Stability and Symmetry Properties for the General Quadrupolar Interaction between Biaxial Molecules

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Summary

Molecular Biaxiality

Interaction Potential

Stability

Symmetry

Ordered Phases

Phase Diagrams

Molecular Biaxiality

molecular tensors

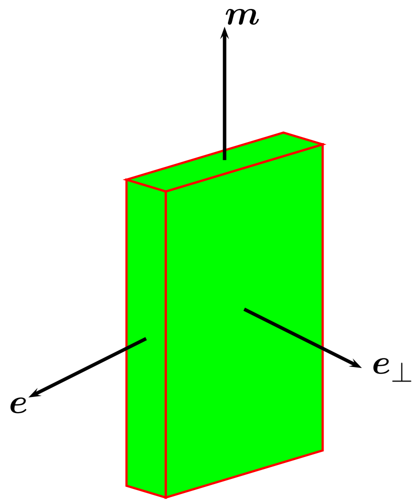
We think of the molecules as being described by a biaxial tensor that can be decomposed into ***two*** traceless, irreducible orthogonal components.

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

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

$\boldsymbol{m}$ long molecular axis

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



Interaction Potential

The most general quadratic pair-potential was introduced by STRALEY (1974)

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

U_0 typical interaction energy

ξ, λ, γ dimensionless parameters

alternative representation

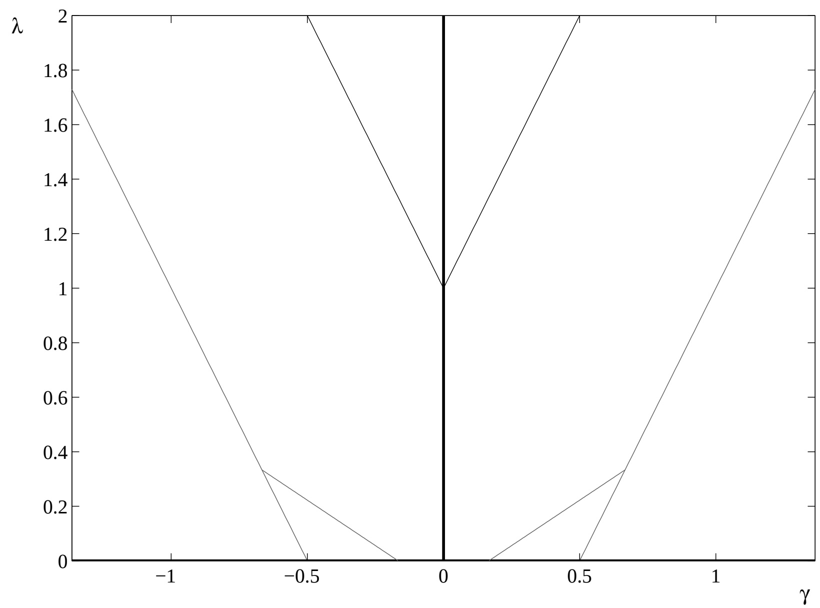
$$V = -U_0\{-(\lambda + \tfrac{1}{3}\xi) + (\xi - \lambda)(\boldsymbol{m} \cdot \boldsymbol{m'})^2$$
$$+2(\lambda + \gamma)(\boldsymbol{e}_\perp \cdot \boldsymbol{e'}_\perp)^2 + 2(\lambda - \gamma)(\boldsymbol{e} \cdot \boldsymbol{e'})^2\}$$

ROMANO (2004), LONGA (2005)

Stability

The local stability of the ***ground state*** of V, where all three molecular axes are equally oriented, is guaranteed by the following conditions

- $\xi = 1 \qquad \lambda > 0 \qquad \lambda - |2\gamma| + 1 > 0$
- $\xi = -1 \qquad \lambda - |2\gamma| - 1 > 0$



symmetric attraction

For $\xi = 1$ and $\lambda = \gamma^2$ the interaction potential V can be given the ***dispersion*** form

