Repertoire of nematic biaxial phases.

Fulvio Bisi

SMMM - Soft Matter Mathematical Modeling

Dip. di Matematica - Univ. di Pavia (Italy)

fulvio.bisi@unipv.it

1 Summary

- Introduction
- Biaxial Interactions
- Mean-Field Theory
- Free Energy and Stability
- Bogolubov Principle
- Tricritical and Triple Points
- Repertoire of Phases

2 Introduction

For more than 30 years has the hunt for nematic biaxial phases been going on.

Strong evidence for existence of this phase recently emerged:

- Acharya *et al.* (2004)
- Madsen *et al.* (2004)
- Merkel *et al.* (2004)

This should open a new era for research, in LC field, eventually ending in new applications.

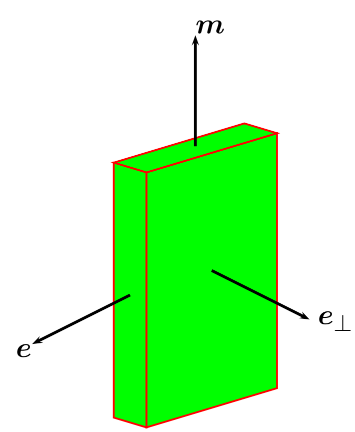
We need a complete model for uniaxial and biaxial nematic phases, and a thorough understanding of how they are related as a function of temperature.

3 Biaxial Interactions

Biaxial Molecules: described by platelets in which we distinguish three axes: $\boldsymbol{m}$, "major" axis, and $\boldsymbol{e}$, $\boldsymbol{e}_\perp$ (eigenvectors of any molecular polarizability tensor).

Two components for the anisotropic part of every molecular biaxial tensor:

$$\mathbf{q} := \boldsymbol{m} \otimes \boldsymbol{m} - \frac{1}{3}\mathbf{I}, \qquad \mathbf{b} := \boldsymbol{e} \otimes \boldsymbol{e} - \boldsymbol{e}_\perp \otimes \boldsymbol{e}_\perp \tag{1}$$



Interaction Energy between two molecules (Straley's potential):

$$V = -U_0[\mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b}' + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}'], \quad (2)$$

- *Remark 1*:

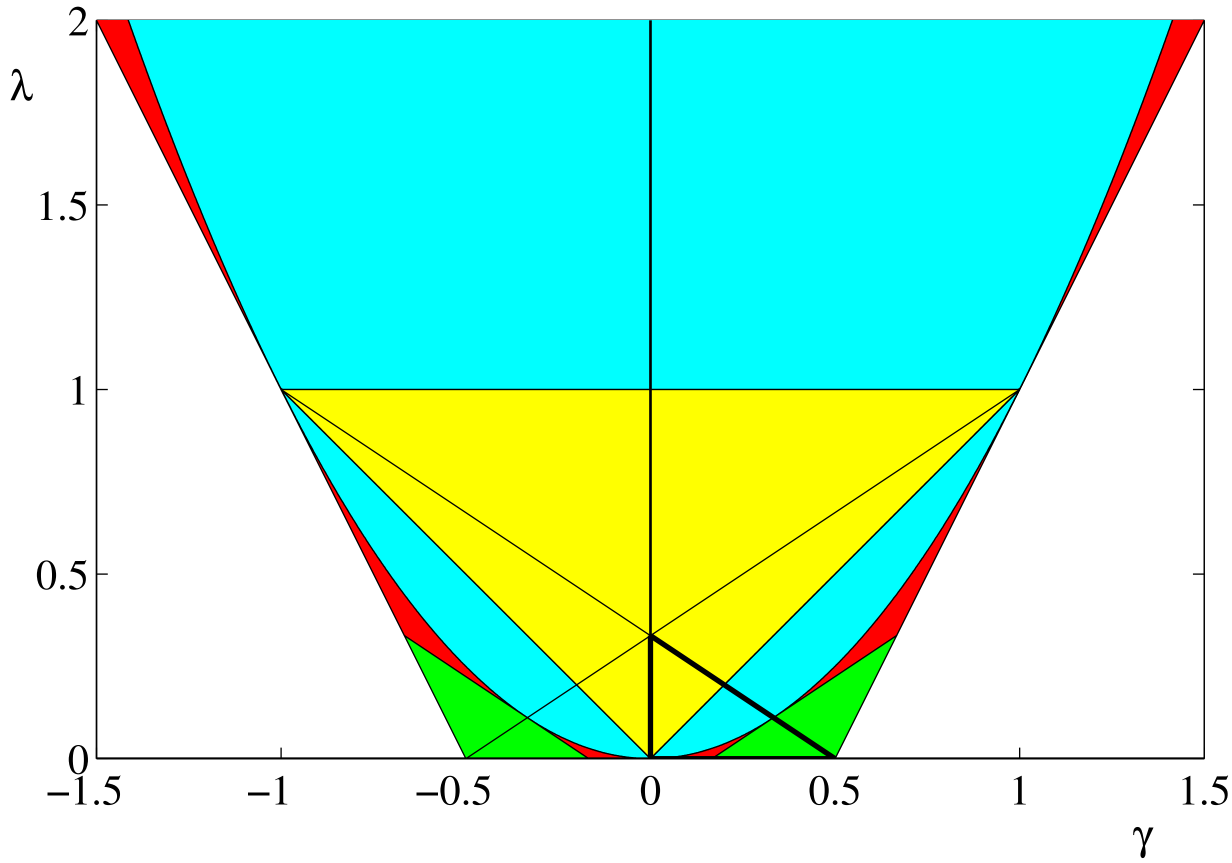
  $\lambda = \gamma = 0$ $\Rightarrow$ Maier-Saupe interaction energy.

- *Remark 2*:

  $\lambda = \gamma^2$ $\Rightarrow$ London's dispersion forces approximation.

- There exist $V-$invariant transformations (Longa et al., 2005; De Matteis et al., 2005)

Conjugation Chart



Ensemble Averages:

$$\mathbf{Q} := \langle \mathbf{q} \rangle =: S\left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I}\right) + T(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y) \tag{3a}$$

$$\mathbf{B} := \langle \mathbf{b} \rangle =: S'\left(\boldsymbol{e}_z \otimes \boldsymbol{e}_z - \frac{1}{3}\mathbf{I}\right) + T'(\boldsymbol{e}_x \otimes \boldsymbol{e}_x - \boldsymbol{e}_y \otimes \boldsymbol{e}_y) \tag{3b}$$

- *Remark 1*:
  unlike $\mathbf{q}$ and $\mathbf{b}$, $\mathbf{Q}$ and $\mathbf{B}$ are NOT orthogonal.

Terminology:

- Uniaxial Phases have $T = T' = 0$ (both $\mathbf{Q}$ and $\mathbf{B}$ uniaxial.
- Phase Biaxiality occurs when $S' = T' = 0$ (cylindrical molecules).
- Intrinsic Biaxiality occurs whenever $T' \neq 0$.

