\mathbf{U}/\text{tr}(\mathbf{U}) - \mathbf{I}/2) : (\mathbf{U}/\text{tr}(\mathbf{U}) - \mathbf{I}/2)}. \quad (6)$$



The left figure shows the equilibrium pdf for different nanorod semi-flexibility  $r_f$ . The peak of the pdf solution is lowered as  $r_f$  increases, indicating the enhanced semi-flexibility reduces the local degree of orientation. The right figure shows the bifurcation diagram of the nanorod orientational order parameter  $s$  as a function of the effective concentration  $N(1 - \phi)$ . The effect of increasing  $r_f$  is shown to delay the formation of the nematic phase in the nanocomposite to higher concentration.

### 4.2 Planar elongation

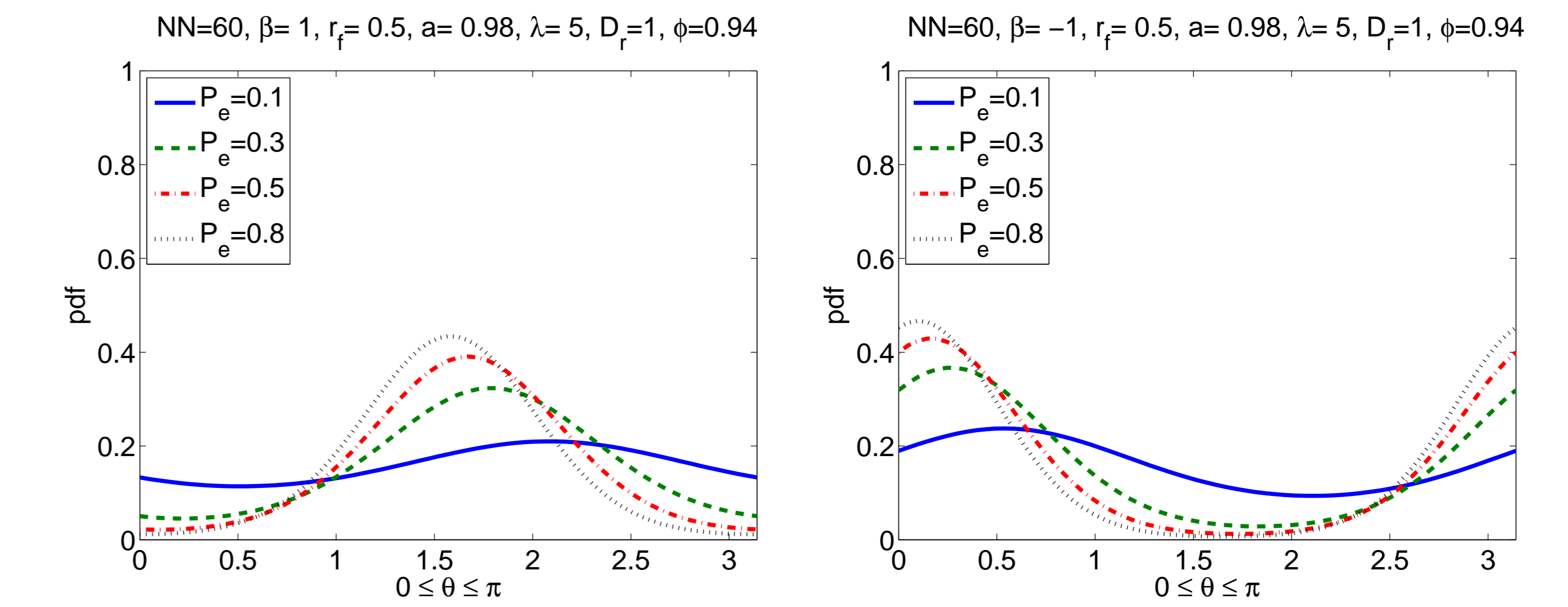
For an imposed elongational flow  $\mathbf{v} = (P_e x, -P_e y)$ , where  $P_e$  is the Peclet number. Elongation is a strong flow, in which all the sustainable solutions are stable steady states.



