Drops of Twist-Bend Nematic Liquid Crystals

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Summary

Twist-Bend Nematics

Surface Energy Functional

Two-Dimensional Drops

Mathematical Model

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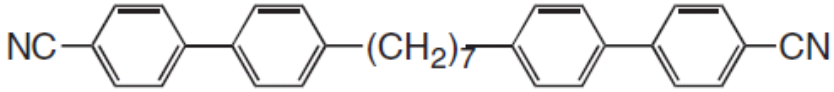

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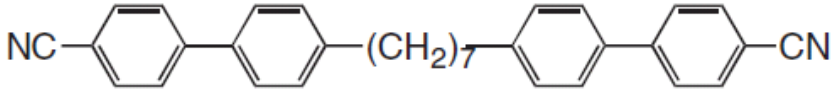
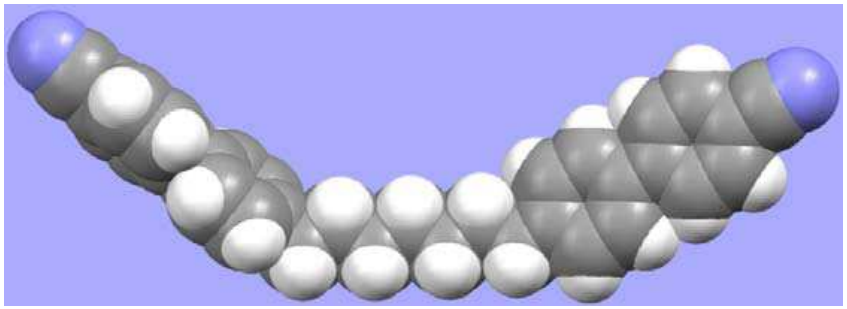


A CB7CB molecule can be viewed as having three parts, each $\approx 1\,\mathrm{nm}$ in length: two rigid end groups connected by a flexible spacer.



transition temperatures

First transition, on cooling, at $T_{\mathrm{NI}} = 116 \pm 1\,^{\circ}\mathrm{C}$, with ***transitional entropy*** $\Delta S_{\mathrm{NI}}/R = 0.34$, where $R \approx 8.31\,\mathrm{J(mol\,K)^{-1}}$ is the ideal gas constant.

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Second transition, on further cooling, at $T_{\mathrm{NN_{tb}}} = 103 \pm 1\,^{\circ}\mathrm{C}$, with $\Delta S_{\mathrm{NN_{tb}}}/R = 0.31$.

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Second transition, on further cooling, at $T_{\mathrm{NN_{tb}}} = 103 \pm 1\,^{\circ}\mathrm{C}$, with $\Delta S_{\mathrm{NN_{tb}}}/R = 0.31$.

Both transitions are ***weakly first-order***, with at ***two-phase coexistence*** at each transition of approximately $0.1\,^{\circ}\mathrm{C}$.

heliconical ground states

The N_{tb} ground states are ***conical*** twists, in which the long molecular axis performs uniform precessions, making the angle ϑ with the ***twist*** axis $\boldsymbol{t}$.

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Letting $\boldsymbol{t} = \boldsymbol{e}_3$ in a Cartesian frame,

$$\boldsymbol{m}^{\pm} = \sin\vartheta\cos(\pm qz)\,\boldsymbol{e}_1 + \sin\vartheta\sin(\pm qz)\,\boldsymbol{e}_2 + \cos\vartheta\,\boldsymbol{t},$$

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helicity

$\boldsymbol{m}$ molecular director

$\eta := \operatorname{curl}\boldsymbol{m}^{\pm}\cdot\boldsymbol{m}^{\pm} = \mp q\sin^2\vartheta$

$q > 0$ twist parameter

$p := \frac{2\pi}{q}$ pitch $\quad\vartheta$ cone angle

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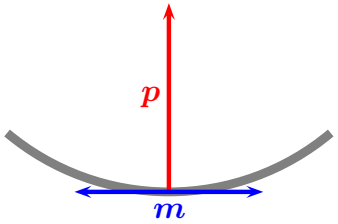

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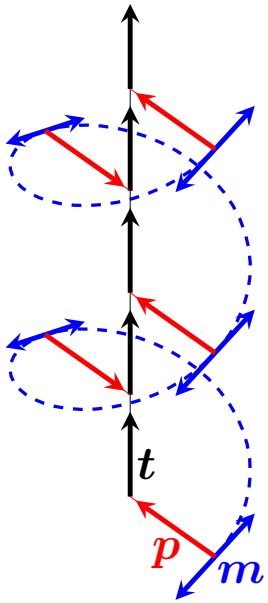

Recent Experimental Evidence

A ***visual*** direct evidence for the N_{tb} phase in ***CB7CB*** (and allied mixtures) has been recently provided with accurate measurements of both p and ϑ.