Order Parameter Manifold:

EULER ANGLES $(\vartheta, \varphi, \psi)$ representing the rotation that take $\{\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z\}$ into $\{\boldsymbol{m}, \boldsymbol{e}, \boldsymbol{e}_\perp\}$. Then:

$$S = \frac{3}{2} < \cos^2\vartheta - 1/3 > \Rightarrow -1/2 \leq S \leq 1 \tag{4a}$$

$$T = \frac{1}{2} < \sin^2\vartheta \cos 2\varphi > \Rightarrow -(1/3)(1-S) \leq T \leq (1/3)(1-S) \tag{4b}$$

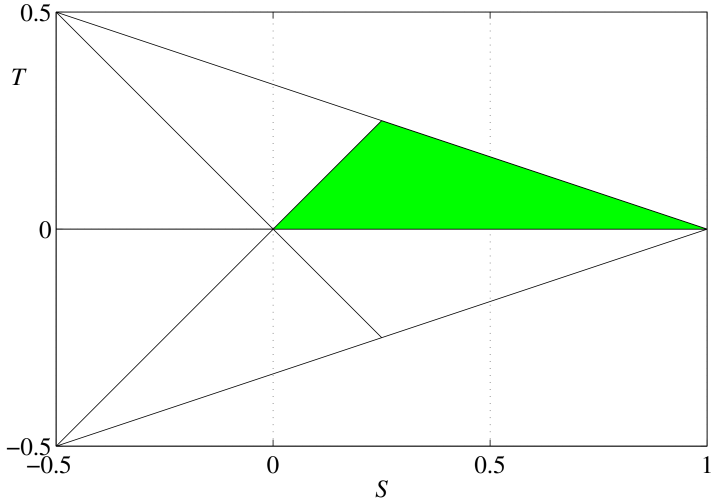
$$S' = \frac{3}{2} < \sin^2\vartheta \cos 2\psi > \Rightarrow -(1-S) \leq S' \leq (1-S) \tag{4c}$$

$$\begin{aligned} T &= \frac{1}{2} < (1+\cos^2\vartheta)\cos 2\varphi \cos 2\psi - 2\cos\vartheta \sin 2\varphi \sin 2\psi > \\ &\Rightarrow -1 \leq T' \leq 1 \end{aligned} \tag{4d}$$

Different set of order parameters may describe the same state: we recast (S, T, S', T') in a selected region of the order parameter manifold by using the mappings:

$$(S, T, S', T') \mapsto (S, -T, S', -T') \quad (5a)$$

$$(S, T, S', T') \mapsto \left(\frac{\pm 3T - S}{2}, \frac{T \pm S}{2}, \frac{\pm 3T' - S'}{2}, \frac{T' \pm S'}{2}\right) \quad (5b)$$



4 Mean-Field Model

Pseudopotential:

$$U = -U_0[\mathbf{q}\cdot\mathbf{Q} + \gamma(\mathbf{q}\cdot\mathbf{B} + \mathbf{b}\cdot\mathbf{Q}) + \lambda\mathbf{b}\cdot\mathbf{B}]\,, \tag{6}$$

Partition Function:

$$Z := \int_{\mathbb{T}} \exp[\beta(\mathbf{q}\cdot\mathbf{Q} + \gamma(\mathbf{q}\cdot\mathbf{B} + \mathbf{b}\cdot\mathbf{Q}) + \lambda\mathbf{b}\cdot\mathbf{B}]\,, \tag{7}$$

where $\mathbb{T} = \mathbb{S}^2 \times \mathbb{S}$ is the toroidal manifold, $\beta := U_0/(k_B T)$, with k_B being the Boltzmann constant and T the absolute temperature.

Free Energy:

$$\mathcal{F}^* := \mathcal{F}/U_0 = \frac{1}{2}(\mathbf{Q}\cdot\mathbf{Q} + 2\gamma\mathbf{Q}\cdot\mathbf{B} + \lambda\mathbf{B}\cdot\mathbf{B}) - \frac{1}{\beta}\log\frac{Z}{8\pi^2}$$

$$\frac{1}{3}S^2 + T^2 + 2\gamma(\frac{1}{3}SS' + TT') + \lambda(\frac{1}{3}(S')^2 + (T')^2) - \frac{1}{\beta}\log\frac{Z}{8\pi^2} \qquad (8)$$

The states corresponding to equilibrium point of F in (8) satisfy the compatibility conditions

$$\mathbf{Q} = \int_{\mathbb{T}} f\mathbf{q} = <\mathbf{q}> \qquad \mathbf{B} = \int_{\mathbb{T}} f\mathbf{b} = <\mathbf{b}> \qquad (9)$$

5 Bogolubov Principle

We can write the the interaction potential V as a function of new tensor variables:

$$V = -U_0(a^+\mathbf{q}^+ \cdot \mathbf{q}^{+\prime} + a^-\mathbf{q}^- \cdot \mathbf{q}^{-\prime}) \,, \tag{10}$$

with $\mathbf{q}^\pm := \mathbf{q} \pm \gamma^\pm \mathbf{b}$ and $\mathbf{q}^+ \cdot \mathbf{q}^- = 0$. Hence:

$$\mathcal{F}^*(\mathbf{Q}^+, \mathbf{Q}^-) = (a^+\mathbf{Q}^+ \cdot \mathbf{Q}^+ + a^-\mathbf{Q}^- \cdot \mathbf{Q}^-) - \frac{1}{\beta} \log \frac{Z}{8\pi^2} \,; \tag{11}$$

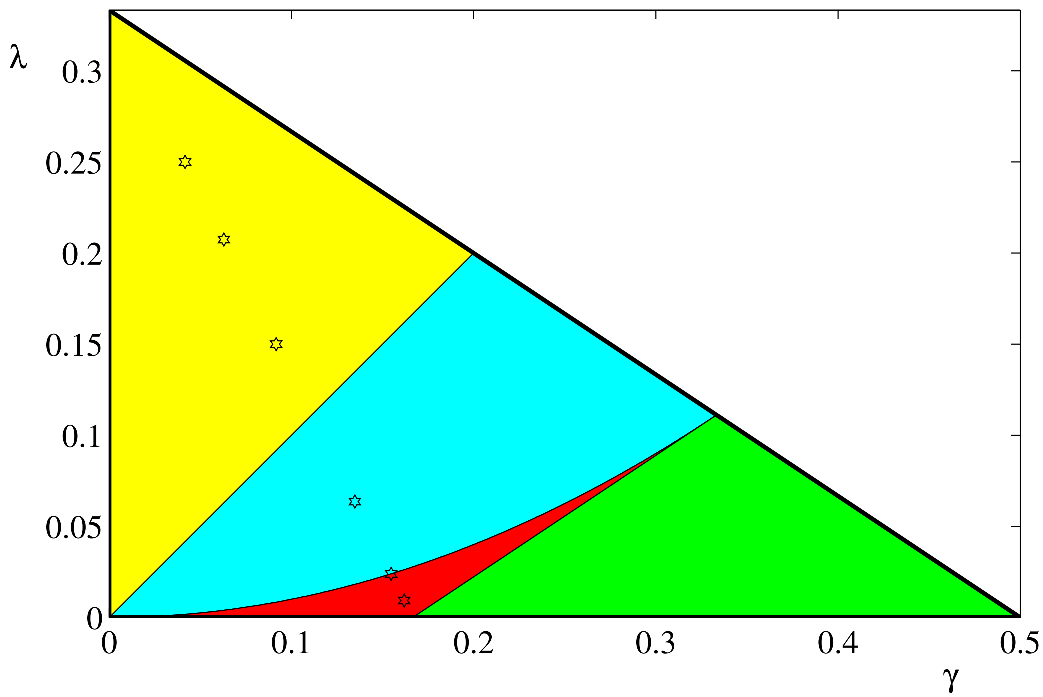
- Above the parabola, both a^+ and a^- are positive: stable states are local minima.
- Below the parabola, one coefficient is negative: $a^- < 0$. It can be shown that for all stationary states $\mathcal{F}$ has a maximum in $\mathbf{Q}^-$ at given $\mathbf{Q}^+$.

