Biaxial Phase Transitions in Nematic Liquid Crystals

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Summary

General quadrupolar interaction: Straley's potential

Mean-field model and Phase diagram for $\gamma = 0$

Reference model parameters domain

Conjugated phase diagram

Extension to a mildly repulsive model

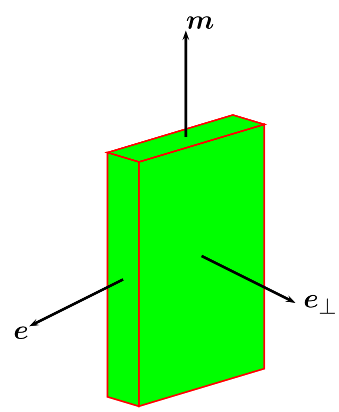
Molecular Biaxiality

We consider a homogeneous nematic liquid crystal intrinsically biaxial in the absence of any external field. It is made up of biaxial molecules which we can imagine as being described by a biaxial tensor decomposed into two traceless, irreducible orthogonal components

$$\mathbf{q} := \mathbf{m} \otimes \mathbf{m} - \frac{1}{3}\mathbf{I}$$

$$\mathbf{b} := \mathbf{e} \otimes \mathbf{e} - \mathbf{e}_{\perp} \otimes \mathbf{e}_{\perp}$$

$\mathbf{m}$, $\mathbf{e}$, $\mathbf{e}_{\perp}$ axes of any molecular polarizability



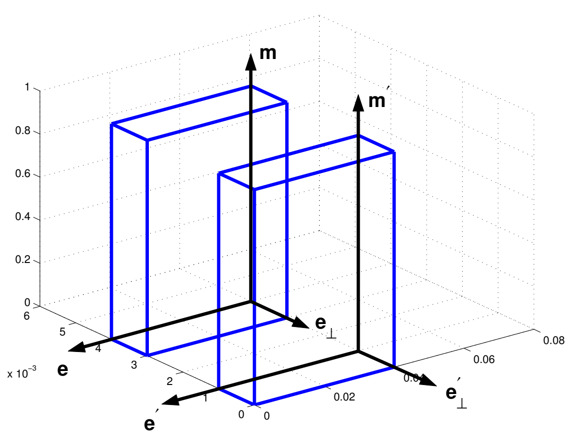
Interaction potential

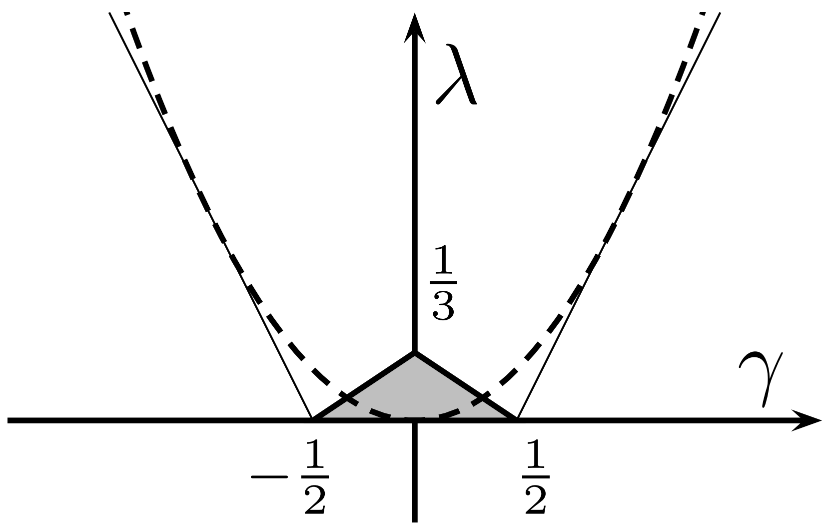
Letting $(\mathbf{q}, \mathbf{b})$ and $(\mathbf{q}', \mathbf{b}')$ represent two interacting molecules, the most general quadrupolar interaction potential coupling them is

$$V = -U_0 \{\mathbf{q} \cdot \mathbf{q}' + \gamma(\mathbf{q} \cdot \mathbf{b}' + \mathbf{b} \cdot \mathbf{q}') + \lambda \mathbf{b} \cdot \mathbf{b}'\}$$

$U_0 > 0$ and λ, γ model parameters

Ground State





Model $\gamma = 0$

$$V = -U_0 \{\mathbf{q}\cdot\mathbf{q}' + \lambda \mathbf{b}\cdot\mathbf{b}'\}$$

$$\frac{V}{U_0} = -\left\{-\left(\lambda + \frac{1}{3}\right) + (1-\lambda)\left(\mathbf{m}\cdot\mathbf{m}'\right)^2 + 2\lambda\left[\left(\mathbf{e}'_\perp\cdot\mathbf{e}_\perp\right)^2 + \left(\mathbf{e}'\cdot\mathbf{e}\right)^2\right]\right\}$$

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

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

pseudo-potential

$$U = -U_0(\mathbf{q}\cdot\mathbf{Q} + \lambda\mathbf{b}\cdot\mathbf{B})$$

Mean-field equations

partition and distribution functions

$$Z(\mathbf{Q},\mathbf{B},\beta,\lambda)=\int_{\mathbb{T}}\exp\left(\beta\left(\mathbf{Q}\cdot\mathbf{q}+\lambda\mathbf{B}\cdot\mathbf{b}\right)\right)$$

$$f=\frac{1}{Z}\exp\left[\beta(\mathbf{q}\cdot\mathbf{Q}+\lambda\mathbf{b}\cdot\mathbf{B})\right]$$