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

superposition

By superimposing

$$V_1 = -U_1(\mathbf{q} + \gamma_1\mathbf{b}) \cdot (\mathbf{q'} + \gamma_1\mathbf{b'})$$

$$V_2 = -U_2(\mathbf{q} + \gamma_2\mathbf{b}) \cdot (\mathbf{q'} + \gamma_2\mathbf{b'})$$

we obtain

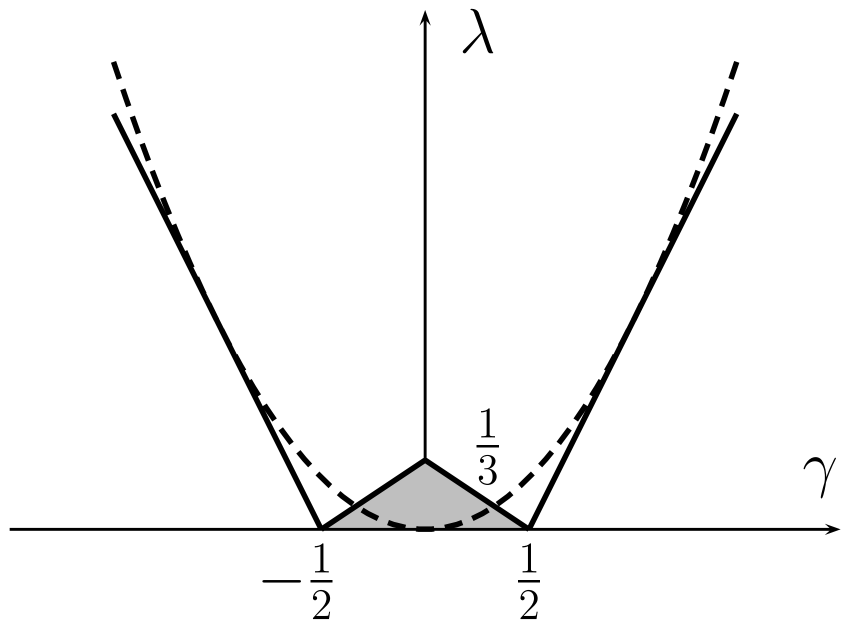
$$V = V_1 + V_2 = -U_0\left\{\mathbf{q} \cdot \mathbf{q}' + \gamma\left(\mathbf{q} \cdot \mathbf{b'} + \mathbf{b} \cdot \mathbf{q'}\right) + \lambda\mathbf{b} \cdot \mathbf{b'}\right\}$$

where

$$U_0 = U_1 + U_2, \qquad \gamma = \frac{U_1\gamma_1 + U_2\gamma_2}{U_1 + U_2}, \qquad \lambda = \frac{U_1\gamma_1^2 + U_2\gamma_2^2}{U_1 + U_2}$$

The point (γ, λ) lies on the segment joining the points (γ_1, λ_1) and (γ_2, λ_2), within the dispersion parabola