In this latter case, according to Bogolubov principle, the best approximation to the stable equilibrium state are given by:

$$\min_{\mathbf{Q}^+} \max_{\mathbf{Q}^-} \mathcal{F}(\mathbf{Q}^+, \mathbf{Q}^-)\,; \tag{12}$$

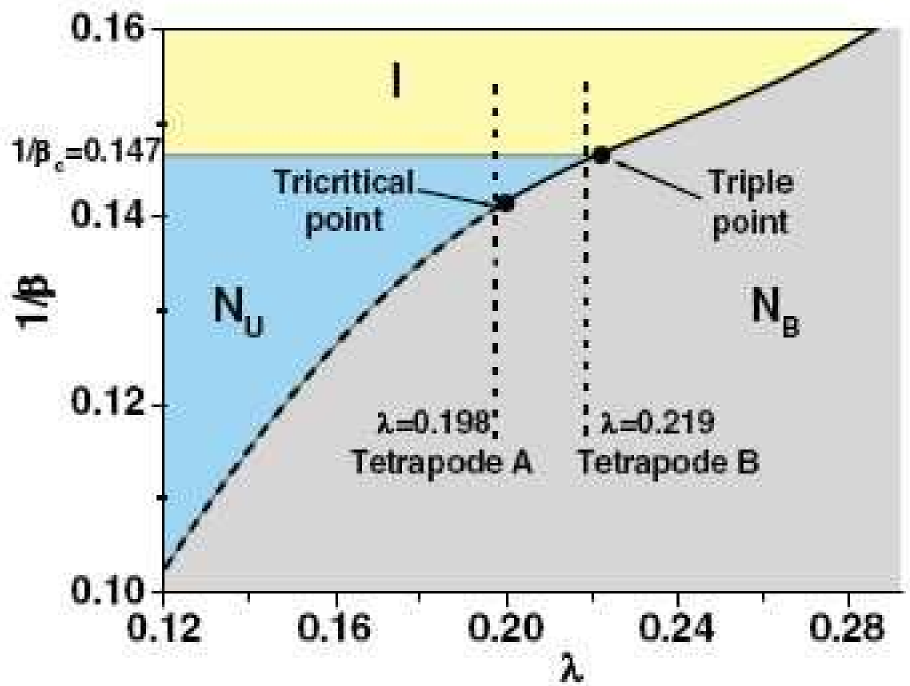
As the dimension of the eigenspace associated to $\mathbf{Q}^-$ is 2, assessing the stability of an equilibrium solution below the parabola boils down to the third eigenvalue criterion.

Essential Triangle



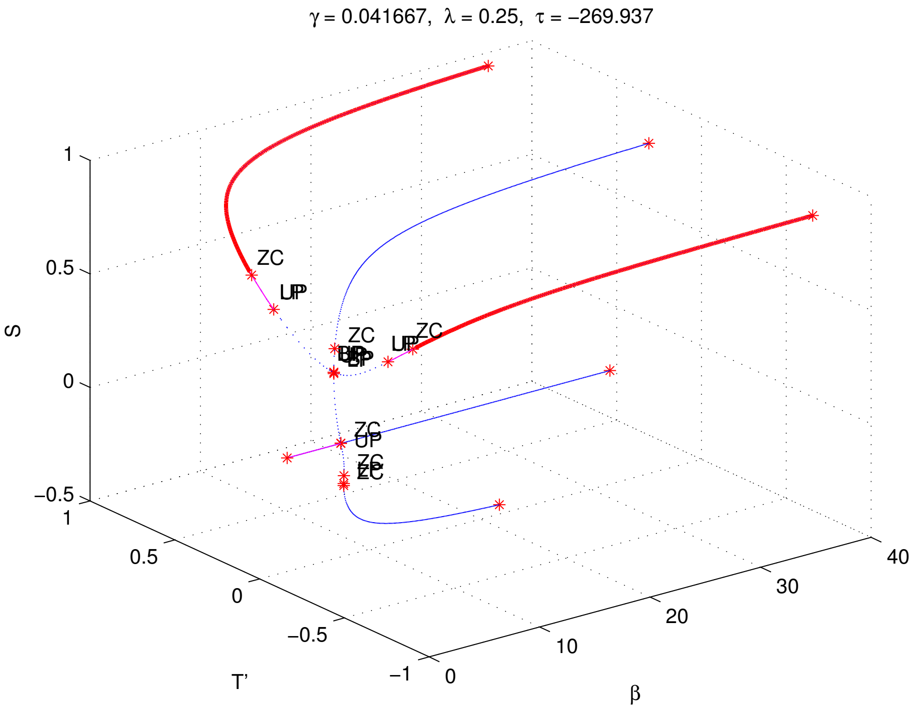
We explore some points inside the essential triangle to assess the effect of several flavours in the interaction potential.