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measured pitch and cone angle

$$p \approx 10\,\mathrm{nm} \qquad \vartheta \approx 20^\circ$$

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interfacial energy density

$$W_{\mathrm{s}} = W_0 \left[1 + w(\boldsymbol{m} \cdot \boldsymbol{\nu})^2\right]$$

$\boldsymbol{\nu}$ outer unit normal

W_0 isotropic surface tension

$w \geqq -1$ anisotropy dimensionless parameter

$w > 0$ degenerate tangential alignment

$w < 0$ homeotropic alignment

outside the drop

The molecular director $\boldsymbol{m}$ must to be ***continuous*** across the N_{tb} /nematic interface and agree with the uniform $\boldsymbol{n}$ outside the drop.

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inside the drop

Inside the drop $\boldsymbol{m}$ is expected to comply, at least locally, with the heliconical ground state

$$\boldsymbol{m} = \cos\vartheta\,\boldsymbol{t} + \sin\vartheta\,(\cos\varphi\,\boldsymbol{e}_1 + \cos\varphi\,\boldsymbol{e}_2)$$

φ phase varying over a nanoscopic length-scale

ϑ cone angle

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coarse-graining W_{s}

$$\langle W_{\mathrm{s}}\rangle = W_0\left\{1 + \frac{1}{2}w\sin^2\vartheta - \frac{1}{2}w\left(1 - 3\cos^2\vartheta\right)(\boldsymbol{t}\cdot\boldsymbol{\nu})^2\right\}$$

degenerate tangential anchoring

Assuming $w > 0$ and $\cos\vartheta > \frac{1}{\sqrt{3}}$, $\langle W_{\mathrm{s}} \rangle$ is ***minimized*** by letting $\boldsymbol{t}$ be tangent to the interface, however oriented upon it.

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geometric compatibility

In view of the uniform alignment of the nematic director $\boldsymbol{n}$ outside the drop and the continuity of the molecular alignment across the interface, the degenerate tangential anchoring of $\boldsymbol{t}$ becomes geometrically compatible only if the cone angle is allowed to ***vary*** along the ***interface***.

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elastic mismatch energy

$$f_{\rm a} = \frac{1}{2} W_{\rm a} \left[(\boldsymbol{t}\cdot\boldsymbol{n})^2 - c^2 \right]^2$$

$W_{\rm a} > 0$ elastic constant

$\vartheta = \arccos c$ ***ideal*** cone angle

surface energy functional

$$\mathscr{F}_{\mathrm{s}} = W_0 \int_{\mathscr{S}} \left\{ 1 + \frac{1}{2}\omega \left[(\boldsymbol{t}\cdot\boldsymbol{n})^2 - c^2 \right]^2 \right\} da$$

a area measure

$\omega := \frac{W_{\mathrm{a}}}{W_0} > 0$ anisotropy dimensionless parameter

$\mathscr{S}$ surface separating the phases

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isoperimetric constraint

As the $\mathrm{N_{tb}}$ phase, like the classical nematic phase, can be regarded as incompressible, $\mathscr{F}_{\mathrm{s}}$ is subject to the constraint that the ***volume enclosed*** by $\mathscr{S}$ be ***fixed***.

neglecting distortion energy

Clearly, the ***t*** field will also be ***distorted*** in the interior of the drop. We shall hereafter ***neglect*** the ***elastic energy*** associated with such a distortion, as we believe that it plays a little role in determining the ***equilibrium shape*** of a N_{tb} drop, which is mainly driven by the ***interfacial energy***.