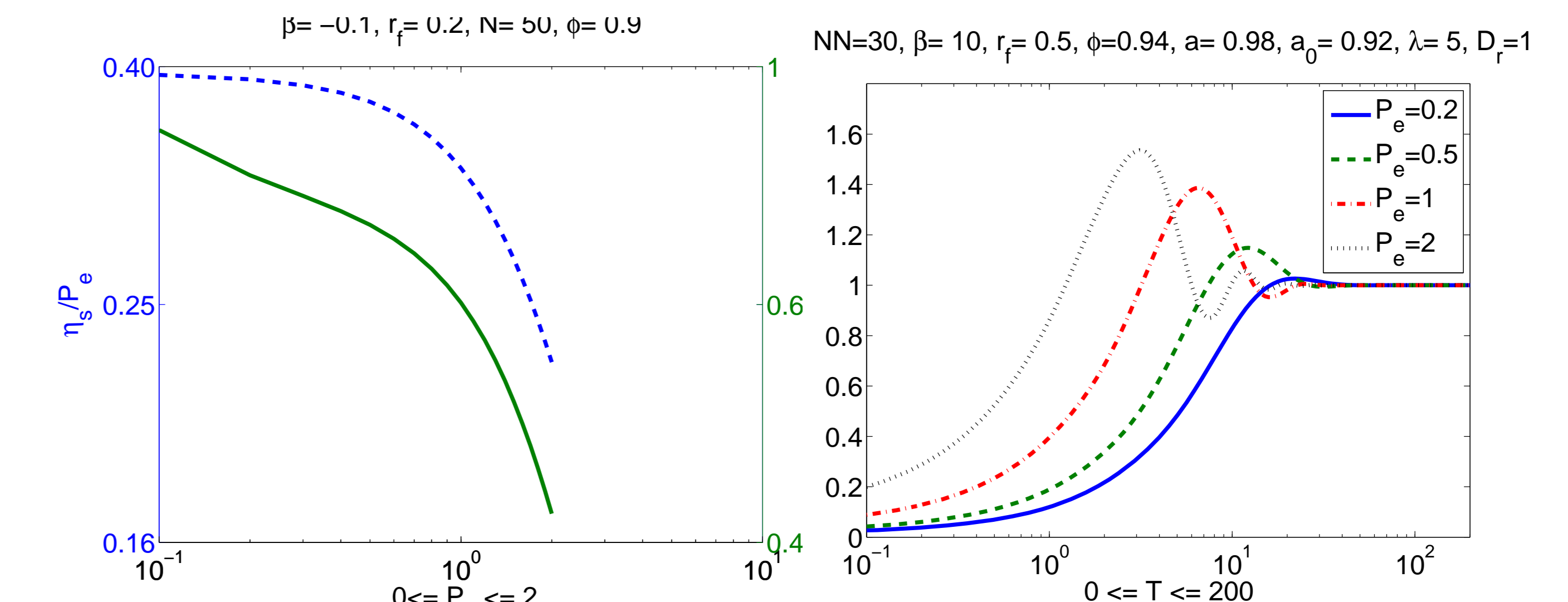
In above figures, the orientation tensor  $\mathbf{Q}$  (left) and structure tensor  $\mathbf{U}$  (right) are depicted as ellipses. The right figure shows that the flow aligns the polymer matrix to the flow (i.e. the stretching direction or the x-axis). However, the nanorod alignment is slaved by the detail of the nanorod-polymer interaction (left). When  $\beta > 0$ , the interaction favors an orthogonal alignment between the nanorod phase and the flow-aligning polymer matrix; When  $\beta < 0$ , the nanorod phase aligns with the polymer matrix in the flow direction.