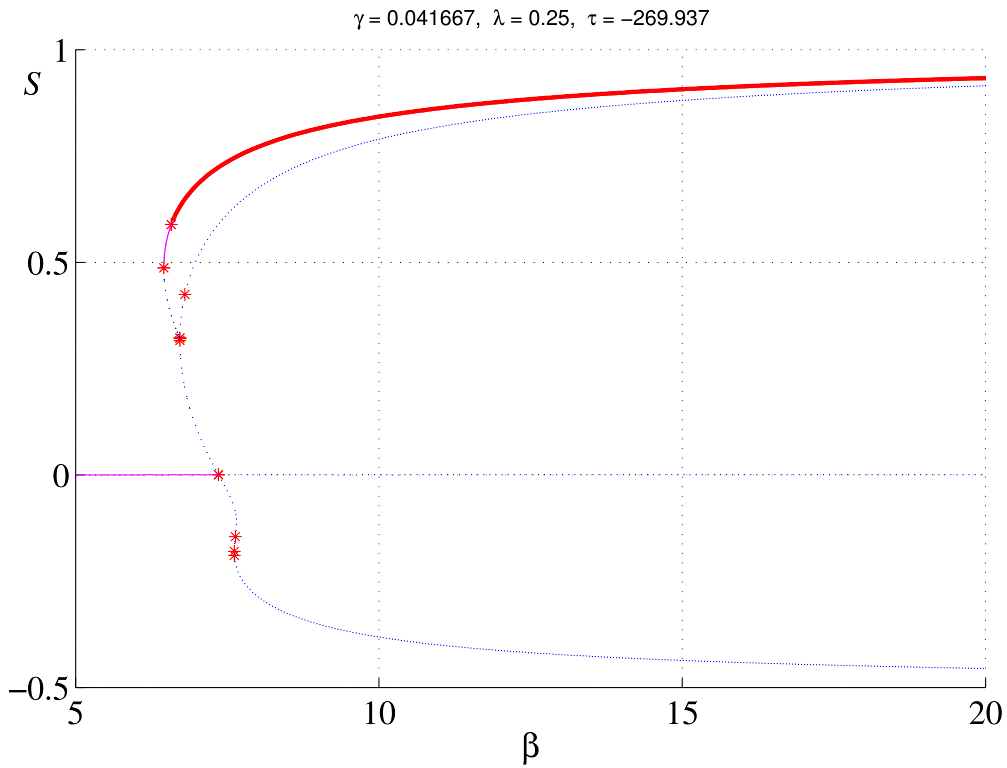
Experimental Evidence

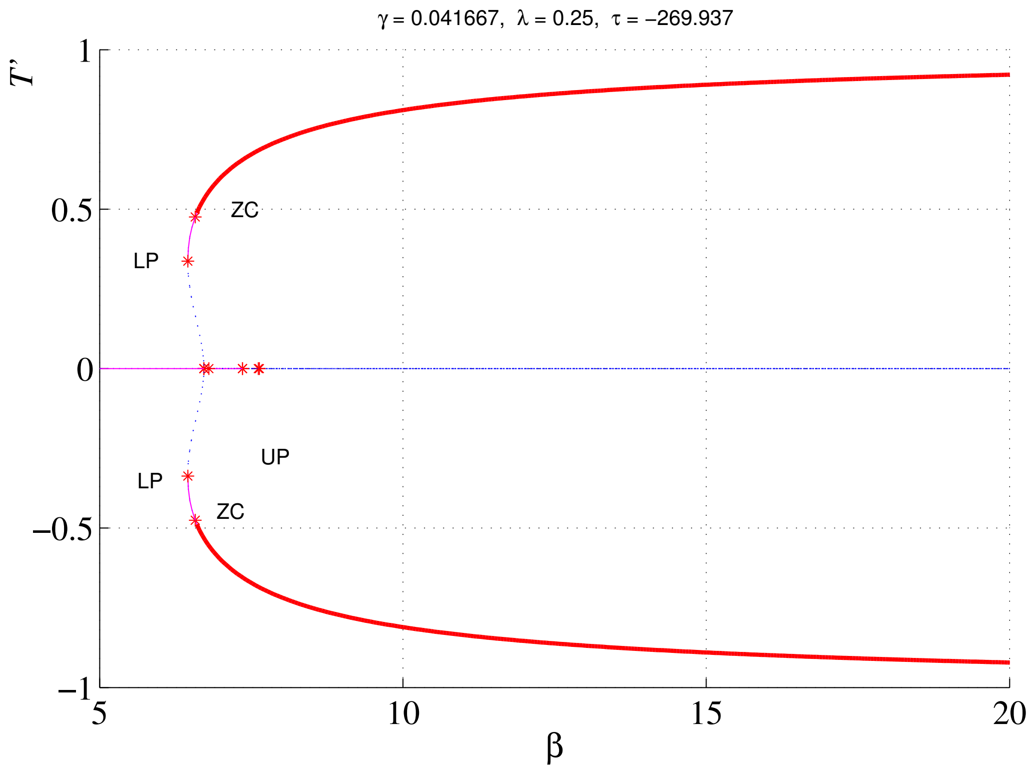


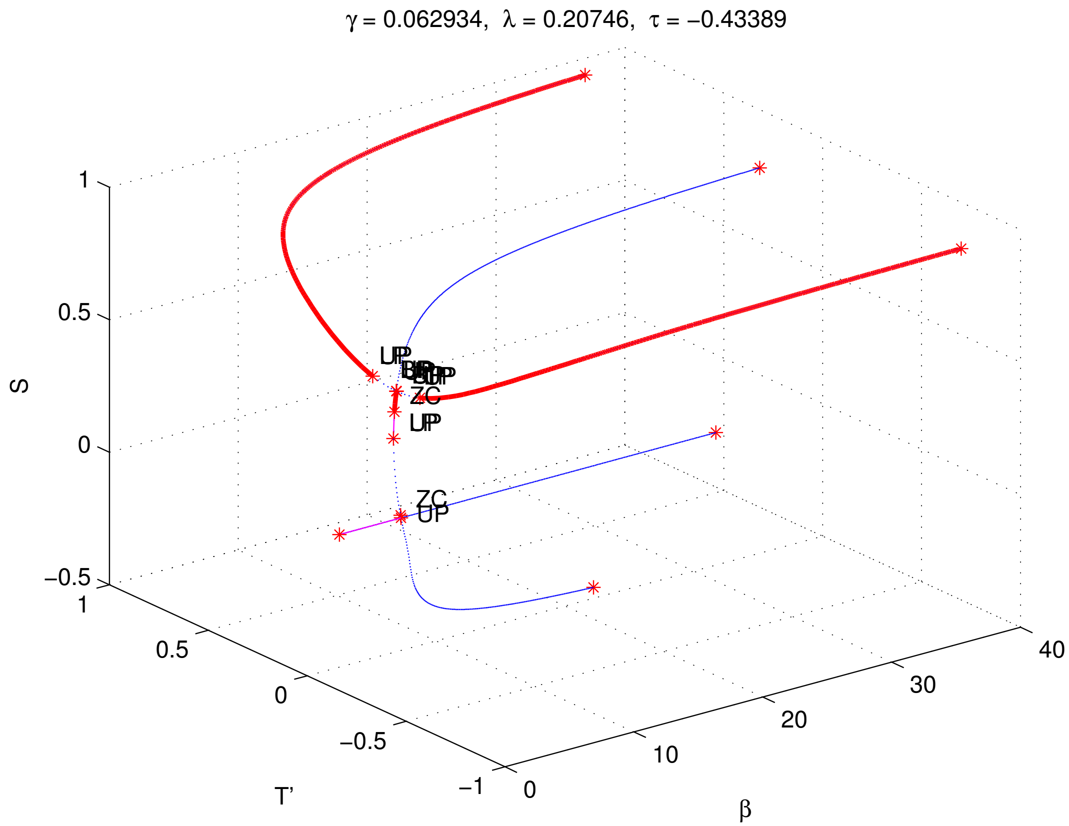
Recently experimental results obtained on tetrapodes seem to be in agreement with the prediction of the model with $\gamma = 0$ (Merkel, Vij et al., 2004). What if $\gamma \neq 0$?