Two-Dimensional Drops

K.S. Krishnamurthy has shown that the equilibrium shape of N_{tb} drops surrounded by their ***oriented*** nematic phase are ***tactoids*** with their pointed corners ***aligned*** with the ***outside director***.

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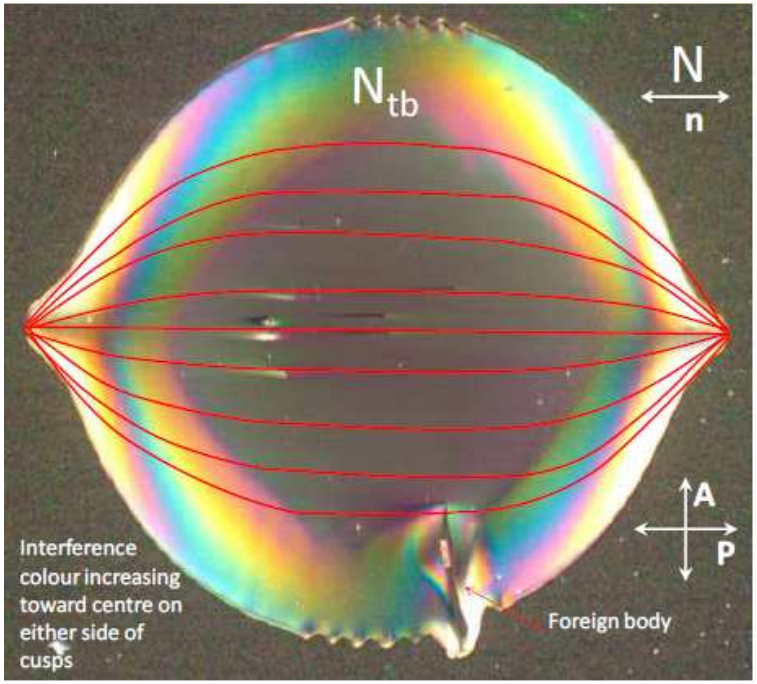
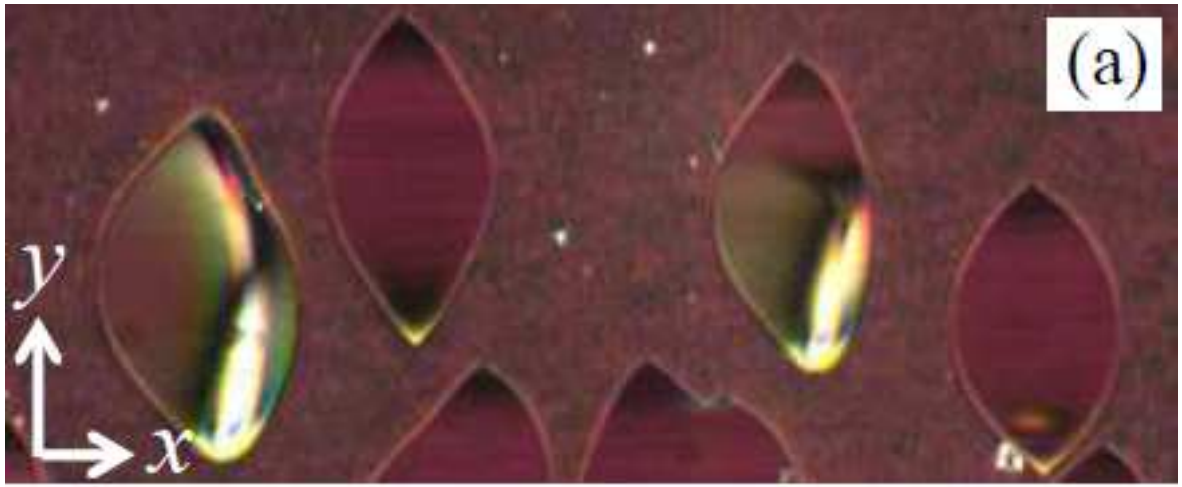
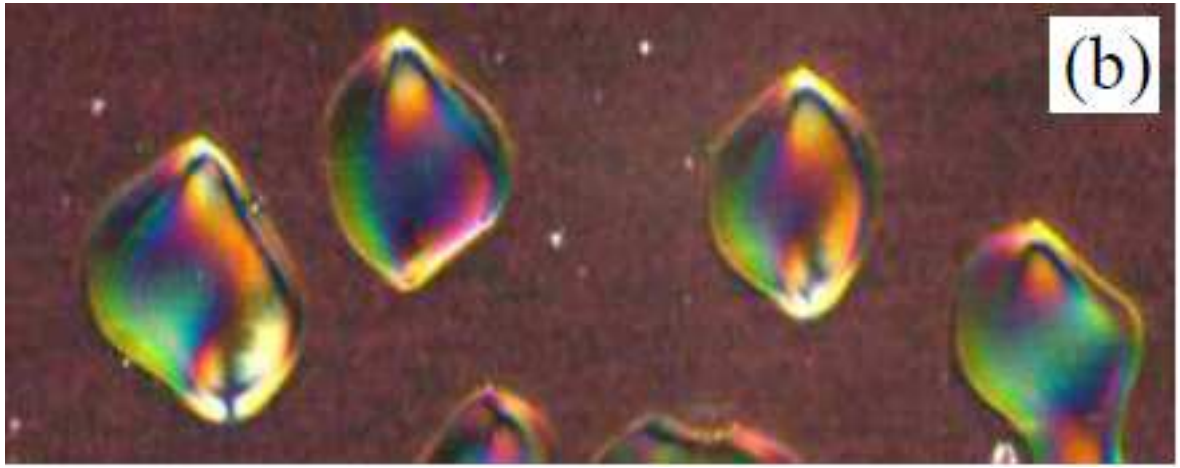


