Critical Thresholds in Kinetic Equations for Polymers

Hailiang Liu

Department of Mathematics
Iowa State University
http://orion.math.iastate.edu/hliu
hliu@iastate.edu

CSCAMM, April 16-20, 2007

Outline

- Mathematical models
- Equilibrium solutions

  —Uniaxial symmetry

  —Number and type of equilibrium solutions
- Global orientation dynamics

  —Dynamics of orientation tensor

  —Stability and global dynamics
- The FENE dumbbell models

  —Dumbbell models for semi-flexible polymers

  — Boundary conditions and trace

Phenomena in complex fluids

- Fluids with complex microstructure abound in daily life and in many industrial processes, peculiar phenomena appear due to many effects such as
  normal stress – a tension force in flow direction
  elongational viscosity — large elastic force
  flow contraction — corner singularity
  viscoelastic flow instability — pattern formation
- Detection of critical thresholds for physical parameters is particularly helpful in understanding various peculiar behaviors.

Mathematical models

- Balance laws for fluid motion

$$\nabla \cdot u = 0, \quad u = velocity$$
$$\rho(u_t + u \cdot \nabla u) = \nabla \cdot (\tau) - \nabla p + \nu \Delta u.$$

  where $\tau =$extra stress tensor, forces where material develops in response to being deformed.

- Orientation dynamics for polymers
  At the molecule level, Brownian forces are more important than the inertial force. Let m denote the orientation vector of assumed shape (rod or dumbbell) of polymer molecules, then orientation dynamics is governed by the Langevin equation

$$\zeta dm = -\nabla_m U dt + g dW_t, \quad dx = u dt.$$

Fokker-Planck equations

- The Fokker-Planck equation

$$\partial_t f(t, x, m) + ... = D_m \cdot (f D_m U) + D_m \cdot D_m f.$$

  Different potential leads to different models.

- Two widely accepted kinetic models for polymers:
  (i) Doi-Onsager models for rigid rod-like polymers

$$D_m = \mathcal{R}, \quad \mathcal{R} := m \times \frac{\partial}{\partial m}, \quad |m| = 1.$$

  (ii) FENE Dumbbell models for polymer chains

$$D_m = \nabla_m, \quad |m|^2 \leq b.$$

The Doi-Onsager equation

- Consider the Doi-Onsager equation

$$\mathcal{R} \cdot (\mathcal{R}f + f\mathcal{R}U) = 0, \quad \int_{|m|=1} f(m)dm = 1,$$

or the Boltzmann relation: $f = Z^{-1}e^{-U}$, with the Maier-Saupe potential (1958)

$$U(m) = \alpha \int |m \times m'|^2 f(m')dm'.$$

- Our goal (w/H. Zhang and P. Zhang): give a complete classification of phase transitions to equilibrium solutions in terms of α
  — Uniaxial symmetry of all equilibrium solutions
  — Phase transition in terms of critical intensities

Orientation tensor

Let $f(m)$ be a general local distribution of molecular orientations, the traceless order tensor is

$$Q := \int_{|m|=1} (m \otimes m - \frac{1}{3} I) f(m) dm.$$

It is uniaxial if two eigenvalues of Q coincide.

- Eigen-decomposition

$$Q = \lambda_1 e_1 \otimes e_1 + \lambda_2 e_2 \otimes e_2 + \lambda_3 e_3 \otimes e_3.$$

- Relation with two free parameters

$$3aQ : e_3 \otimes e_3 + bQ : (e_1 \otimes e_1 - e_2 \otimes e_2) = 0,$$

where $a = \alpha(\lambda_2 - \lambda_1)/2$ and $b := 3\alpha\lambda_3/2$.