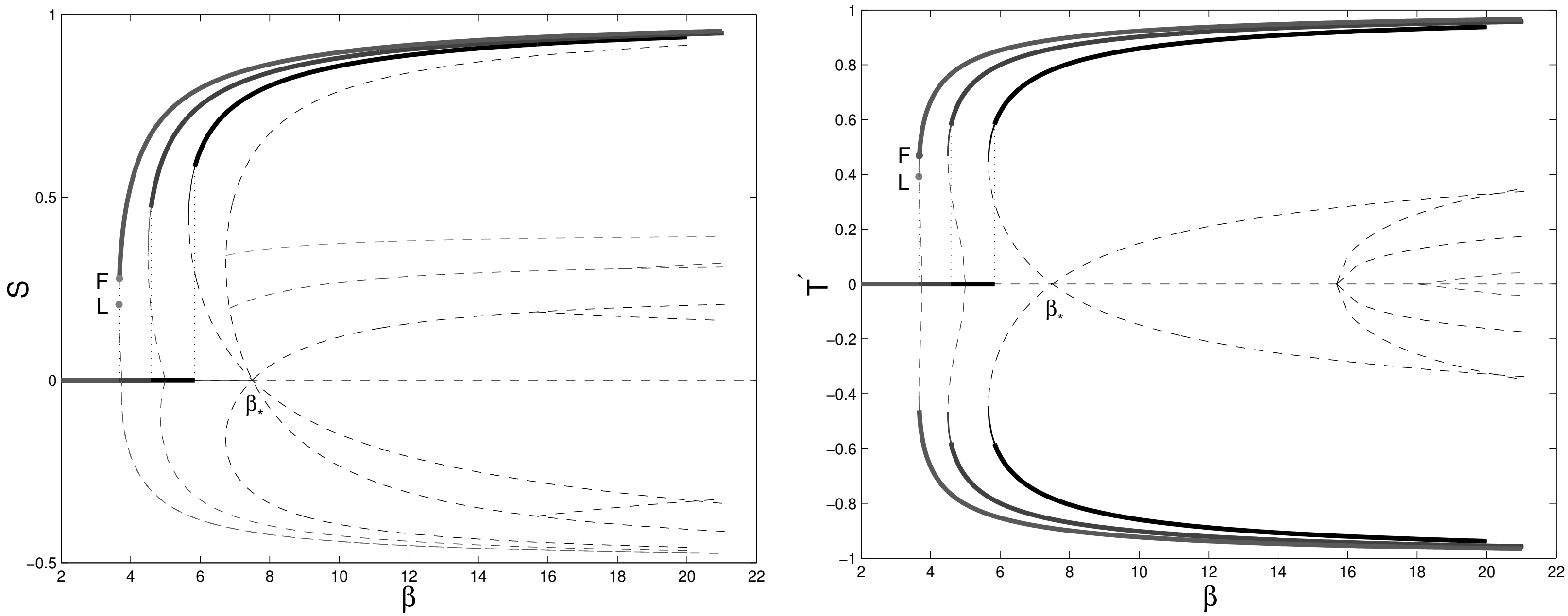
$$\mathbb{T}:=\mathbb{S}^2\times\mathbb{S}^1,\quad \beta:=\frac{U_0}{k_B t}$$

k_B Boltzmann constant and t absolute temperature

$$\mathbf{Q}=\langle\mathbf{q}\rangle=\int_{\mathbb{T}}f\mathbf{q}\qquad \mathbf{B}=\langle\mathbf{b}\rangle=\int_{\mathbb{T}}f\mathbf{b}$$

$$\mathcal{F}(\mathbf{Q},\mathbf{B},\beta,\lambda)=U_0\left\{\frac{1}{2}\mathbf{Q}\cdot\mathbf{Q}+\frac{\lambda}{2}\mathbf{B}\cdot\mathbf{B}-\frac{1}{\beta}\ln\left(\frac{Z(\mathbf{Q},\mathbf{B},\beta,\lambda)}{8\pi^2}\right)\right\},$$

$$\lambda = 1/3, 1/2, 2/3$$



dominant stable biaxial states $(S, 0, 0, T')$

$$\mathbf{Q} = S(\mathbf{e}_z \otimes \mathbf{e}_z - \frac{1}{3}\mathbf{I}) \qquad \mathbf{B} = T'(\mathbf{e}_x \otimes \mathbf{e}_x - \mathbf{e}_y \otimes \mathbf{e}_y)$$

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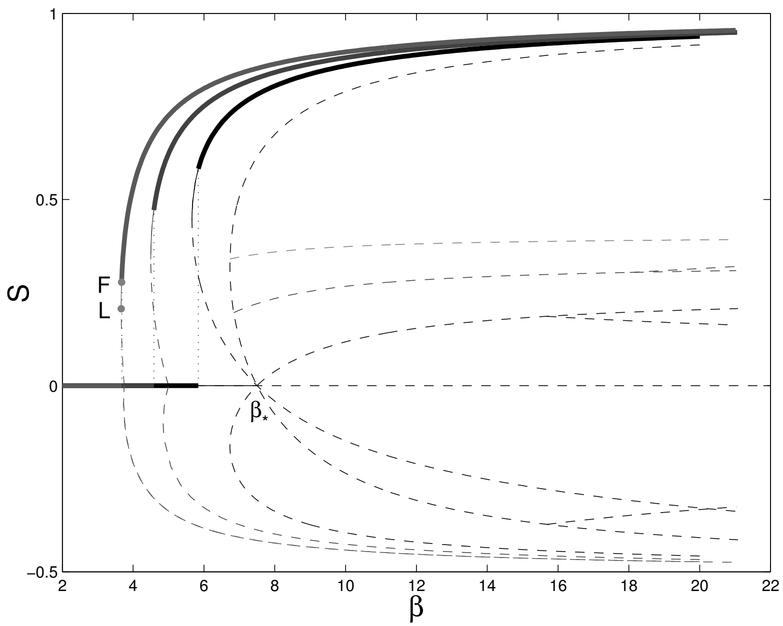
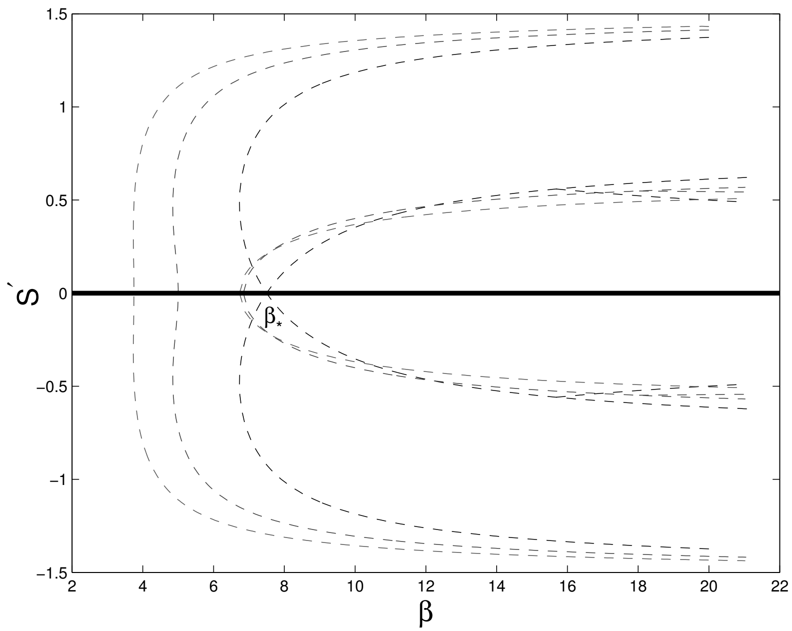