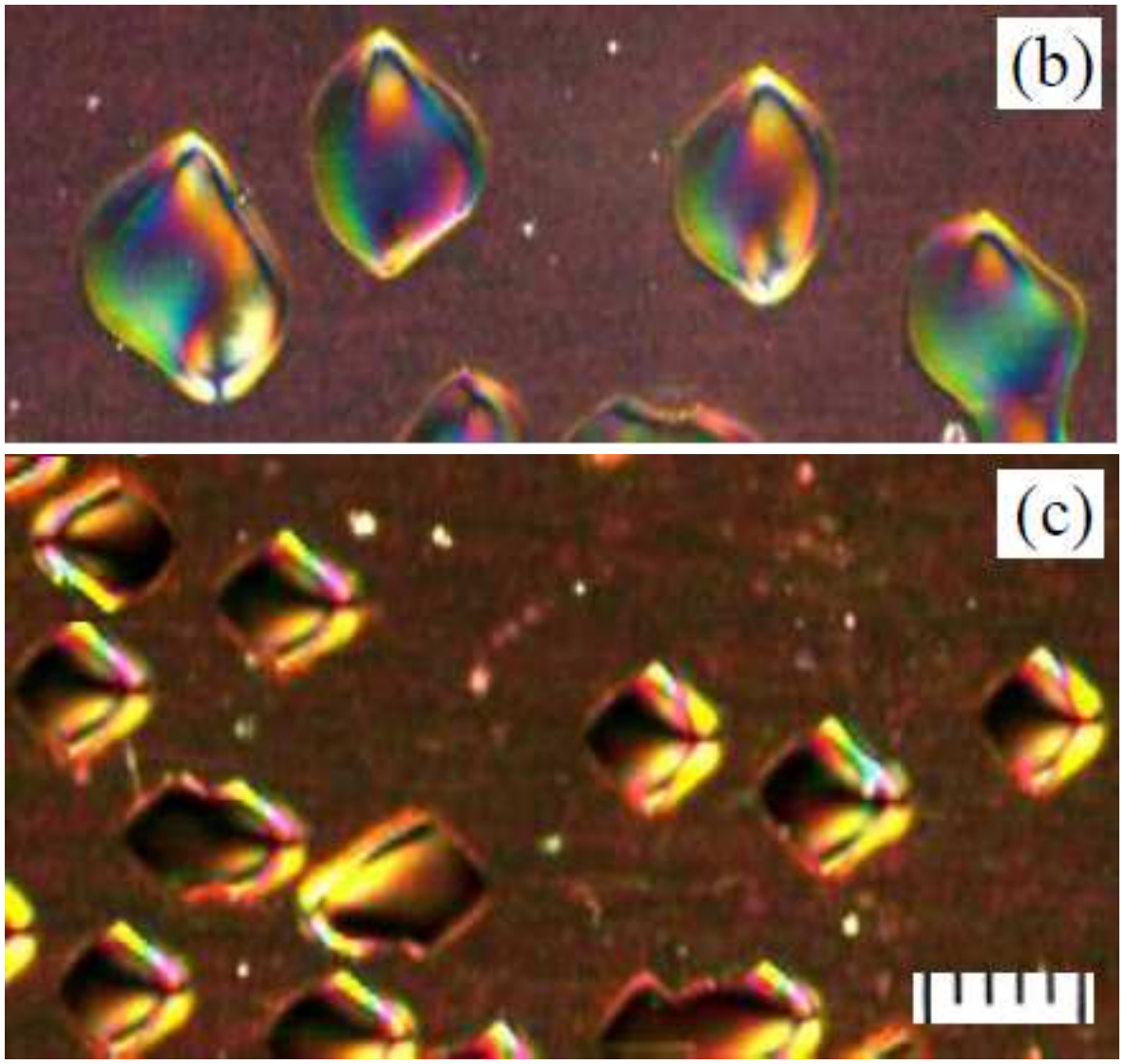
Two-dimensional drop, 2 mm long in a gap 20 μm wide