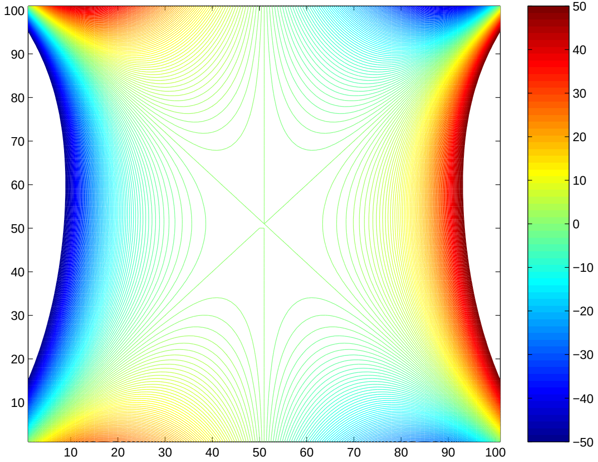
The Maier-Saupe potential

- Boltzmann's relation: $f = Z^{-1}e^{-U}, \quad Z = \int e^{-U} dm.$
- For the Maier-Saupe potential $U = V + \frac{2}{3}\alpha$ with

$$V = -m \otimes m : (\alpha Q) = a\left(m_1^2 - m_2^2\right) + b\left(\frac{1}{3} - m_3^2\right).$$

- leading to an $\alpha-$free relation $F(a,b) = 0$ where

$$F(a,b) := \int_{|m|=1} [b(m_1^2 - m_2^2) + a(3m_3^2 - 1)]e^{-V} dm.$$


100
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
100
50
40
30
20
10
0
−10
−20
−30
−40
−50

Uniaxial Symmetry

- It is shown that for any b the only zeros of F are $a = \{0, \pm b\}$ — Comm. Math. Sci. Vol 3(2)(2005), 201-218.
- **Theorem (w/H. Zhang and P. Zhang)**
  Consider the Doi-Onsager equation on a sphere with the normalization. Let U be the Maier-Saupe potential. Then such a potential is necessarily invariant with respect to rotations around a director $\mathbf{n} \in \mathbb{S}^2$, i.e., it is uniaxially symmetric. Moreover, this potential must have the following form
  $$U = \frac{2\alpha}{3} - b\left((\mathbf{m} \cdot \mathbf{n})^2 - \frac{1}{3}\right),$$
  where $b \in \mathbb{R}$ is an orientation parameter.

References:

1. **P. Constantin, I. Kevrekidis and E.S. Titi**, *Arch. Rat. Mech. Anal.,* **174** *(2004), 365-384.*
Solutions of the Doi-Onsager model were classified in the high concentration limit. The isotropic state is shown to be the only possible solution at low enough concentration.
2. **I. Fatkullin and V. Slastikov** (2005)
A different proof of the uniaxial symmetry was given at about the same time.
3. **H. Zhou, H. Wang, G. Forest and Q. Wang**
A new proof ...

Number and type of equilibria

Assume the axis of uniaxial symmetry is e_3, i.e., $a = 0$. Thus

$$V = b\left(\frac{1}{3} - m_3^2\right).$$

Thereby the Boltzmann distribution becomes

$$f = ke^{bm_3^2}, \quad k = \left[4\pi \int_0^1 e^{bz^2} dz\right]^{-1}.$$

Note that b has to satisfy

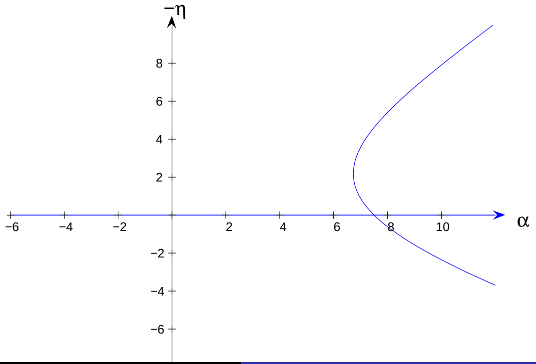
$$b = \frac{3\alpha}{2} Q : (e_3 \otimes e_3) = \frac{\alpha}{2}\left(3\int_{|m|=1} m_3^2 f(m) dm - 1\right).$$

Phase transitions

- A simple calculation gives

$$\alpha = G(b) := \frac{\int_0^1 e^{bz^2} dz}{\int_0^1 (z^2 - z^4) e^{bz^2} dz}.$$

- Critical Intensity α vs. $b = -\eta$



Explicit representation of all solutions

Theorem (w/H. Zhang and P. Zhang)
(i) The number of equilibrium solutions hinges on whether the intensity α crosses two critical values: $\alpha^* \approx 6.7314$ and 7.5.
(ii) All solutions are given explicitly by

$$f = k\, e^{b(\mathbf{m}\cdot\mathbf{n})^2}, \quad k = [4\pi \int_0^1 e^{bz^2} dz]^{-1},$$

where $\mathbf{n} \in \mathbb{S}^2$ is a dominated director, $\alpha = G(b)$.