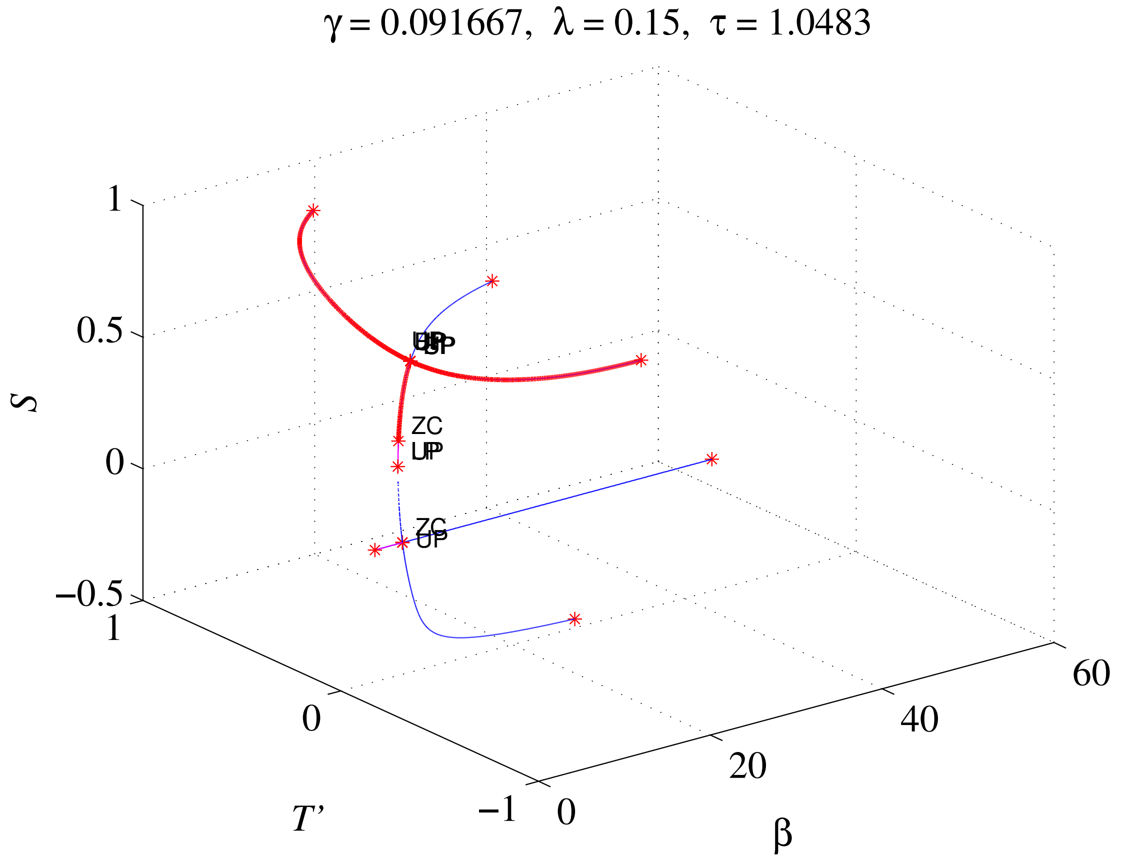
6 Bifurcation plots

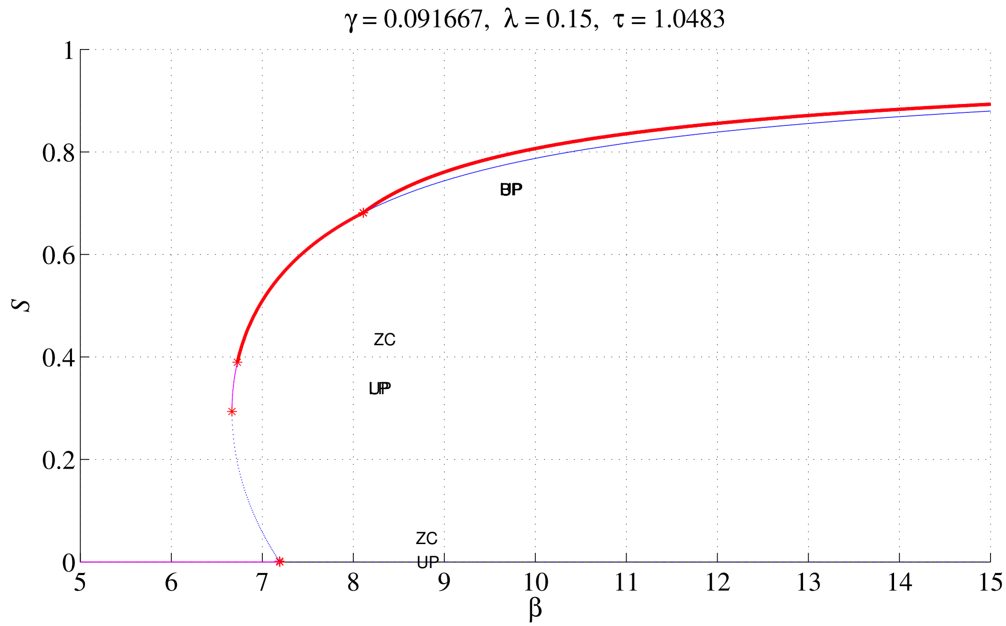


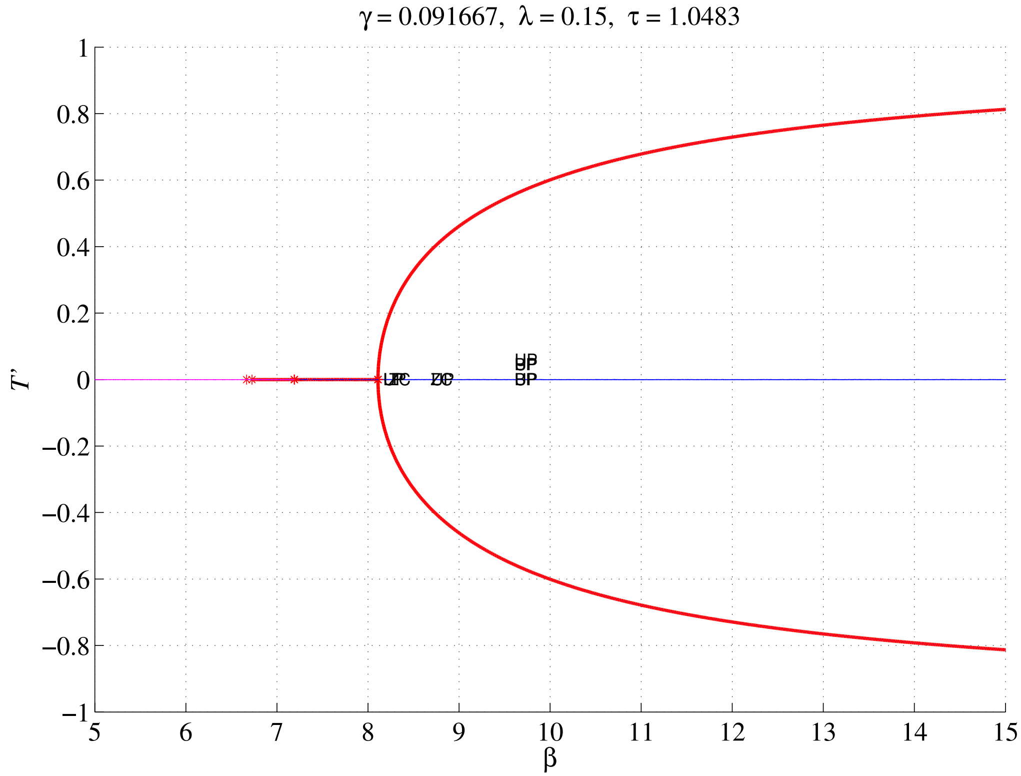

γ = 0.041667, λ = 0.25, τ = −269.937