$$\lambda > \gamma^2$$

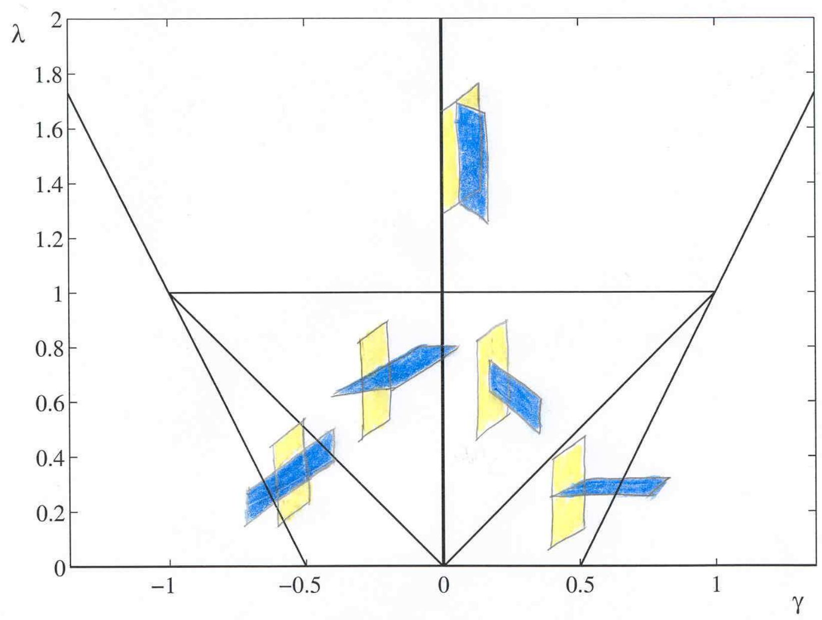


potential extrema

The stability region can be further characterized by identifying all extrema of V

- V attains its absolute minimum at $(\mathbf{q}, \mathbf{b}) = (\mathbf{q'}, \mathbf{b'})$
- $(\mathbf{q}, \mathbf{b})$ and $(\mathbf{q'}, \mathbf{b'})$ have one and the same eigenframe at all extrema of V

maxima chart



strongest attraction

The inner triangle, where V attains its maxima when all corresponding molecular axes are mutually orthogonal, is interpreted as the region of strongest molecular attraction.

mild repulsion

The interactions within the stability region that fall outside the dispersion parabola are called ***mildly repulsive***.

Symmetry

V-invariant transformations

$$V = -U_0\{\xi^* \mathbf{q^*} \cdot \mathbf{q^{*\prime}} + \gamma^*(\mathbf{q^*} \cdot \mathbf{b^{*\prime}} + \mathbf{q^{*\prime}} \cdot \mathbf{b^*}) + \lambda^* \mathbf{b^*} \cdot \mathbf{b^{*\prime}}\}$$

$$\boldsymbol{e} = \boldsymbol{e}^*$$

$$\xi_1^* = 9\lambda + 6\gamma + 1$$
$$\gamma_1^* = 1 - 3\lambda + 2\gamma$$
$$\lambda_1^* = 1 + \lambda - 2\gamma$$

$$\boldsymbol{e}_\perp = \boldsymbol{e}^*{}_\perp$$

$$\xi_2^* = 9\lambda - 6\gamma + 1$$
$$\gamma_2^* = 1 - 3\lambda - 2\gamma$$
$$\lambda_2^* = 1 + \lambda + 2\gamma$$

$$\boldsymbol{m} = \boldsymbol{m}^*$$

$$\xi_3^* = 1$$
$$\gamma_3^* = -\gamma$$
$$\lambda_3^* = \lambda$$

Longa(2005), De Matteis (2005)

rescaling

Provided that $\xi^* \neq 0$, we can set either $\xi^* = 1$ or $\xi^* = -1$, depending on whether $\xi^* > 0$ or $\xi^* < 0$. Correspondingly, the pairs $(\gamma_1^*, \lambda_1^*)$ and $(\gamma_2^*, \lambda_2^*)$ become

$$\gamma_1^* = \frac{1 - 3\lambda + 2\gamma}{9\lambda + 6\gamma + 1} \qquad \lambda_1^* = \frac{1 + \lambda - 2\gamma}{9\lambda + 6\gamma + 1}$$

$$\gamma_2^* = \frac{1 - 3\lambda - 2\gamma}{9\lambda - 6\gamma + 1} \qquad \lambda_2^* = \frac{1 + \lambda + 2\gamma}{9\lambda - 6\gamma + 1}$$