Critical intensities

- If $0 < \alpha < \alpha^*$, there exists one solution $f_0 = 1/4\pi$.
- If $\alpha = \alpha^*$, there exist two distinct solutions $f_0 = 1/4\pi$ and $f_1 = k_1\, e^{b_1(m\cdot n)^2}$, $b_1 > 0$.
- If $\alpha^* < \alpha < 15/2$, there exist three distinct solutions $f_0 = 1/4\pi$ and $f_i = k_i\, e^{b_i(m\cdot n)^2}$, $b_i > 0$ (i=1,2).
- If $\alpha = 15/2$, there exist two distinct solutions $f_0 = 1/4\pi$ and $f_1 = k_1\, e^{b_1(m\cdot n)^2}$, $b_1 > 0$.
- If $\alpha > 15/2$, there exist three distinct solutions $f_0 = 1/4\pi$ and $f_i = k_i\, e^{b_i(m\cdot n)^2}(i = 1, 2)$, $b_1 > 0$, $b_2 < 0$.

Onsager's theory (1949)

- Variational approach:

$$\min_f A(f), \quad \int f d\mathbf{m} = 1,$$

where A is the total free energy

$$A(f) = \int_{|\mathbf{m}|=1} f ln f + \frac{1}{2} f U d\mathbf{m}$$

with the potential U defined by

$$U = \alpha \int_{|\mathbf{m}'|=1} \beta(\mathbf{m}, \mathbf{m}') f(\mathbf{m}') d\mathbf{m}'$$

- Onsager's aim (1949):
  (1) derivation of the function $\beta \sim sin(\theta)$, where θ is the angle between $\mathbf{m}$ and $\mathbf{m}'$
  (2) study of the limit of high concentration ...

Onsager's conjecture

- Uniaxial symmetry of probability distributions

$$f(\mathbf{m}) = \psi(\mathbf{m} \cdot \mathbf{n}), \quad \mathbf{n} \in \mathbb{S}^2.$$

- Phase transition: Based on an assumed remarkable ansatz

$$f = \frac{\eta}{2\pi sinh\eta} \cdot cosh(\eta m \cdot n), \quad \forall n \in \mathbb{S}^2,$$

Onsager (1949, Ann N. Y. Acad. Sci. 51, p.627) was able to argue that in the limit of $\alpha \to \infty$ one has transition from the isotropic uniform distribution to an ordered prolate distribution ...

The Hess-Doi kinetic theory (70'-80')

- Effects from external fields: $\mathbf{m} \in \mathbb{S}^2$ rod orientation, u fluid velocity

$$\frac{\partial f}{\partial t} = \mathcal{R} \cdot \hat{D}_r(\mathcal{R}f + U\mathcal{R}f)) - \mathcal{R} \cdot (\mathbf{m} \times \kappa \cdot \mathbf{m}f).$$

$\mathcal{R} = \mathbf{m} \times \frac{\partial}{\partial \mathbf{m}}$: the rotational operator
$\hat{D}_r$ rotational diffusion coefficient
$\kappa = (\nabla \mathrm{u})^T$, U thermodynamic interaction potential.

- Ignore external field: Doi-Smoluchowski equation

$$\frac{\partial f}{\partial t} = \mathcal{R} \cdot (\mathcal{R}f + U\mathcal{R}f), \quad \int_{|m|=1} f(t, m) = 1.$$

A look at history development

- L. Onsager (1949): Onsager's conjecture
- P.J. Flory (1956): lattice theory
- J. L. Ericksen (1960): stress tensor
- F.M. Leslie (1968): director equation
- S. Hess (1976): kinetic description
- M. Doi (1981): kinetic equation
- G. Marrucci (1982): derive EL theory from the Doi theory
- N. Kuzuu and M. Doi (1983): constitutive equation
- ...
- P. Constantin et al (2004): revisit Onsager's conjecture