S
1
0.5
0
−0.5
5
10
15
20
β

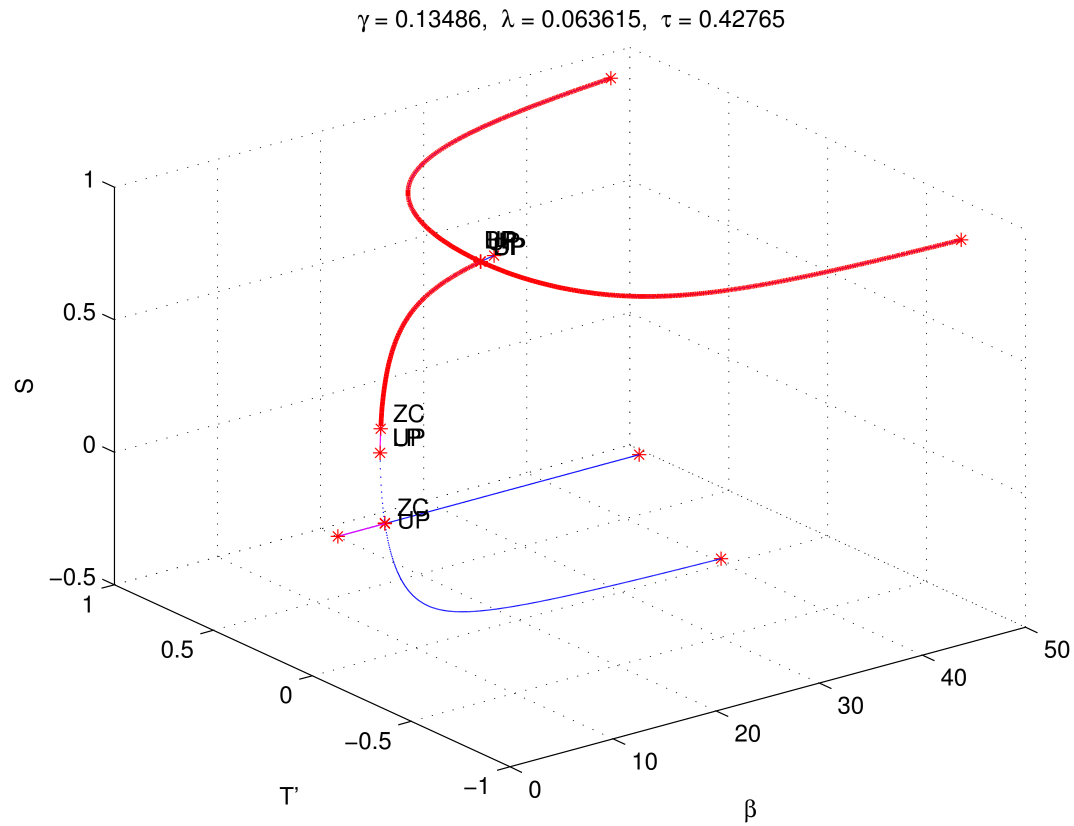

γ = 0.041667, λ = 0.25, τ = −269.937
T'
1
0.5
0
−0.5
−1
5
10
15
20
β
ZC
LP
LP
ZC
UP