disintegration of large drops

Under heating, the millimeter-size drop breaks into small, tactoid-shaped drops with corners now on the y axis




(b)

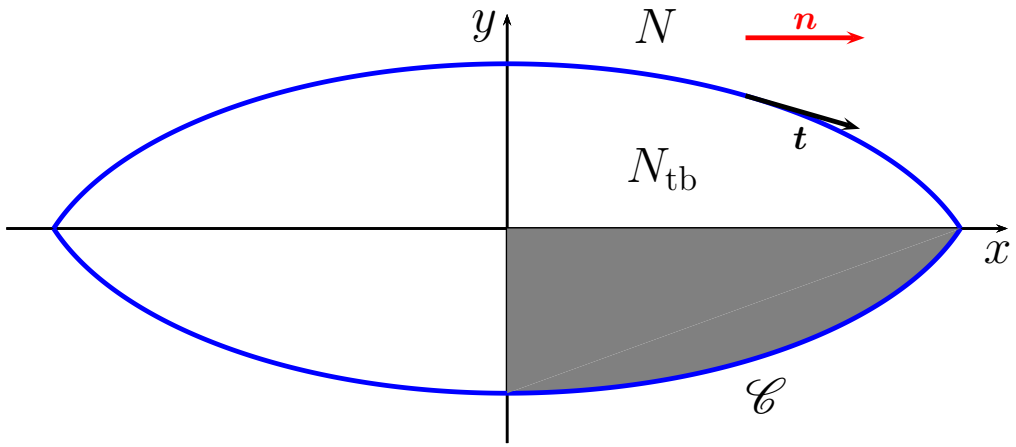


each scale division 10 μm

Mathematical Model

In two space dimension, the drop is bounded by a curve $\mathscr{C}$ described by $s \mapsto \boldsymbol{r}(s)$

$$F[\boldsymbol{r}] := \int_0^L \left\{ 1 + \frac{1}{2}\omega \left[(\boldsymbol{t}\cdot\boldsymbol{n})^2 - c^2 \right]^2 \right\} ds$$



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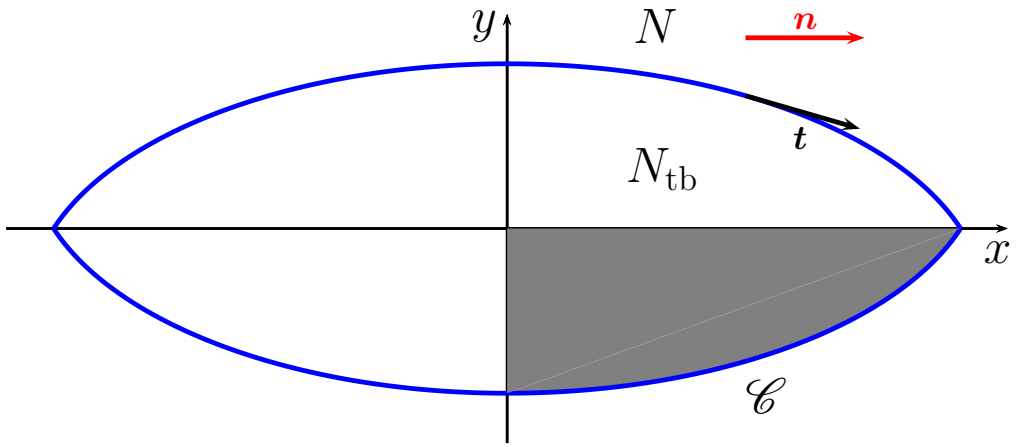
s arc-length co-ordinate along $\mathscr{C}$