A look at level of models

- The Onsager equation

$$\ln f(m) + U[f](m) = Const$$

- The Doi-Onsager equation

$$\frac{\partial f}{\partial t} = \mathcal{R} \cdot (\mathcal{R} f + U \mathcal{R} f).$$

- The Smoluchowski equation

$$\frac{\partial f}{\partial t} = \mathcal{R} \cdot \hat{D}_r(\mathcal{R} f + U \mathcal{R} f)) - \mathcal{R} \cdot (\mathbf{m} \times \kappa \cdot \mathbf{m} f).$$

- Coupling with Navier Stokes systems

$$u_t + u \nabla_x \cdot u + \nabla_x p = \nu \Delta_x u + \nabla_x \cdot \tau, \quad div(u) = 0.$$

- Effects of imposed external fields such as electric, magnetic fields

Questions of stability

Are these equilibria stable?

- Stability of equilibria via energy comparison (Onsager's program)
- Global orientation dynamics via the kinetic equation

How do external fields affect the orientation dynamics?

- How are polymers oriented by: magnetic and electric fields?
- Effects of fluids: shear flow, elongation flow ...

Stability via energy comparison

- Let $A(a,b)$ be the free energy for $f(t,m;a,b)$ with $(0,b^*)$ being the equilibrium, we have

$$A(a,b) = A(0,b^*) + X^\top D^2 A X/2, \quad X = (a, b-b^*)^\top.$$

Here $A_{ab}(0,b) = 0$ and

$$Diag(D^2A)(0,b) = \begin{cases} \left(\frac{4(7.5-\alpha)}{15\alpha}, \frac{4(7.5-\alpha)}{45\alpha}\right), & b=0 \\ \left(\frac{1}{3\alpha}(7.5-\alpha+b), \frac{2b}{3\alpha^2}G'(b)\right), & G(b)=\alpha. \end{cases}$$

- Stability

– $0 < \alpha < \alpha^*$, isotropic phase is stable;

– $\alpha^* < \alpha < 7$, both the isotropic and larger nematic prolate are stable;

– $\alpha > 7.5$, only the nematic prolate phase is stable.

Dynamic energy and orientation tensor

- Dynamic energy

$$\mathcal{A}[f](t) = \int f\ln f + \frac{1}{2} fU dm.$$

- Asymptotic towards $f_{eq} = ke^{b(\mathbf{m}\cdot\mathbf{n})^2}$

$$\frac{d}{dt}\mathcal{A} = -\int (\mathcal{R}(\ln f + U))^2 f dm \leq 0.$$

- The mesoscopic orientation tensor Q is the traceless matrix

$$Q := \langle m \otimes m \rangle - \frac{1}{3} I.$$

- Spectral dynamics: evolution of eigenvalues of Q.

Orientation tensor dynamics

- Second moment equation

$$\frac{d}{dt}\langle mm\rangle = -6\langle mm - \frac{1}{3}I\rangle - \langle \mathcal{R}\cdot Um + m\mathcal{R}\cdot U\rangle,$$

which for the Maier-Saupe potential leads to

$$\dot{Q} = -6Q + 2\alpha(Q\cdot\langle mm\rangle + \langle mm\rangle\cdot Q) - 4\alpha Q : \langle mmmm\rangle.$$

- Doi's moment closure

$$Q : \langle mmmm\rangle = Q : \langle mm\rangle\langle mm\rangle.$$

$$\dot{Q} = F(Q)$$
$$F(Q) = \left(\frac{4\alpha}{3} - 6\right)Q + 4\alpha Q^2 - 4\alpha Tr(Q^2)\left(Q + \frac{1}{3}I\right).$$

Spectral dynamics of the structure tensor

- Spectral dynamics: Let λ_i be eigenvalues of Q, then

$$\dot{\lambda}_i = \left(\frac{4\alpha}{3} - 6\right)\lambda_i + 4\alpha\lambda_i^2 - 4\alpha\sum_{j=1}^{3}\lambda_j^2\left(\lambda_i + \frac{1}{3}\right), \quad i = 1, 2, 3.$$

- Global invariant

$$\frac{d}{dt}(\lambda_i - \lambda_k) = (\lambda_i - \lambda_k)\left[(\frac{4\alpha}{3} - 6) + 4\alpha(\lambda_i + \lambda_k) - 4\alpha\sum_{j=1}^{3}\lambda_j^2\right].$$

Theorem

The uniaxial symmetry of the orientation distribution function is preserved in time.