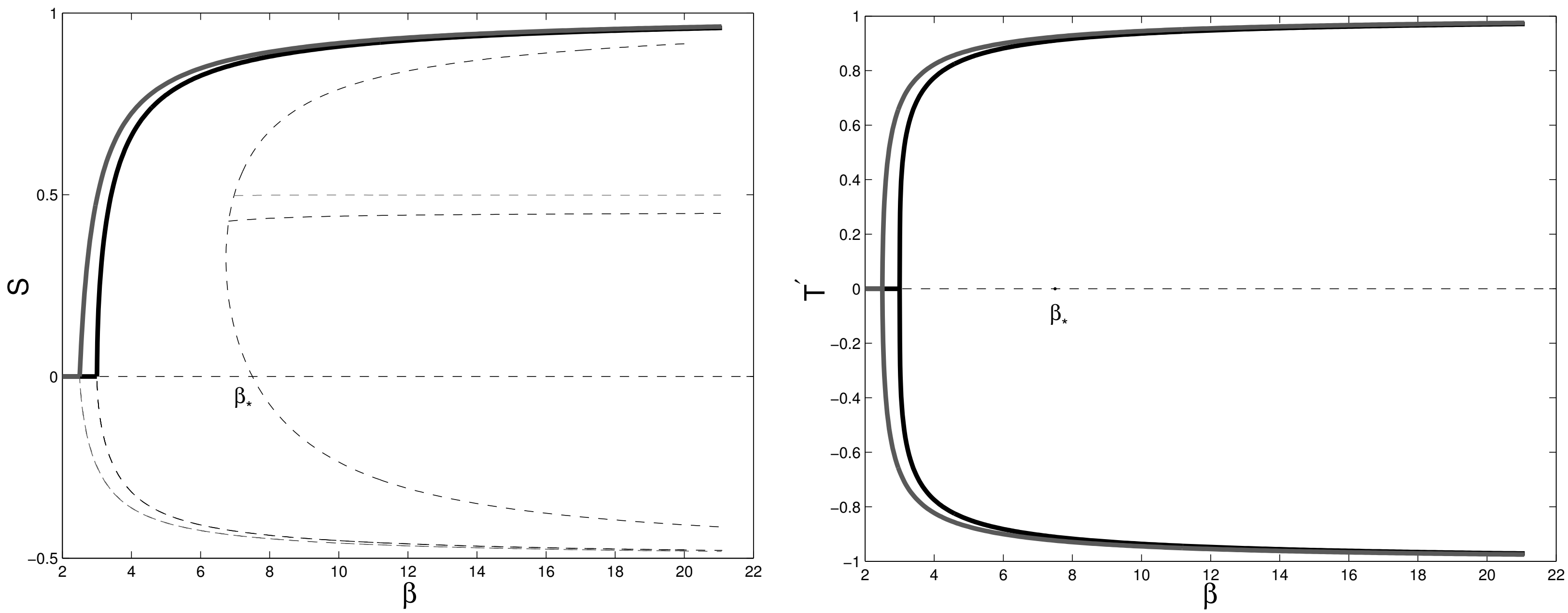


unstable uniaxial states with a greater value of free energy $(S, 0, S', 0)$

$$\mathbf{Q} = -S(\mathbf{e}_y \otimes \mathbf{e}_y - \frac{1}{3}\mathbf{I}) \qquad \mathbf{B} = -S'(\mathbf{e}_y \otimes \mathbf{e}_y - \frac{1}{3}\mathbf{I})$$

$$\mathbf{Q} = -S(\mathbf{e}_x \otimes \mathbf{e}_x - \frac{1}{3}\mathbf{I}) \qquad \mathbf{B} = -S'(\mathbf{e}_x \otimes \mathbf{e}_x - \frac{1}{3}\mathbf{I})$$

$\lambda = 5/6, 1$



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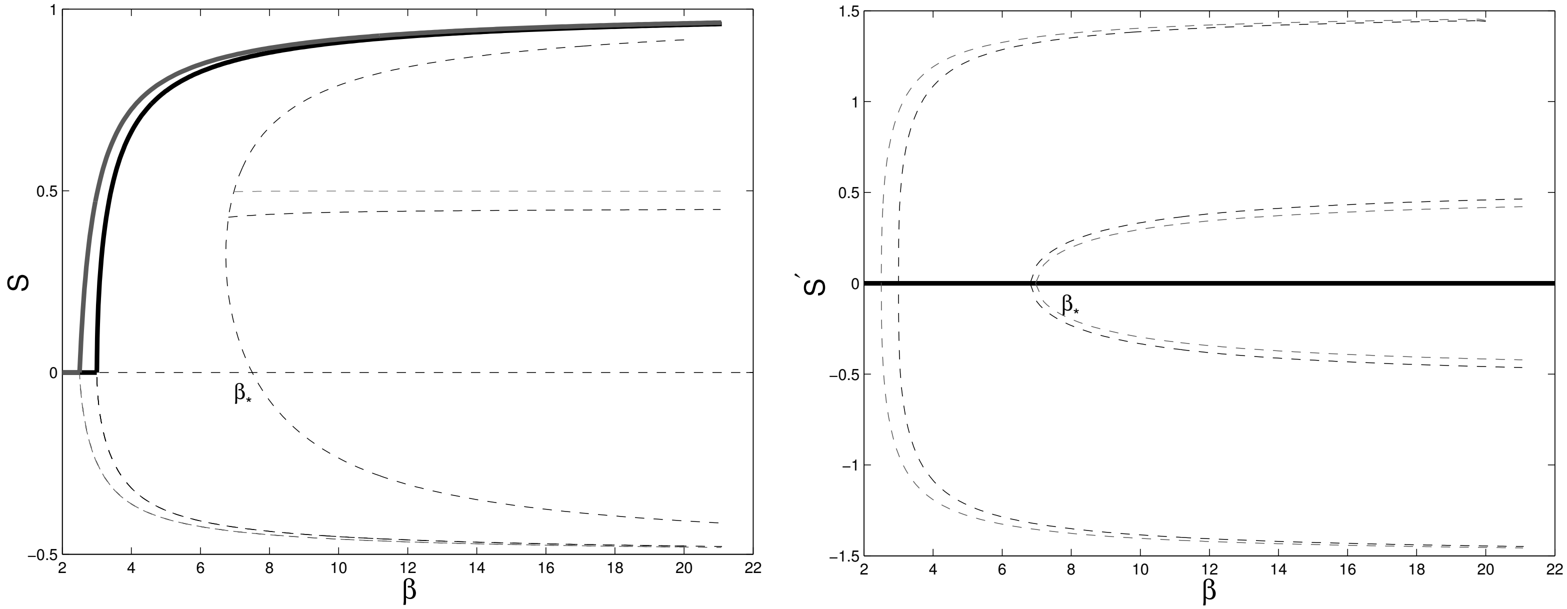