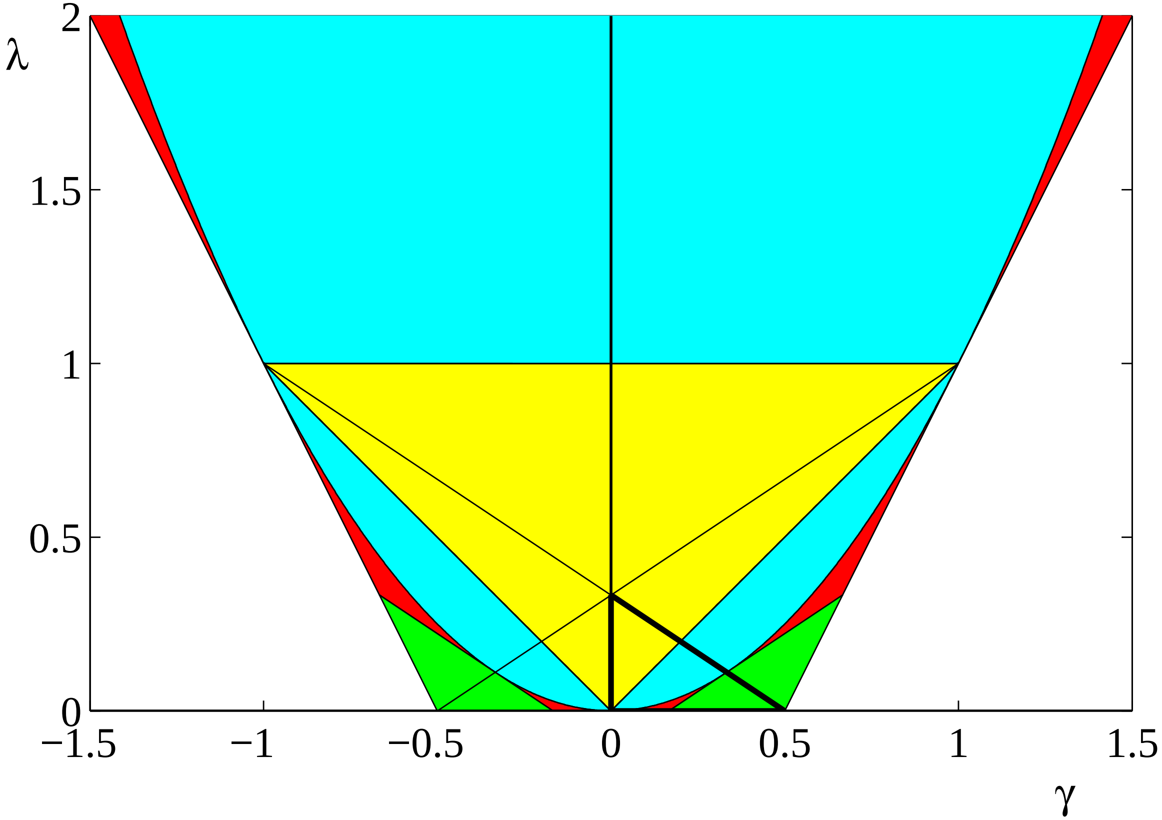
symmetry properties

We denote by τ_1, τ_2, and τ_3 the scaled transformations. They enjoy the following properties:

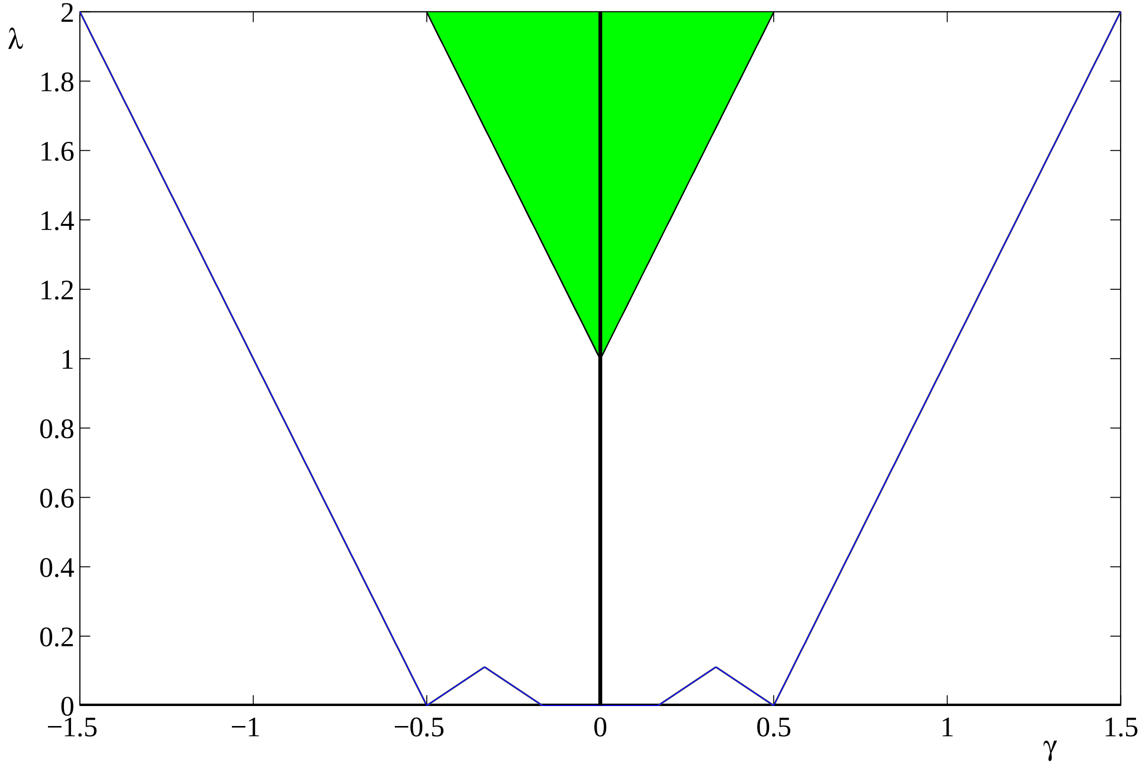
- $\tau_i \circ \tau_i = 1$
- $\tau_i \circ \tau_j \circ \tau_k = 1 \quad \text{for } i \neq j \neq k$
- lines $1 + \lambda + 2\gamma = 0$, $1 + \lambda - 2\gamma = 0$, and $\gamma = 0$ are conjugated
- parabola $\lambda = \gamma^2$ is self-conjugated

De Matteis (2005)

conjugation charts



$\xi = 1$



$\xi = -1$

Ordered Phases

order tensors

$$\mathbf{Q} := \langle \mathbf{q} \rangle \qquad \mathbf{B} := \langle \mathbf{b} \rangle$$

$\langle \cdot \rangle$ ensemble average

We assume that both **Q** and **B** have one and the same ***eigenframe*** $\{\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z\}$.

conjugation

The conjugations involving **q** and **b** are clearly conveyed on the corresponding order tensors. Conjugated macroscopic states are physically equivalent.

general representation

The most general representation of a ***completely*** biaxial state employs ***four*** order parameters STRALEY (1974):

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

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

terminology

- ***uniaxial phase*** occurs whenever both $\mathbf{Q}$ and $\mathbf{B}$ are uniaxial: $T = T' = 0$
- ***phase biaxiality*** compatible with ***cylindrical*** molecules occurs when $S' = T' = 0$
- ***intrinsic biaxiality*** emerges when $T' \neq 0$.

order parameter manifold

Let $(\vartheta, \varphi, \psi)$ be the ***Euler angles*** that represent the rotation taking $\{\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z\}$ into $\{\boldsymbol{m}, \boldsymbol{e}, \boldsymbol{e}_\perp\}$.