A polynomial dynamical system

- $$\frac{2a}{\alpha} = \lambda_2 - \lambda_1, \quad \lambda_3 - \lambda_2 = \frac{c}{\alpha}, \quad c := b - a.$$

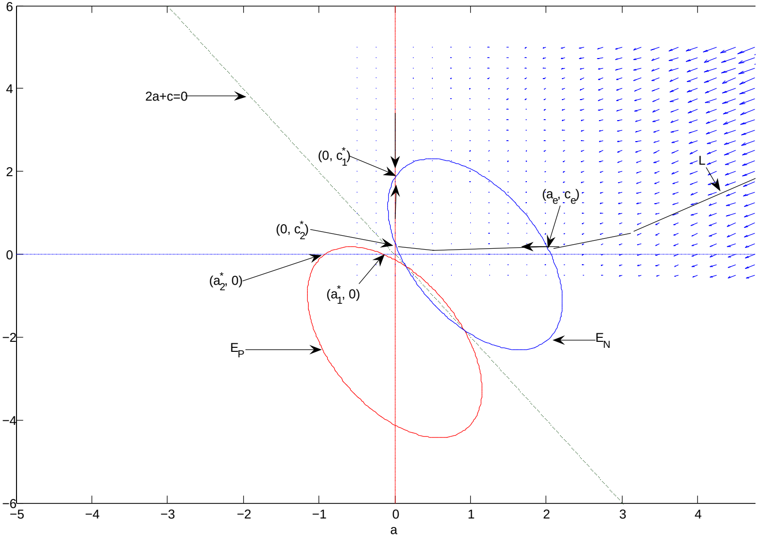
  Invariants: $\lambda_1 = \lambda_2(a = 0)$ and $\lambda_2 = \lambda_3(a = b)$, and $\lambda_1 = \lambda_3(b = -a)$.
- The reduced system for (a, c) is

$$\dot{a} = aP(a,c), \quad P(a,c) := \left[(\frac{4\alpha}{3} - 6) - \frac{8}{3}(a + c) - \frac{8}{3\alpha}(4a^2 + 2ac + c^2) \right], \tag{1}$$

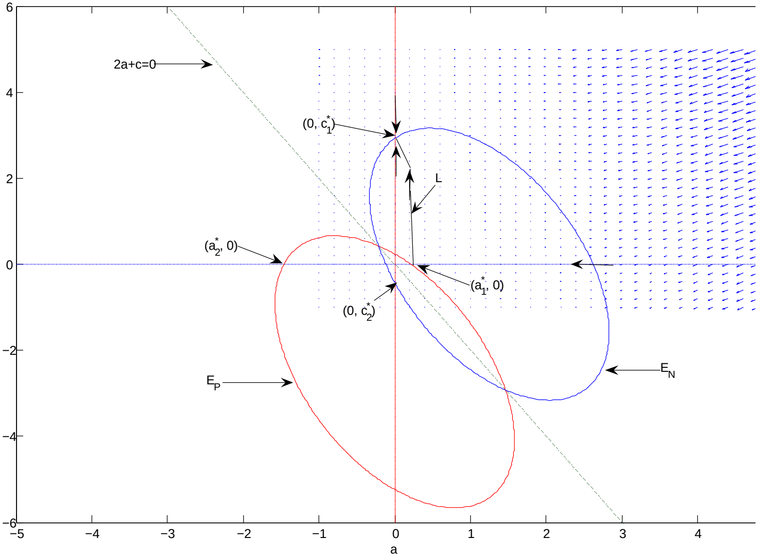
$$\dot{c} = cN(a,c), \quad N(a,c) := \left[(\frac{4\alpha}{3} - 6) + \frac{4}{3}(4a + c) - \frac{8}{3\alpha}(4a^2 + 2ac + c^2) \right] \tag{2}$$

We investigate both the linear stability of equilibria and the global dynamics of general solutions.