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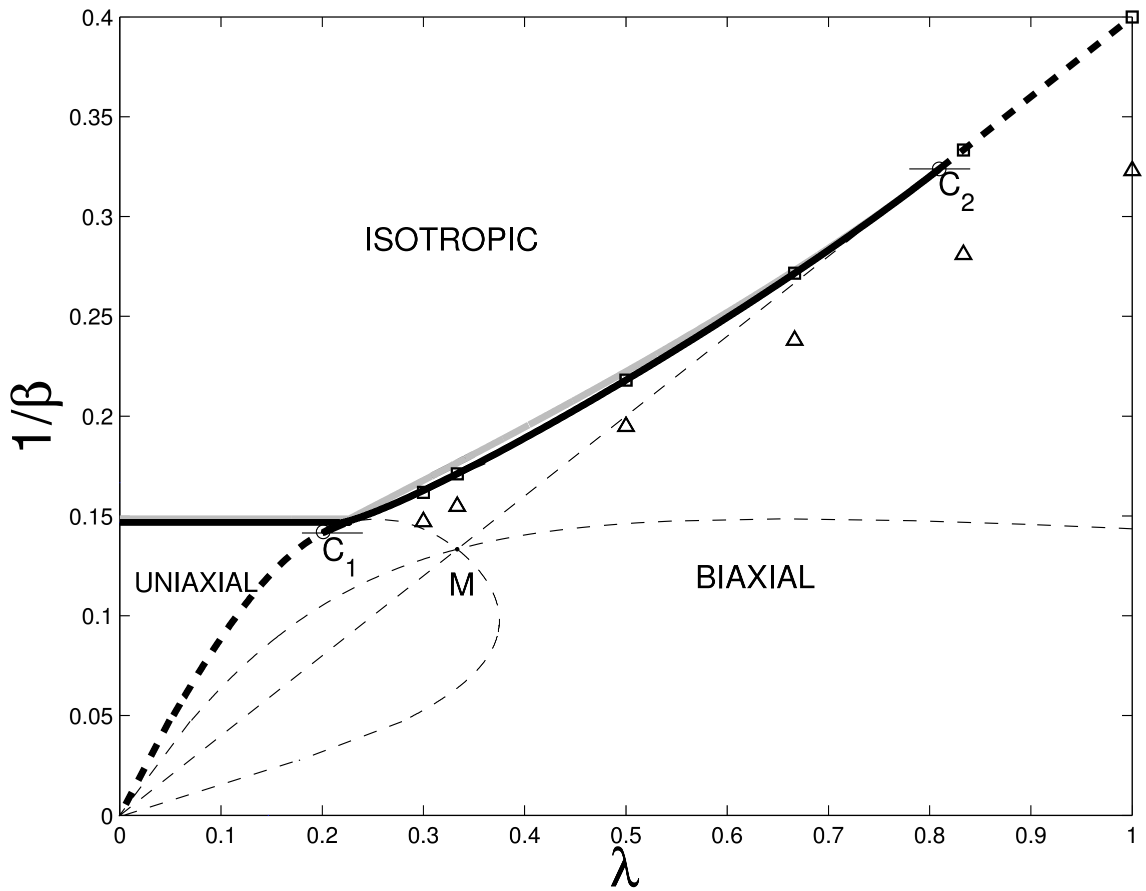
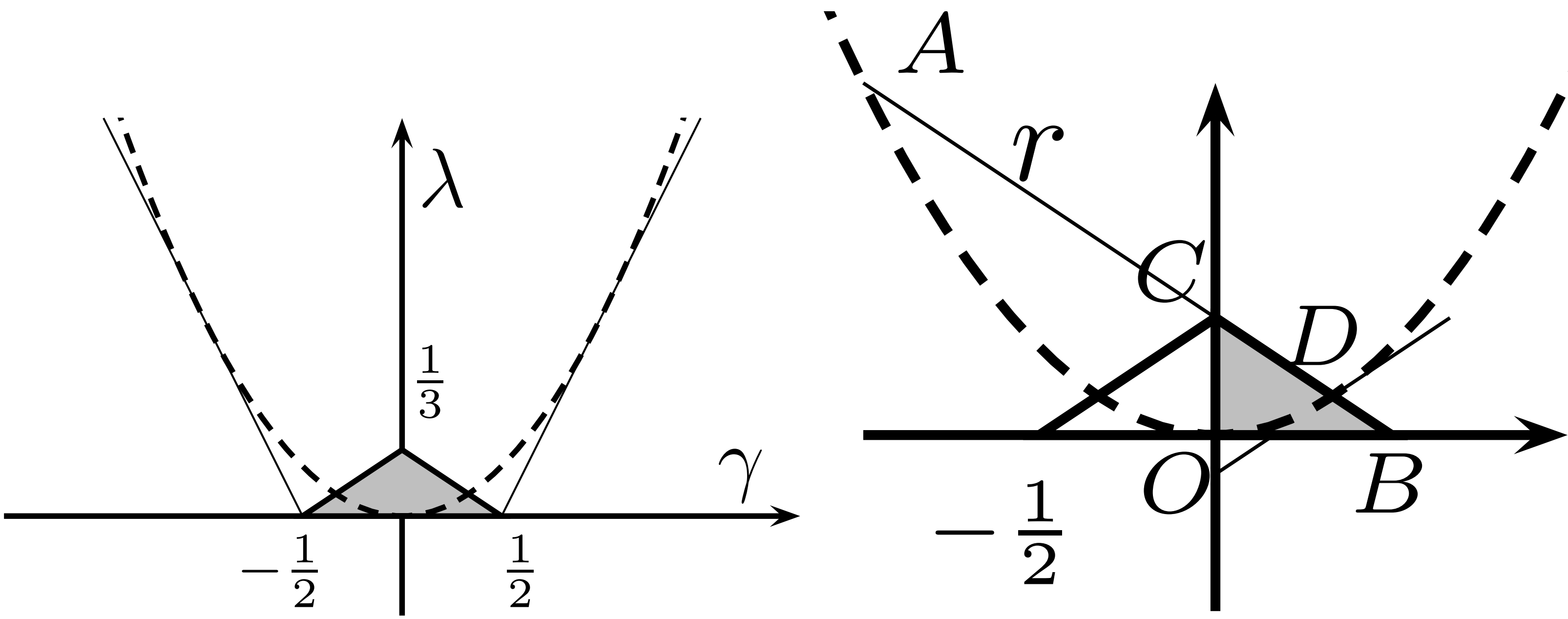
Phase Diagram and Tricritical points