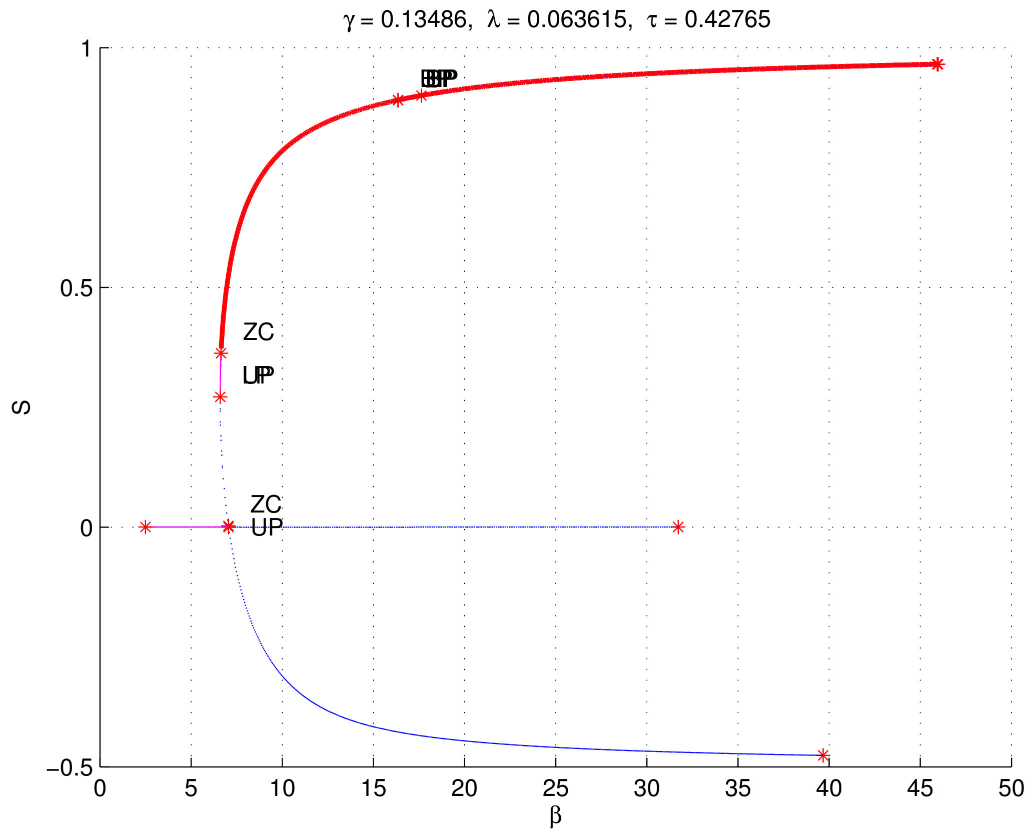

γ = 0.062934, λ = 0.20746, τ = −0.43389
S
T'
β
UP
ZC

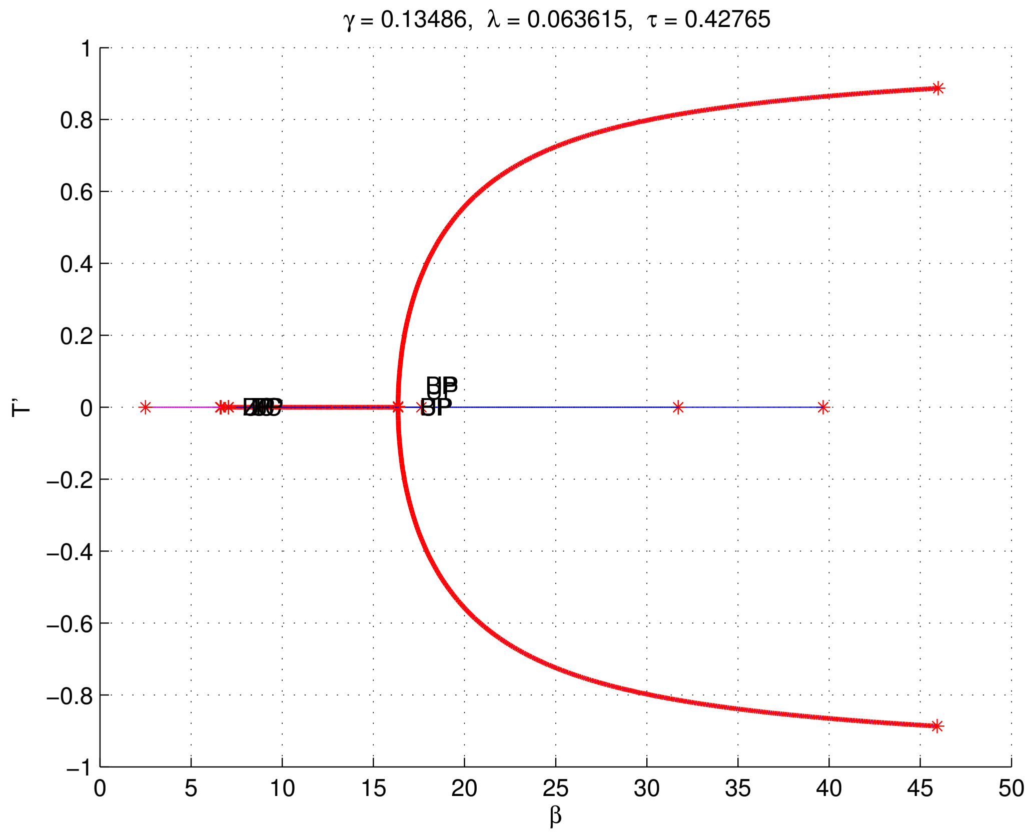

γ = 0.091667, λ = 0.15, τ = 1.0483
S
1
0.5
0
−0.5
T'
1
0
−1
β
0
20
40
60
ZC
UP

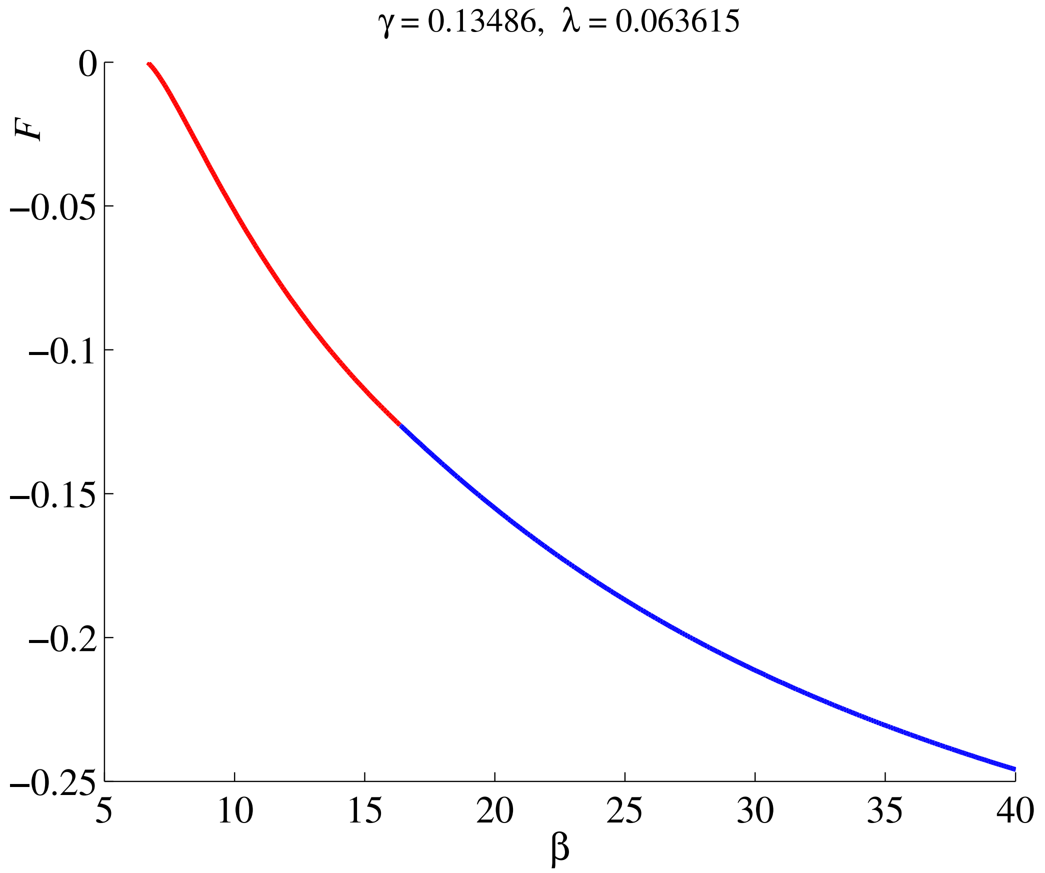

γ = 0.091667, λ = 0.15, τ = 1.0483
S
β
BP
ZC
UP
ZC
UP
0
0.2
0.4
0.6
0.8
1
5
6
7
8
9
10
11
12
13
14
15