Phase field diagram



Phase field diagram



Time-asymptotic stability

Theorem

The number of equilibrium states for the closed orientation model of the Doi-Smoluchowski equation on the sphere hinges on whether the intensity α crosses two critical values: $\alpha = 4$ and 4.5. Moreover,

(i). if $0 < \alpha < 4$, only isotropic phase exists and is stable;
(ii). if $4 < \alpha < 4.5$, there are three equilibrium phases, among which both the isotropic phase and one nematic P phase are stable, another nematic P phase is unstable.
(iii). if $\alpha > 4.5$, there are three equilibrium phases. Only the nematic P phase is stable, both isotropic and nematic O phases are unstable.

Global orientation dynamics in polymers (Liu, Physics D.)

Theorem

Consider the closed orientation model of the Doi-Smoluchowski equation on the sphere. Given initial states lie in any region of a spectral order, then
(i). if $0 < \alpha < 4$*, all initial states will evolve into the isotropic state;*
(ii). if $4 < \alpha < 4.5$*, there exists a critical threshold for the initial configuration. An initial state will evolve into either the isotropic phase or the stable nematic prolate phase, depending on whether such an initial state crosses the critical threshold.*
(iii). if $\alpha > 4.5$*, all initial states will evolve into the nematic prolate phase.*

The Microscopic FENE Models (w/Chun Liu)

- Dumbbell models for flexible polymers
- The FENE potential
- Critical finite extension parameter
- Boundary conditions and traces of the PDF

Microscopic FENE models

- Let m be an end-to-end vector, then

$$dm = (\nabla_x u)^\top m + \left(-\frac{2}{\gamma}\nabla_m U\right) dt + \sqrt{\frac{4k_B T}{\gamma}} dW_t, \quad dx = udt.$$

- The Fokker-Planck equation is

$$\partial_t f + u\cdot\nabla_x f + \nabla_m\cdot(\kappa m f) = \frac{2}{\gamma}\left[(\nabla_m\cdot(\nabla_m U f) + k_B T\Delta_m f)\right],$$

  where $\kappa = \nabla_x u$ is the strain rate tensor; U denotes the spring potential; γ is the friction coefficient, T is the absolute temperature, and k_B is the Boltzmann constant.
- The FENE (Finite Extendible Nonlinear Elasticity) potential:

$$U(m) = -\frac{Hb}{2} log(1 - |m|^2/b).$$

Some basic issues for FENE models

Observe that since the FP equation experiences singularity on the sphere $|m| = \sqrt{b}$, the data may not be necessarily well defined. The main issues of our interest are:

- whether Dirichlet boundary conditions are necessary;
- if the PDF solution is regular enough to have a trace on the boundary, what is its trace, no matter whether the data is pre-imposed or not.

Math results are rather recent

B. Jourdain, T. Lelièvre (2002)[Probability to reach boundary]
B. Jourdain, T. Lelièvre and C. Le Bris (2004)[local existence for SDE models with FENE potential]
J.W. Barrett, C. Schwab and E. Suli (2005) [global existence with zero boundary PDF]
Q. Du, C. Liu and P. Yu (2005) [Moment closure with zero boundary PDF]
C. Le Bris, B. Jourdain, T. Lilièvre and F. Otto (2005)[Large time behavior in weighted Sobolev sapce]
H. Zhang and P. Zhang (2005) [Local existence in weighted Sobolev space].

More on related models: **P. Degond, P. L. Lions, F. Lin,** ,...

The non-dimensional FENE parameter

- The key non-dimensional parameter is

$$Li := \frac{Hb}{k_B T},$$

identified by the following scaling

$$(x, u, t, m, b) \to \left(\frac{x}{L_0}, \frac{u}{U_0}, \frac{t}{T_c}, \frac{m}{l}, \frac{b}{l^2} \right)$$

where $T_c := L_0/U_0$, $l := \sqrt{\frac{k_B T}{H}}$.

$$\partial_t f(t, m) + \nabla_m \cdot (\kappa m f) = \frac{1}{2}(\nabla_m \cdot (\nabla_m U f) + \Delta_m f),$$

where

$$\nabla_m U = \frac{m}{1 - |m|^2/Li}.$$

The Fichera function and boundary conditions

The difficulty of the problem lies in the singularity of the equation occurring at boundary.