Durand, Sonnet, Virga (2003) De Matteis, Romano ,Virga (2005)

Reference triangle



$$D\left(\frac{1}{3},\frac{1}{9}\right),\quad B\left(\frac{1}{2},0\right),\quad C\left(0,\frac{1}{3}\right),\quad A\,(-1,1)$$

$$r: 2\gamma + 3\lambda - 1 = 0$$

Model: $2\gamma = 1 - 3\lambda$

$$\mathbf{q}^* := \mathbf{e} \otimes \mathbf{e} - \frac{1}{3}\mathbf{I}, \quad \mathbf{b}^* := \mathbf{m} \otimes \mathbf{m} - \mathbf{e}_\perp \otimes \mathbf{e}_\perp$$

$$V = -U_0 \left\{ \left(\frac{9\lambda - 1}{2} \right) \mathbf{q}^* \cdot \mathbf{q}^{*\prime} + \left(\frac{1 - \lambda}{2} \right) \mathbf{b}^* \cdot \mathbf{b}^{*\prime} \right\}$$

$$V^* = -U_0 \left(\frac{9\lambda - 1}{2} \right) \left\{ \mathbf{q}^* \cdot \mathbf{q}^{*\prime} + \lambda^* \mathbf{b}^* \cdot \mathbf{b}^{*\prime} \right\}$$

which is equivalent to $\gamma = 0$ model by transforming the model parameter λ and β as follows

$$\beta^* = \beta \left(\frac{9\lambda - 1}{2} \right), \quad \lambda^* = \frac{1 - \lambda}{9\lambda - 1}$$

in the (γ, λ) −plane

$$\left[\frac{1}{9}, 1 \right] \mapsto [0, \infty], \left[\frac{1}{9}, \frac{1}{3} \right] \mapsto \left[\frac{1}{3}, \infty \right] \, i.e. \overline{DA} \mapsto \overline{OP_\infty}, \overline{CD} \mapsto \overline{CP_\infty}$$

$$P_\infty (0, \infty)$$

Order parameters

$$\mathbf{Q}^* = S^*(\mathbf{e}_z \otimes \mathbf{e}_z - \frac{1}{3}\mathbf{I}) + T^*(\mathbf{e}_x \otimes \mathbf{e}_x - \mathbf{e}_y \otimes \mathbf{e}_y)$$

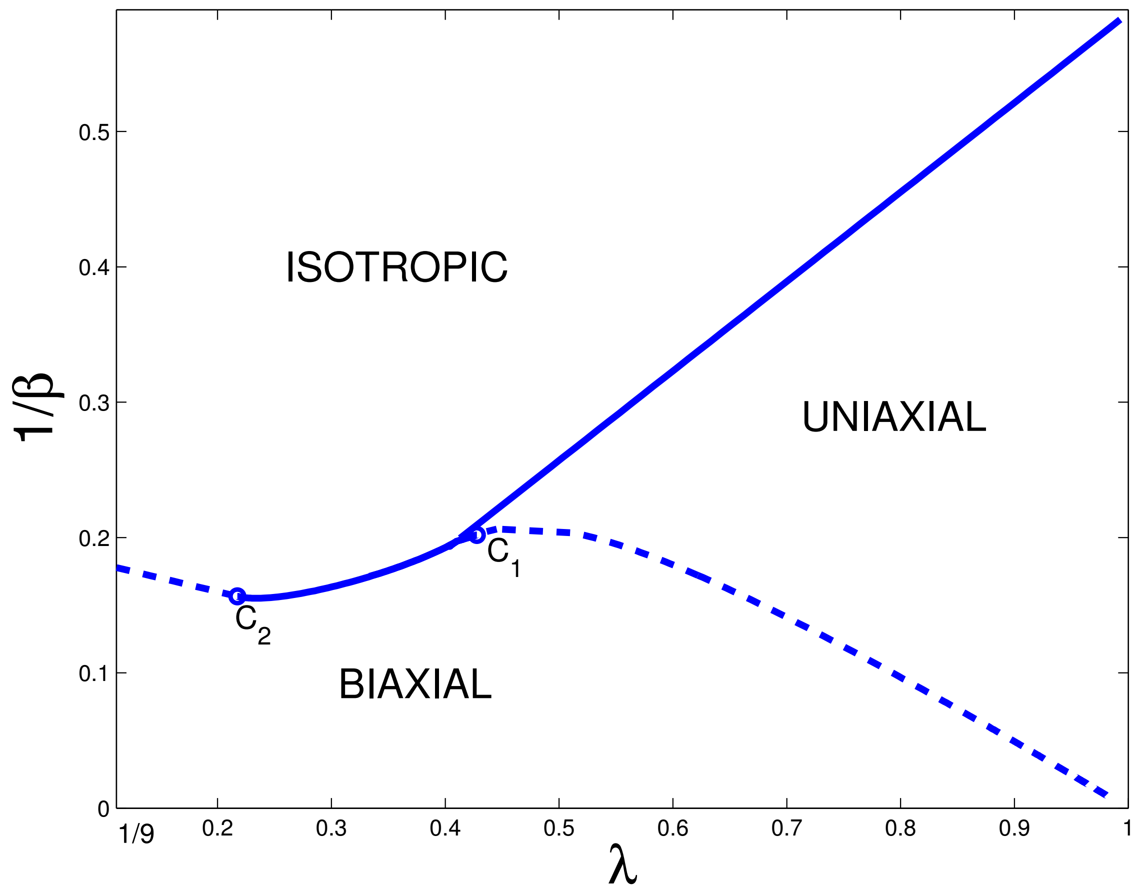
$$\mathbf{B}^* = S'^*(\mathbf{e}_z \otimes \mathbf{e}_z - \frac{1}{3}\mathbf{I}) + T'^*(\mathbf{e}_x \otimes \mathbf{e}_x - \mathbf{e}_y \otimes \mathbf{e}_y)$$