### 4.3 Plane shear

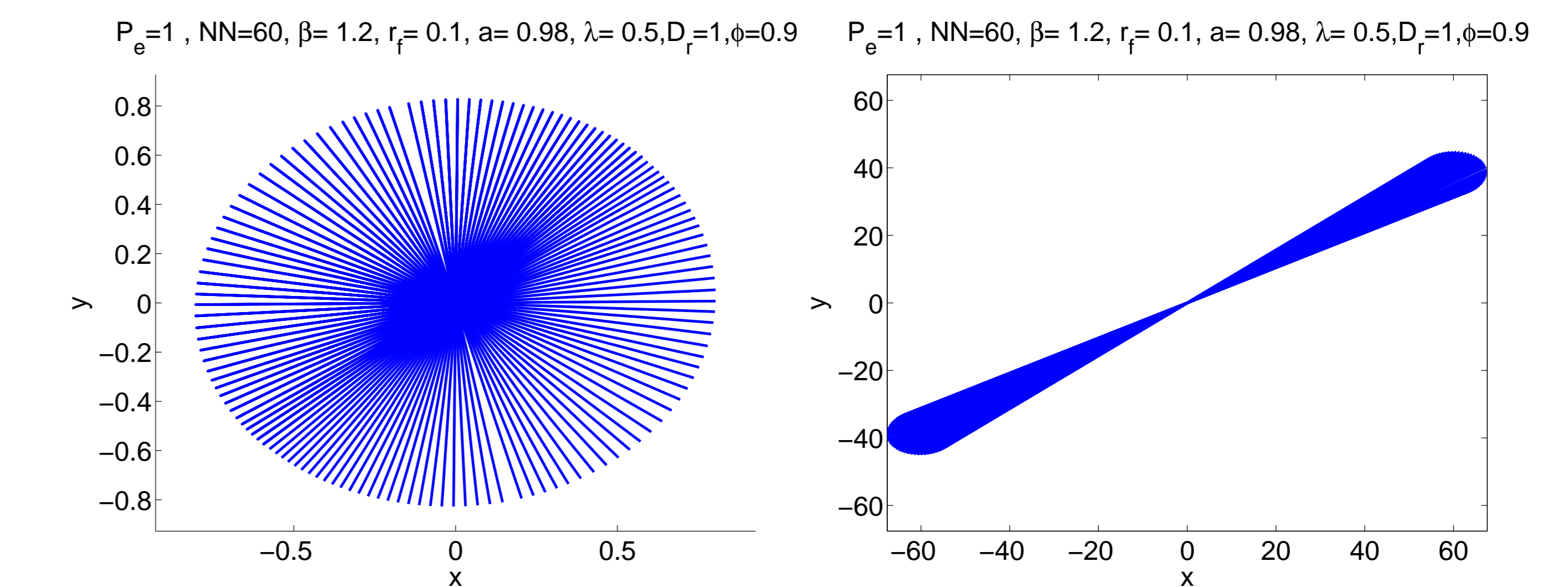
Consider an imposed shear flow  $\mathbf{v} = (P_e y, 0)$ , the nanorod kinetic equation admits either steady or time-periodic solutions in various regimes of the parameter space.



For steady states, above are the pdf solutions for various  $P_e$ , when  $\beta = 1$  (left) and  $\beta = -1$ .



The steady state shear viscosity, defined by  $\eta_s = \frac{\tau_{xy}}{P_e}$ , shows shear thinning behavior consistently (left figure). Transient shear viscosity demonstrates a sequence of actions: initial climbing, overshooting and then reaching a plateau (right figure). The shear viscosity prediction qualitatively captures the behavior observed in experiment [5].



Time-periodic solutions exist in this system at some regimes of  $P_e$  and  $N(1 - \phi)$ . For the time-periodic solutions, we observe either tumbling (left figure) or wagging behavior in the nanorod ensemble. In the meantime, the polymer matrix synchronically exhibits wagging behavior (right figure).

## 5 Acknowledgment

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## References

- [1] M. G. Forest, R. Zhou, and Q. Wang, "Chaotic boundaries of nematic polymers in mixed shear and extensional flows," *Physical Review Letters*, 93 (8) (2004), pp. 088301-088305.
- [2] G. Forest and Q. Wang, Hydrodynamic theories for blends of flexible polymer and nematic polymers, *Physical Review E*, 72 (2005), pp. 041805.
- [3] Alexei R. Khokhlov and Alexander N. Semenov, Liquid-Crystalline Ordering in Solutions of Semiflexible Macromolecules with Rotational-Isomeric Flexibility, *Macromolecules* 1984,17, 2678-2685.
- [4] C. Canuto, M. Y. Hussaini, A. Quarteroni, and T. A. Zang, *Spectral Methods Evolution to Complex Geometries and Applications to Fluid Dynamics*, Springer-Verlag, Berlin-Heidelberg, 2007.
- [5] Defeng Wu, Chixing Zhou, Zheng Hong, Dalian Mao, Zhang Bian, Study on rheological behaviour of poly(butylene terephthalate)/montmorillonite nanocomposites, *European Polymer Journal* 41 (2005), 21992207.