$$S = \tfrac{3}{2}\langle \cos^2\vartheta - \tfrac{1}{3}\rangle \qquad -\tfrac{1}{2} \le S \le 1$$

$$T = \tfrac{1}{2}\langle \sin^2\vartheta \cos 2\varphi\rangle \qquad -\tfrac{1}{3}(1-S) \le T \le \tfrac{1}{3}(1-S)$$

$$S' = \tfrac{3}{2}\langle \sin^2\vartheta \cos 2\psi\rangle$$

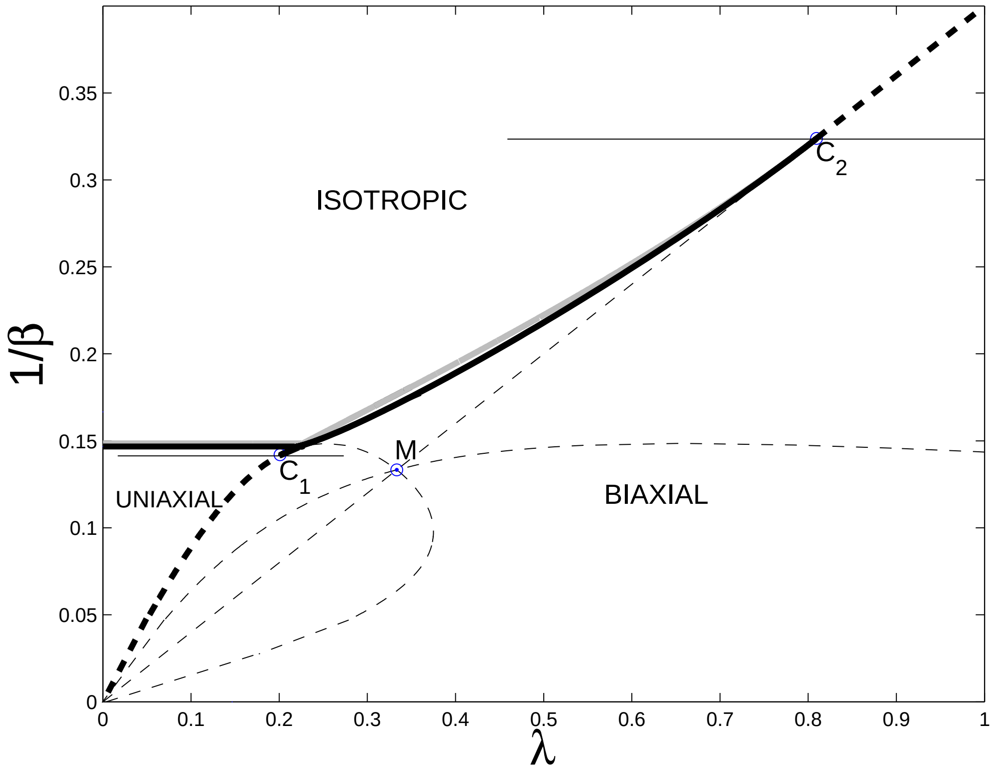
$$-(1-S) \le S' \le (1-S)$$

$$T' = \tfrac{1}{2}\langle \left(1+\cos^2\vartheta\right)\cos 2\varphi \cos 2\psi - 2\cos\vartheta \sin 2\varphi \sin 2\psi\rangle$$