with the following corrispondence on the order parameters

$$S = \frac{S'^* - S^*}{2}, \quad T = \frac{T'^* - T^*}{2},$$

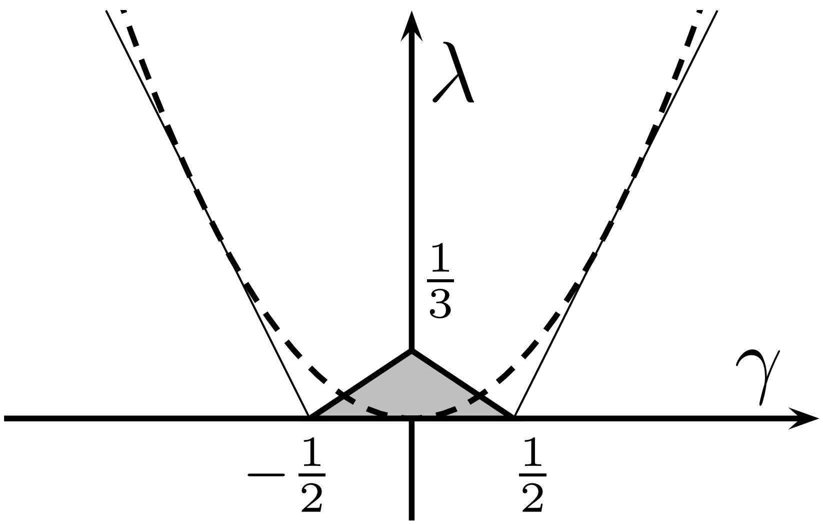
$$S' = \frac{S'^* + 3S^*}{2}, \quad T' = \frac{T'^* + 3T^*}{2}$$

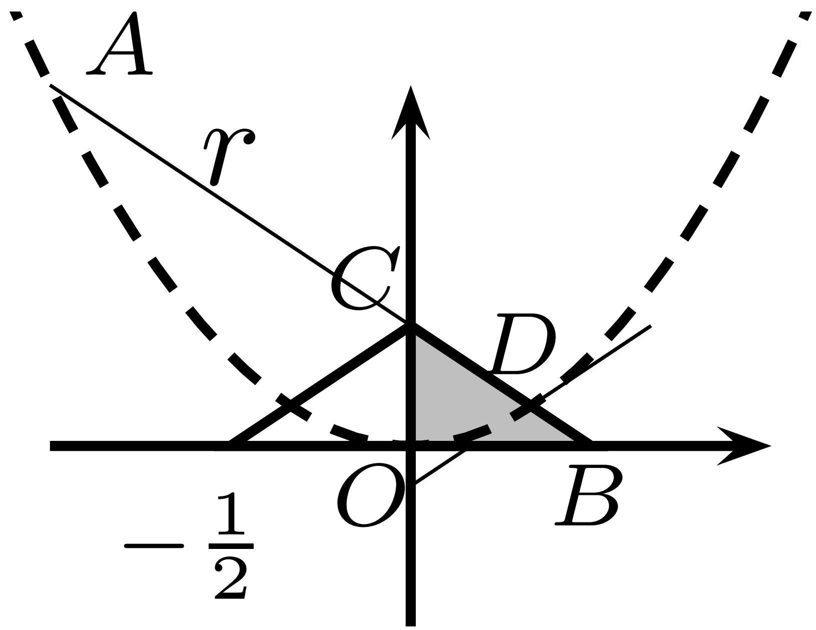
Conjugated phase diagram



$$2\gamma = 1 - 3\lambda \quad \frac{1}{9} \leq \lambda \leq 1$$

Reference triangle





$$D\left(\frac{1}{3},\frac{1}{9}\right),\quad B\left(\frac{1}{2},0\right),\quad C\left(0,\frac{1}{3}\right),\quad A\left(-1,1\right)$$

$$r : 2\gamma + 3\lambda - 1 = 0$$

$2\gamma = 1 - 3\lambda, \quad 0 \leq \lambda \leq \frac{1}{9}$: a mildly repulsive model

$$V_\mu = -U_0 \left(\frac{1-\lambda}{2} \right) \left\{ \mathbf{b}^* \cdot \mathbf{b}^{*\prime} - \mu \mathbf{q}^* \cdot \mathbf{q}^{*\prime} \right\}$$

$$\mu = \frac{1-9\lambda}{1-\lambda}, \quad \beta_\mu = \beta \left(\frac{1-\lambda}{2} \right)$$

$$\lambda \in \left[0, \frac{1}{9} \right] \Leftrightarrow \mu \in [0,1] \Leftrightarrow \overline{BD}$$

mean-field

$$f_\mu = \frac{1}{Z_\mu} \exp\left(\beta_\mu \left(\mathbf{B}^* \cdot \mathbf{b}^* - \mu \mathbf{Q}^* \cdot \mathbf{q}^* \right) \right)$$

$$Z_\mu := \int_{\mathbb{T}} \exp\left(\beta_\mu \left(\mathbf{B}^* \cdot \mathbf{b}^* - \mu \mathbf{Q}^* \cdot \mathbf{q}^* \right) \right)$$

$$\mathcal{F}_{\mu}\left(\mathbf{Q}^{*},\mathbf{B}^{*}\right)=U_{0}\left\{\frac{1}{2}\left(\mathbf{B}^{*}\cdot\mathbf{B}^{*}-\mu\mathbf{Q}^{*}\cdot\mathbf{Q}^{*}\right)-\frac{1}{\beta_{\mu}}\log\left(\frac{Z_{\mu}}{8\pi^{2}}\right)\right\}$$

$$\mathbf{Q}^{*}=\langle\mathbf{q}^{*}\rangle=\int_{\mathbb{T}}f_{\mu}\mathbf{q}^{*}\quad\Leftrightarrow\quad\frac{\partial\mathcal{F}_{\mu}}{\partial\mathbf{Q}^{*}}=0$$

$$\mathbf{B}^{*}=\langle\mathbf{b}^{*}\rangle=\int_{\mathbb{T}}f_{\mu}\mathbf{b}^{*}\quad\Leftrightarrow\quad\frac{\partial\mathcal{F}_{\mu}}{\partial\mathbf{B}^{*}}=0$$

Bogoliubov's *minimax principle*

All the phases are characterized at least by two negative eigenvalues in the Hessian matrix of $\mathcal{F}_{\mu}$. In this case we adopt a minimax principle to determine the effective phases.

$$\min_{\mathbf{B}^{*}}\max_{\mathbf{Q}^{*}}\mathcal{F}_{\mu}\left(\mathbf{Q}^{*},\mathbf{B}^{*}\right)$$

which is equivalent to finding a solution of the mean-field equations giving $\mathcal{F}_{\mu}$ a smaller value than do any other solutions