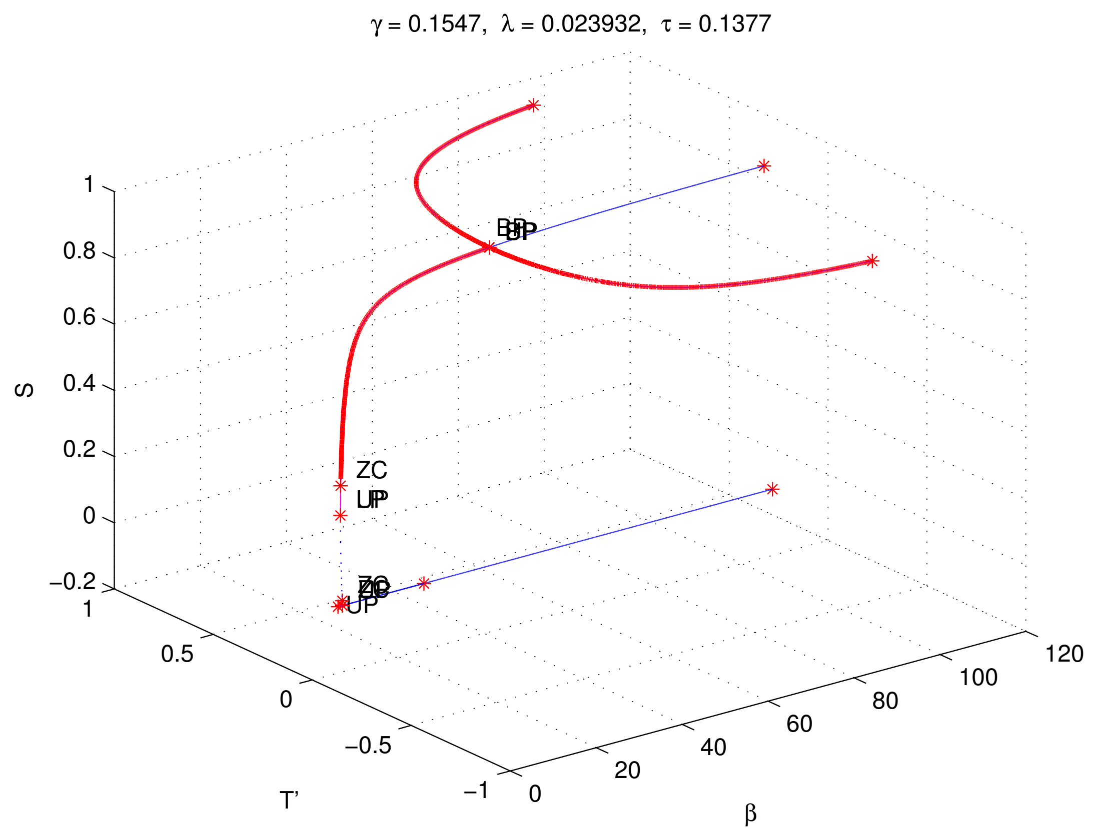

γ = 0.091667, λ = 0.15, τ = 1.0483
T'
β
LP
TC
UP
BP

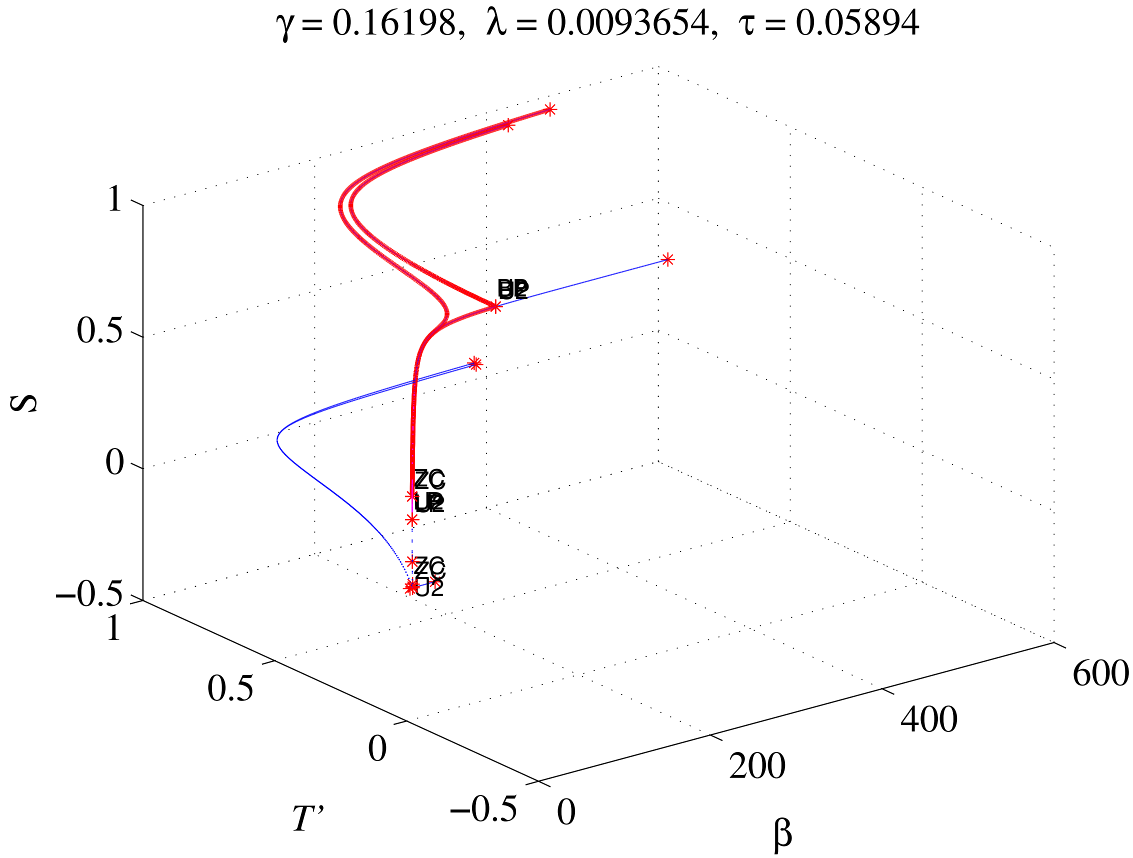

γ = 0.13486, λ = 0.063615, τ = 0.42765
S
1
0.5
0
–0.5
1
0.5
0
–0.5
–1
T'
0
10
20
30
40
50
β
ZC
UP
ZC
UP


γ = 0.13486, λ = 0.063615, τ = 0.42765
S
β
ZC
UP
ZC
UP
1
0.5
0
−0.5
0
5
10
15
20
25
30
35
40
45
50

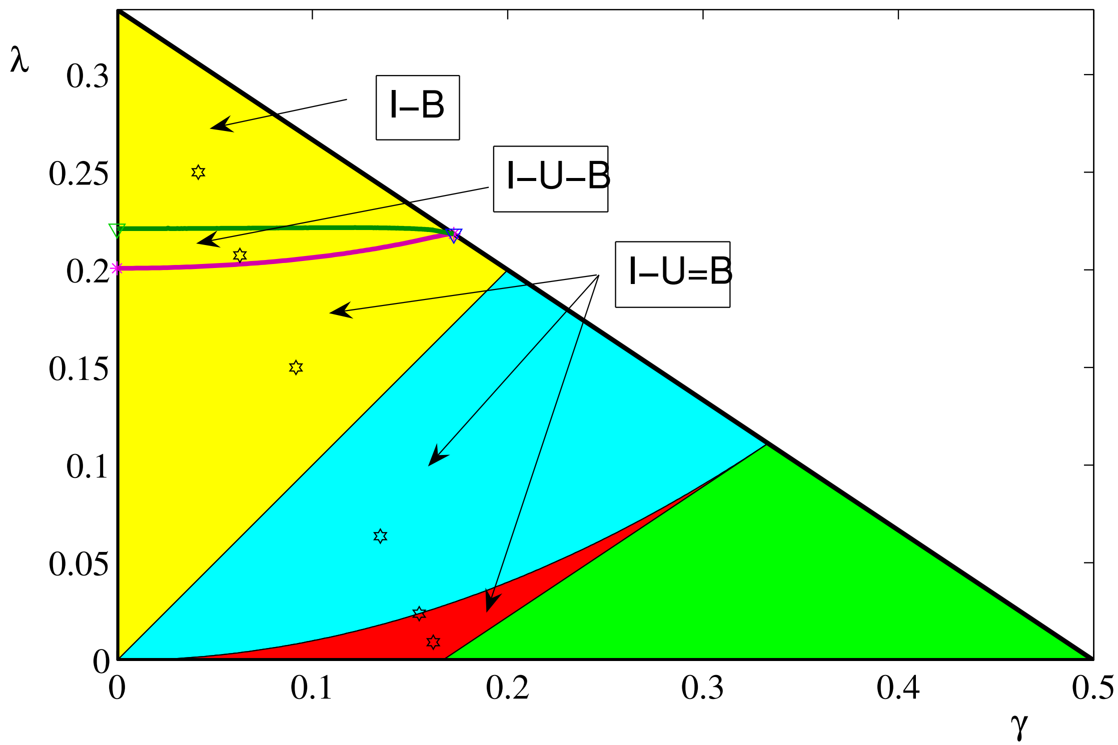

γ = 0.13486, λ = 0.063615, τ = 0.42765
1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
−1
T'
0
5
10
15
20
25
30
35
40
45
50
β
BP
BP


γ = 0.13486, λ = 0.063615
F
0
−0.05
−0.1
−0.15
−0.2
−0.25
5
10
15
20
25
30
35
40
β


γ = 0.1547, λ = 0.023932, τ = 0.1377
S
T'
β
ZC
UP
BP


γ = 0.16198, λ = 0.0093654, τ = 0.05894
S
1
0.5
0
−0.5
1
0.5
0
−0.5
T'
0
200
400
600
β
BP
ZC
LP
ZC
LP

7 Tricritical and Triple Lines



8 Final Remarks

- 1: above the parabola, the sequence of phases somehow mimicks the one predicted for $\gamma = 0$
- 2: upon crossing the high-degeneracy line of the parabola, the bifurcation diagramme unfolds.
- 3: more detail on some aspects of the model can be discussed during this afternoon's Round Table on Biaxial Nematics (see E.G. Virga's and G. De Matteis' presentations).

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