Attraction and Repulsion in Biaxial Molecular Interactions

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Summary

Molecular Biaxiality
Interaction Potential
Stability
Symmetry

Molecular Biaxiality

molecular tensors

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

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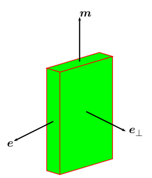
$$\mathbf{q} := \boldsymbol{m} \otimes \boldsymbol{m} - \frac{1}{3}\mathbf{I}$$

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

$\boldsymbol{m}$ 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

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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

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

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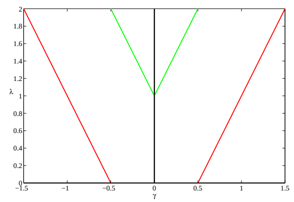

potential extrema

For $\xi = 1$ the stability region enjoys further properties that can be phrased in terms of the 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 maxima of V
- there are extrema of V at which $(\mathbf{q}, \mathbf{b})$ and $(\mathbf{q}', \mathbf{b}')$ do ***not*** share the same eigenframe, but they are neither minima nor maxima. Gartland (2005)

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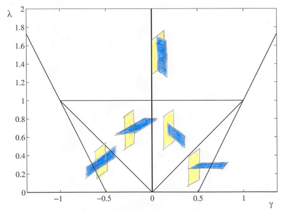
maxima chart



strong 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.

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symmetric attraction

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

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

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symmetric superposition

The pair-potential V can uniquely be written as superposition of two orthogonal symmetric components

$$V = -U_0 \left\{ a^+ \mathbf{q}^+ \cdot \mathbf{q}^{+\prime} + a^- \mathbf{q}^- \cdot \mathbf{q}^{-\prime} \right\}$$

with

$$\mathbf{q}^+ \cdot \mathbf{q}^- = 0$$

Precisely,

$$\mathbf{q}^+ = \mathbf{q} + \gamma^+ \mathbf{b} \qquad \mathbf{q}^- = \mathbf{q} + \gamma^- \mathbf{b}$$

with

$$\gamma^\pm = \frac{3\lambda - 1 \pm \sqrt{(3\lambda - 1)^2 + 12\gamma^2}}{6\gamma}$$

and

$$a^+ = \frac{\gamma - \gamma^-}{\gamma^+ - \gamma^-} \qquad a^- = \frac{\gamma^+ - \gamma}{\gamma^+ - \gamma^-}$$

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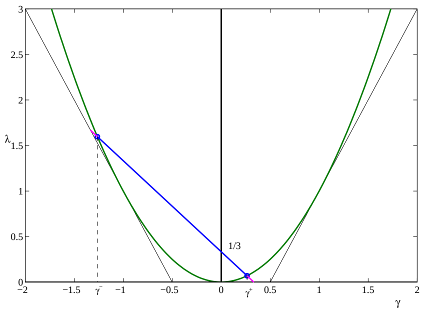
graphical construction



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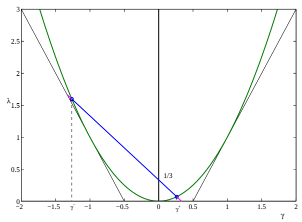
- Each point (γ, λ) represents an interaction potential which can be written as a linear superposition of two orthogonal, purely quadratic (symmetric) potentials represented by points (γ^+, λ^+) and (γ^-, λ^-) on the dispersion parabola $\lambda = \gamma^2$.
- Each point (γ, λ) on a straight line through the point $(0, \frac{1}{3})$ is associated with the same pair (γ^+, λ^+) and (γ^-, λ^-), but with different coefficients a^+ and a^-.



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full attraction

Both a^+ and a^- are ***positive*** whenever $\lambda > \gamma^2$. All potentials represented by points within the dispersion parabola are ***fully attractive***, as they are superpositions of attractive, symmetric potentials.

mild repulsion

Either a^+ or a^- is ***negative*** whenever $\lambda < \gamma^2$ within the stability region. The potentials represented by these points are ***mildly repulsive***.

All ***excluded-volume*** potentials so far studied seem to fall within this category.

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Symmetry

V-invariant transformations

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

$\boldsymbol{e} = \boldsymbol{e}^*$	$\boldsymbol{e}_\perp = \boldsymbol{e}^*{}_\perp$
$\xi_1^* = 9\lambda + 6\gamma + 1$	$\xi_2^* = 9\lambda - 6\gamma + 1$
$\gamma_1^* = 1 - 3\lambda + 2\gamma$	$\gamma_2^* = 1 - 3\lambda - 2\gamma$
$\lambda_1^* = 1 + \lambda - 2\gamma$	$\lambda_2^* = 1 + \lambda + 2\gamma$

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

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

Longa(2005), De Matteis (2005)

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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

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

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

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symmetry properties

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

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

De Matteis (2005)

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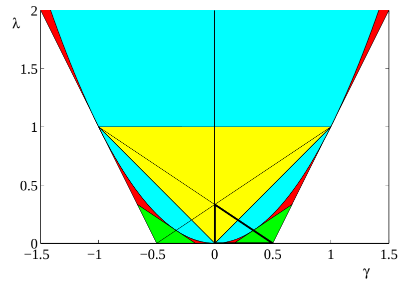
conjugation charts



$\xi = 1$

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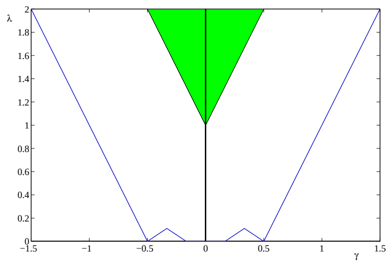

$\xi = -1$

Acknowledgements

Co-Authors

Fulvio Bisi
Giovanni De Matteis
Georges Durand
Chuck Gartland
Silvano Romano
André M. Sonnet

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Institutions

Royal Society of London
Sothampton-Pavia Collaborative Project

Italian MIUR
PRIN Grant No. 2004024508

More information

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