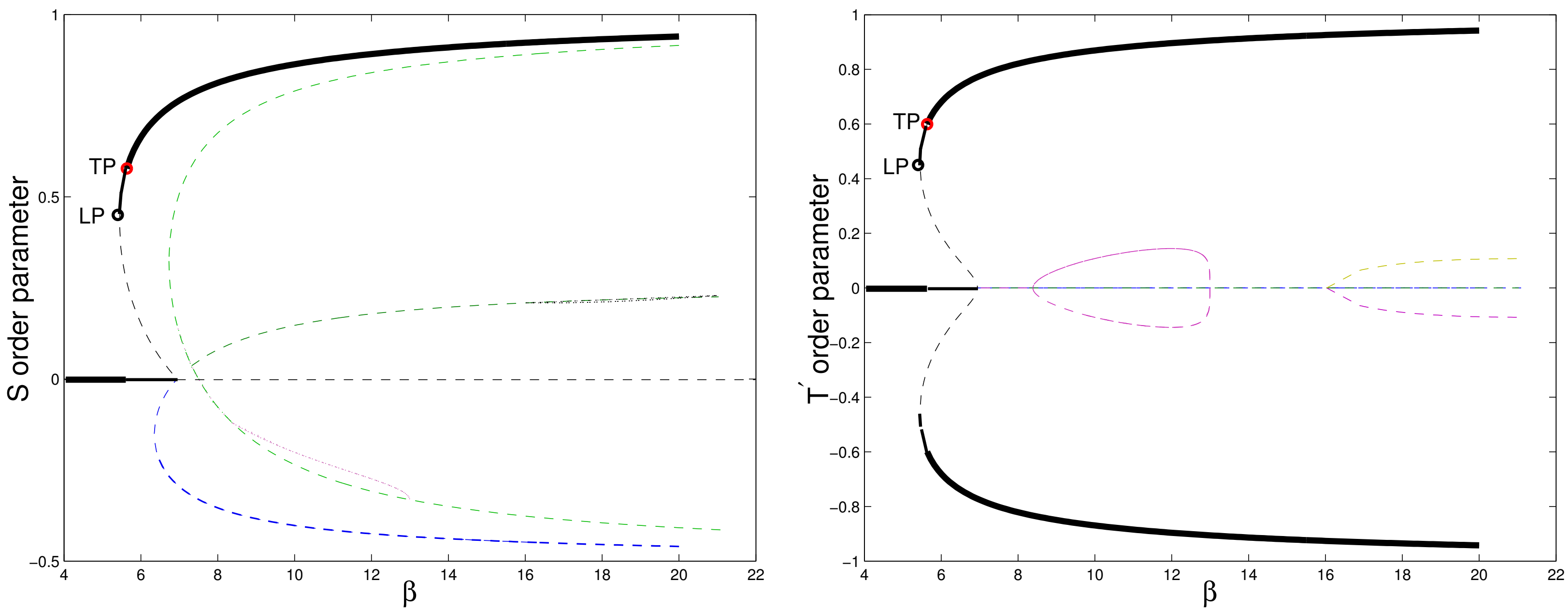
Future work

- Numerical continuation and Bifurcation Analysis for the mildly repulsive model (also with a $\gamma-$crossing term in the interaction)
- Landau theory for both attractive and mildly repulsive cases

.... and finally I would thank

- my PhD thesis advisor Prof. E. Virga
- Prof. Gartland, Prof. Durand, Prof. S. Romano and M. Osipov during my PhD research activity in Pavia

$\lambda = 0.36$



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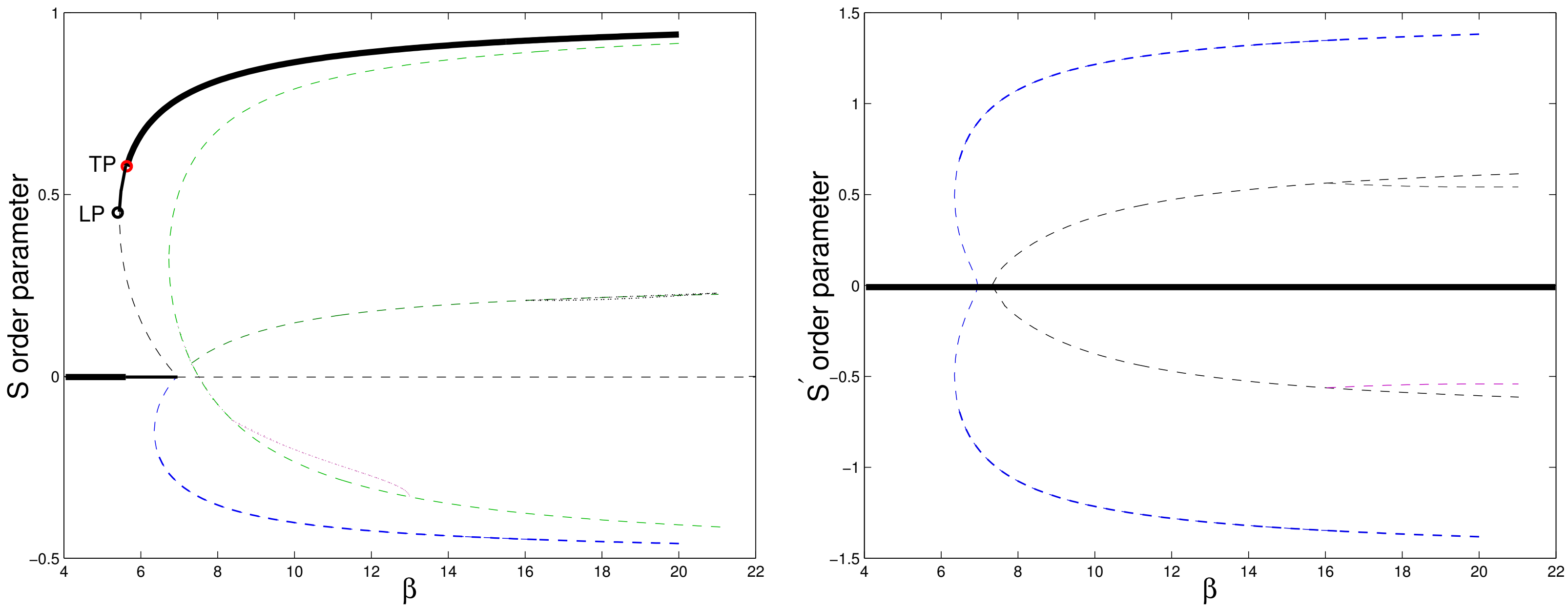