$$-1 \le T' \le 1$$

Phase Diagrams

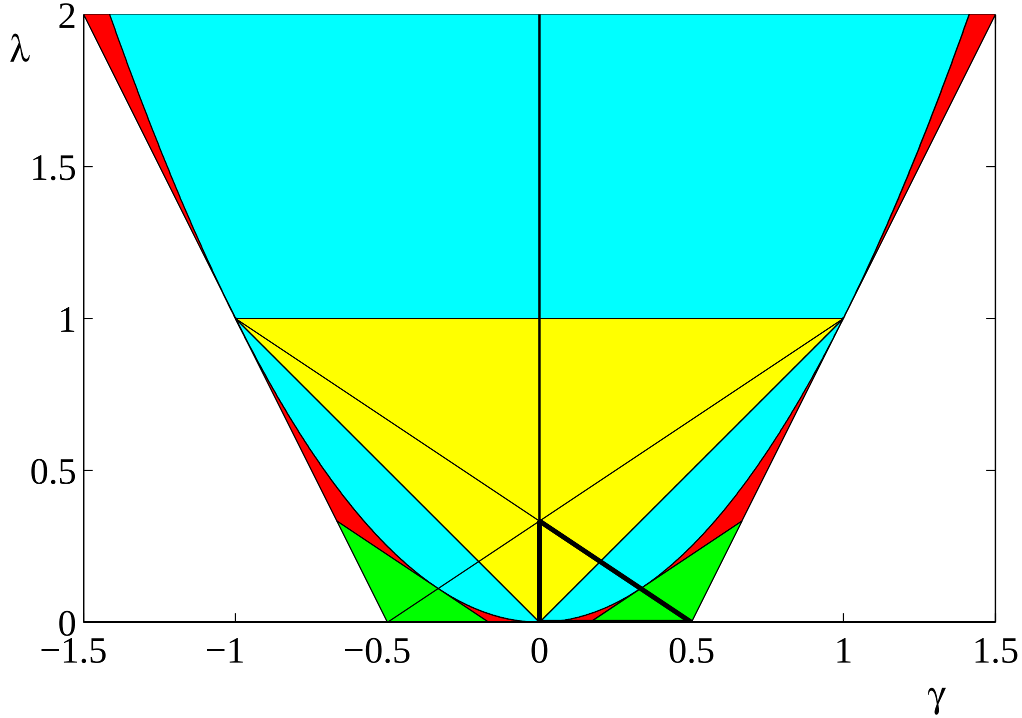
Within a mean-field approximation the following diagram has recently been established for $\gamma = 0$.