Our idea is to introduce v by

$$f(t,m) = v(t,x)e^{-U(m)}, \quad x = \sqrt{2}m,$$

then rewrite the equation into a second order equation

$$\begin{aligned} L(v) &:= (r^2 - |x|^2)\Delta_x v - (r^2 - |x|^2)v_t \\ &\quad -(Lix + (r^2 - |x|^2)\kappa x) \cdot \nabla_x v + Lix^\top \kappa x v, \quad r = 2Li^2. \end{aligned}$$

This has a standard form

$$L(v) :\equiv a^{kj}(\xi)v_{\xi_k\xi_j} + b^k(\xi)v_{\xi_k} + c(\xi)v = 0, \quad k,j = 0\cdots d,$$

for which the boundary condition is needed only when the Fichera function $\Gamma(t,x) = (b^k - a^{kj}_{\xi_j})n_k$ is negative.

Boundary conditions

For the underlying Fokker-Planck equation, any Dirichlet boundary condition will become redundant once the non-dimensional parameter $Li \geq 2$;

Theorem

Let $T^* > 0$ be any fixed number. Consider the FP equation in the domain $\Omega(T^*) := \{(t, m),\ 0 \leq t \leq T^*, |m| < \sqrt{Li}\}$.
(i) When $Li < 2$, Dirichlet boundary conditions imposed on $|m|^2 = Li$ lead to a well-posed problem.
(ii) When $Li \geq 2$, any Dirichlet boundary condition on $|m|^2 = Li$ will become redundant.

Transformation and maximum principle

We further investigate the trace of the PDF on the sphere $|m| = \sqrt{Li}$ where no data is pre-imposed. Our approach is to convert the equation by a transformation

$$f(t,m) = v(t,\sqrt{2}m)(1-|m|^2/(Li))^{Li/2-\alpha}e^{Kt},$$

in such a way that the resulting equation $A(w) = 0$ supports a maximum principle. The operator $A(w)$ is defined as

$$\begin{aligned} A(w) \quad := \quad & (r^2-|x|^2)^2\Delta_x w + (4\alpha - Li)(r^2-|x|^2)x\cdot\nabla_x w \\ & -(r^2-|x|^2)^2\partial_t w + c(x)w, \end{aligned}$$

in which the coefficient

$$c(x) = -K(r^2-|x|^2)^2 + 2\alpha[dr^2 + (2\alpha+2-d-Li)|x|^2] < 0?$$

Trace

If the probability density function f is regular enough for its trace to be defined on the sphere $|m| = \sqrt{Li}$, then the trace is necessarily zero when $Li > 2$.

Theorem

Let $f_0(m)$ be a bounded measurable function in $|m| \le \sqrt{Li}$ with $\mathrm{supp}(f_0(m)) \subset \{m, |m| \le \sqrt{Li^*}\}$, $Li^* < Li$. Then for $Li > 2$ the solution $f(t,m)$ of the FP equation remains bounded and satisfies

$$|f| \le |f_0| \left(\frac{Li - |m|^2}{Li - Li^*} \right)^{Li/2-\alpha} e^{Kt},$$

where α and K satisfy

$$0 < \alpha < \frac{Li}{2} - 1, \quad K > K^* := \frac{\beta^2}{16 Li \alpha (Li - 2 - 2\alpha)} - \rho(Li - 2\alpha)$$

with $\beta = \rho(Li - \alpha) r^2 + 2\alpha(d + Li - 2 - 2\alpha)$ and $\rho = \sqrt{Tr(\kappa^\top \kappa)}$.

Summary

- For the MS potential detection of two critical intensities enables us to conclude:

  (1) All equilibria are necessarily uniaxial;

  (2) A sharp characterization in terms of two critical intensities is given.
- Global orientation dynamics via the Doi kinetic equation is delicate... results obtained so far for a moment closure model are expected to hold for the full model.
- For the FENE Dumbbell model we answered a fundamental question of whether Dirichlet boundary conditions are necessary.