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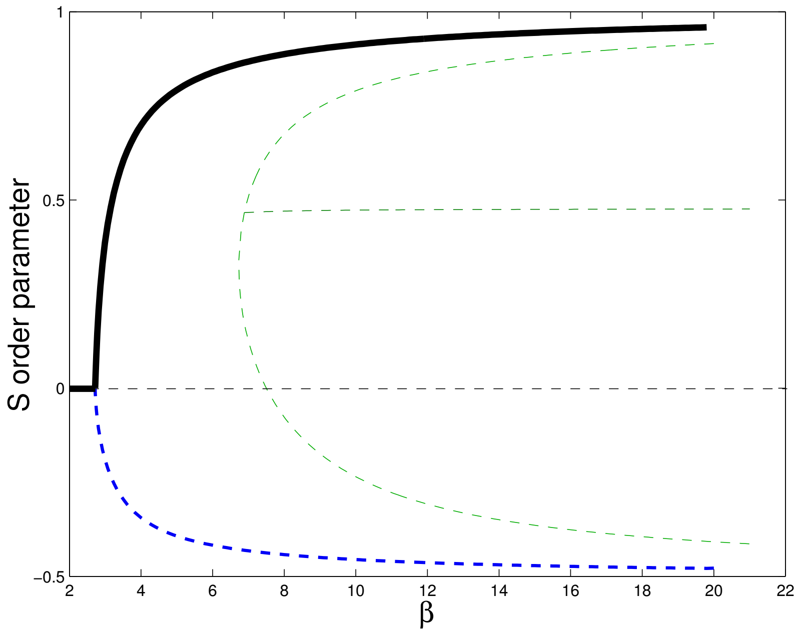
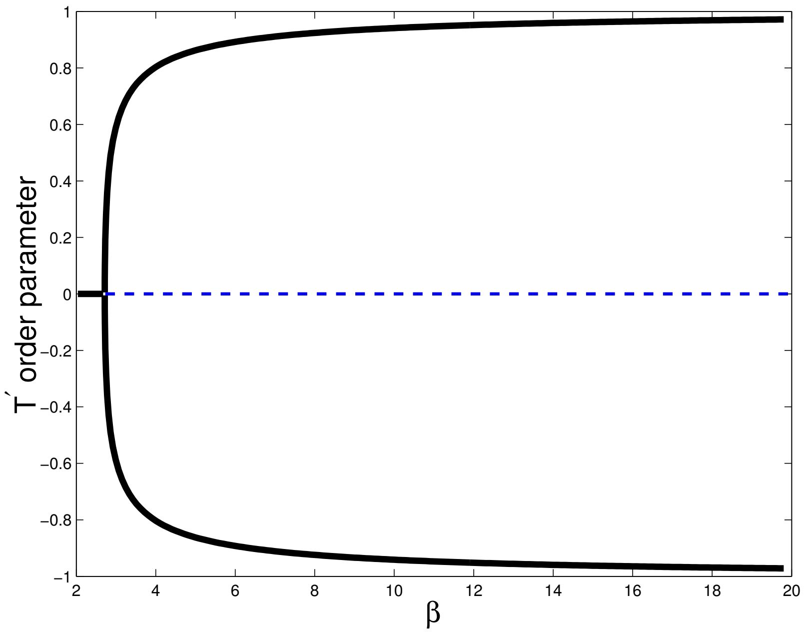
$\lambda = 0.92$





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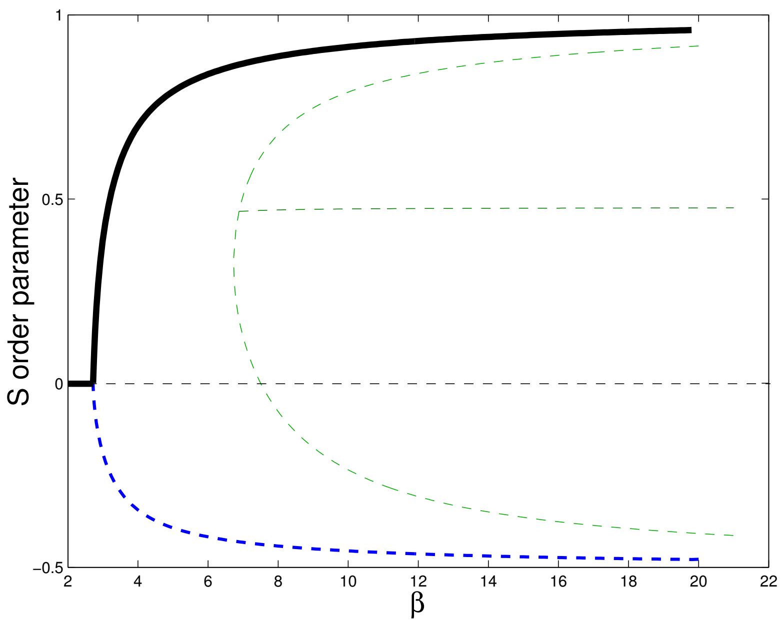

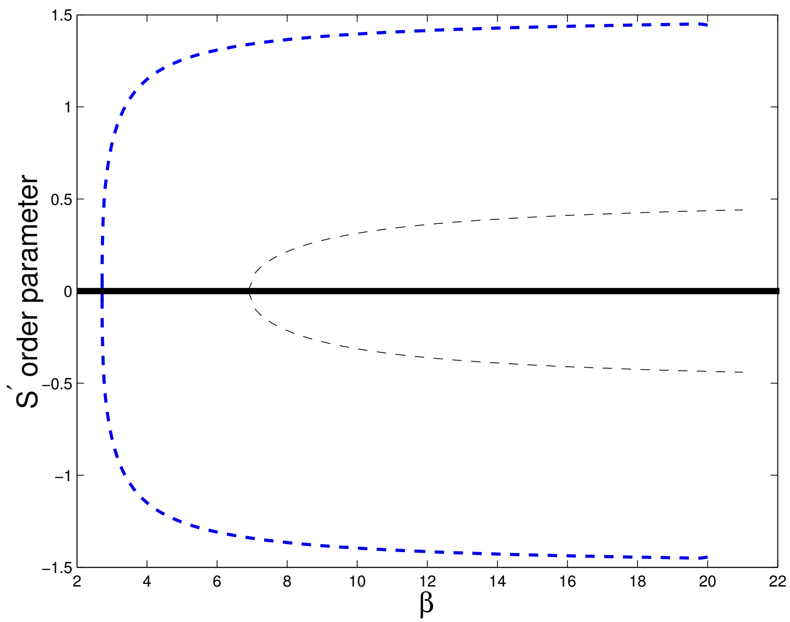

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