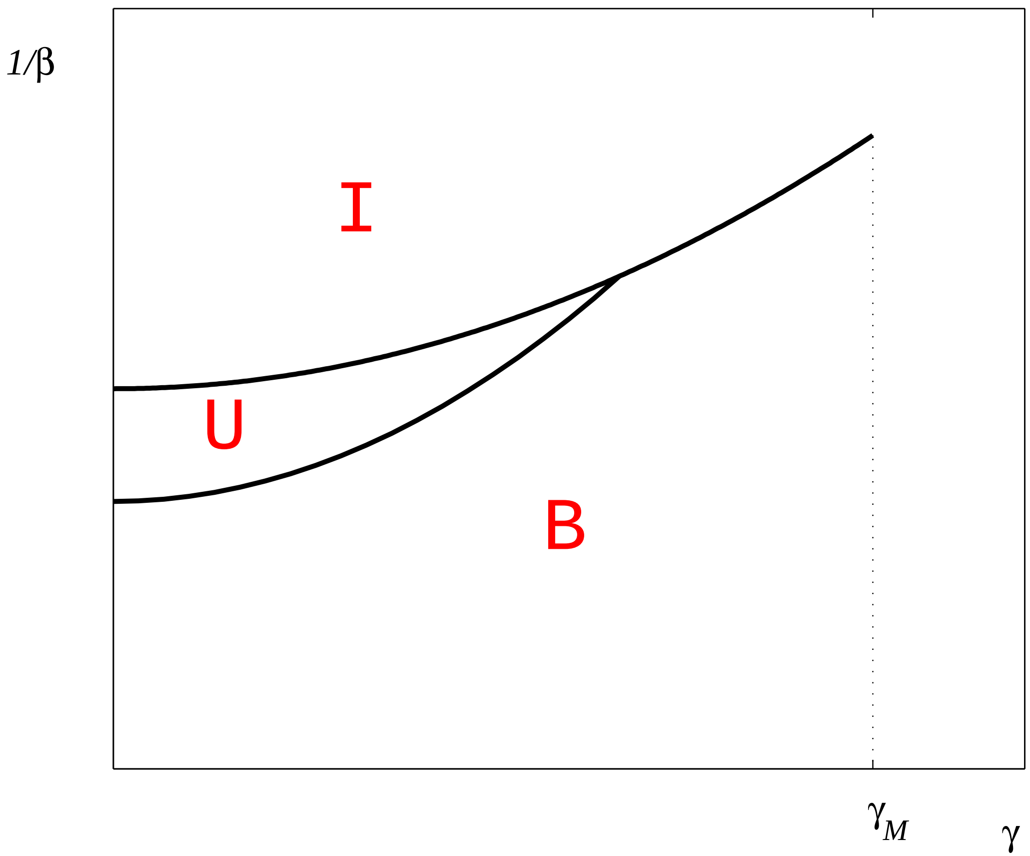


Sonnet, Durand & Virga (2003)
De Matteis & Virga (2005)

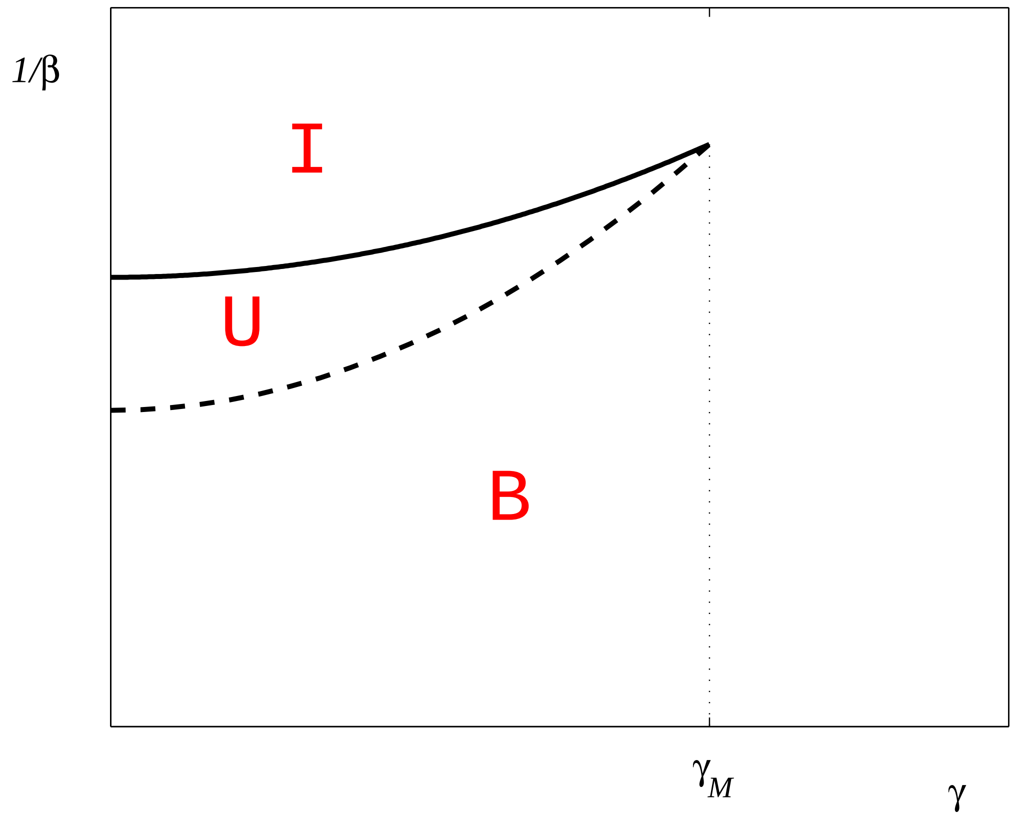
educated guesses

Preliminary numerical explorations suggest that within the attractive parabola there are only two qualitatively different phase diagrams.





For λ constant ***above*** the tricritical trajectory



For λ constant ***below*** the tricritical trajectory

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More information

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