L (undetermined) length of $\mathscr{C}$

$\boldsymbol{t} = \boldsymbol{r}'$ $'$ denotes s differentiation



area functional

$$A[\boldsymbol{r}] := -\frac{1}{2}\int_0^L \boldsymbol{r} \times \boldsymbol{t} \cdot \boldsymbol{e}_z ds$$

$$\boldsymbol{e}_z := \boldsymbol{e}_x \times \boldsymbol{e}_y$$

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constrained equilibrium

$$\delta F = \lambda \delta A$$

λ Lagrange multiplier

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equilibrium regular arcs

$$\boldsymbol{f}' + \lambda\boldsymbol{\nu} = \boldsymbol{0}$$

$$\boldsymbol{f} := 2\omega[(\boldsymbol{t}\cdot\boldsymbol{e}_x)^2 - c^2](\boldsymbol{t}\cdot\boldsymbol{e}_x)(\mathbf{I} - \boldsymbol{t}\otimes\boldsymbol{t})\boldsymbol{e}_x + \left(1 + \frac{1}{2}\omega[(\boldsymbol{t}\cdot\boldsymbol{e}_x)^2 - c^2]^2\right)\boldsymbol{t}$$

$\boldsymbol{f}$ line stress

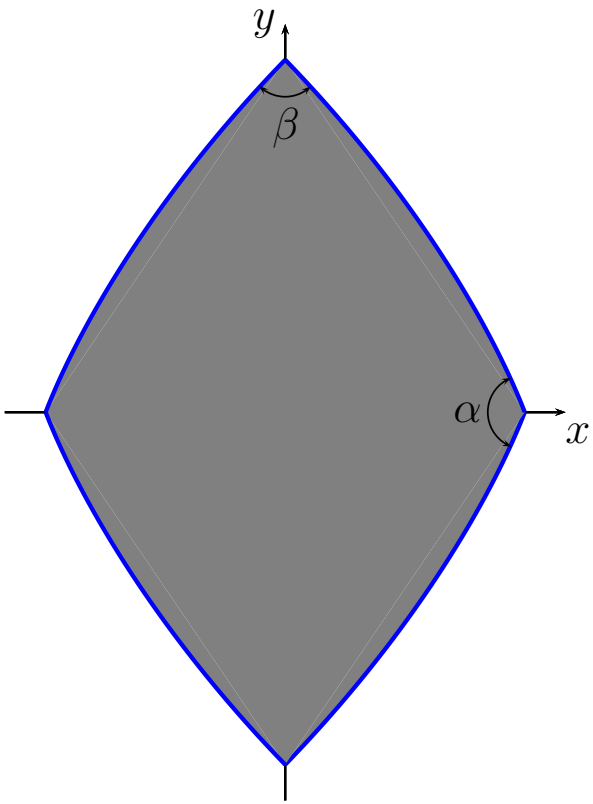
equilibrium corners

$$[\![f]\!] = 0$$

equilibrium corners

$$[\![\boldsymbol{f}]\!] = \mathbf{0}$$

We assume that in equilibrium corners may occur only on the symmetry axes x or y of $\mathscr{C}$.



corner on y

$$\omega \geqq \omega_{\mathrm{c}}^{(1)}(c) := \frac{2}{(1-c^2)(3+c^2)}$$

$$\beta = 2\arcsin\sqrt{\frac{1}{3}\left(c^2+\sqrt{4c^4+\frac{6}{\omega}}\right)}$$

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corner on x

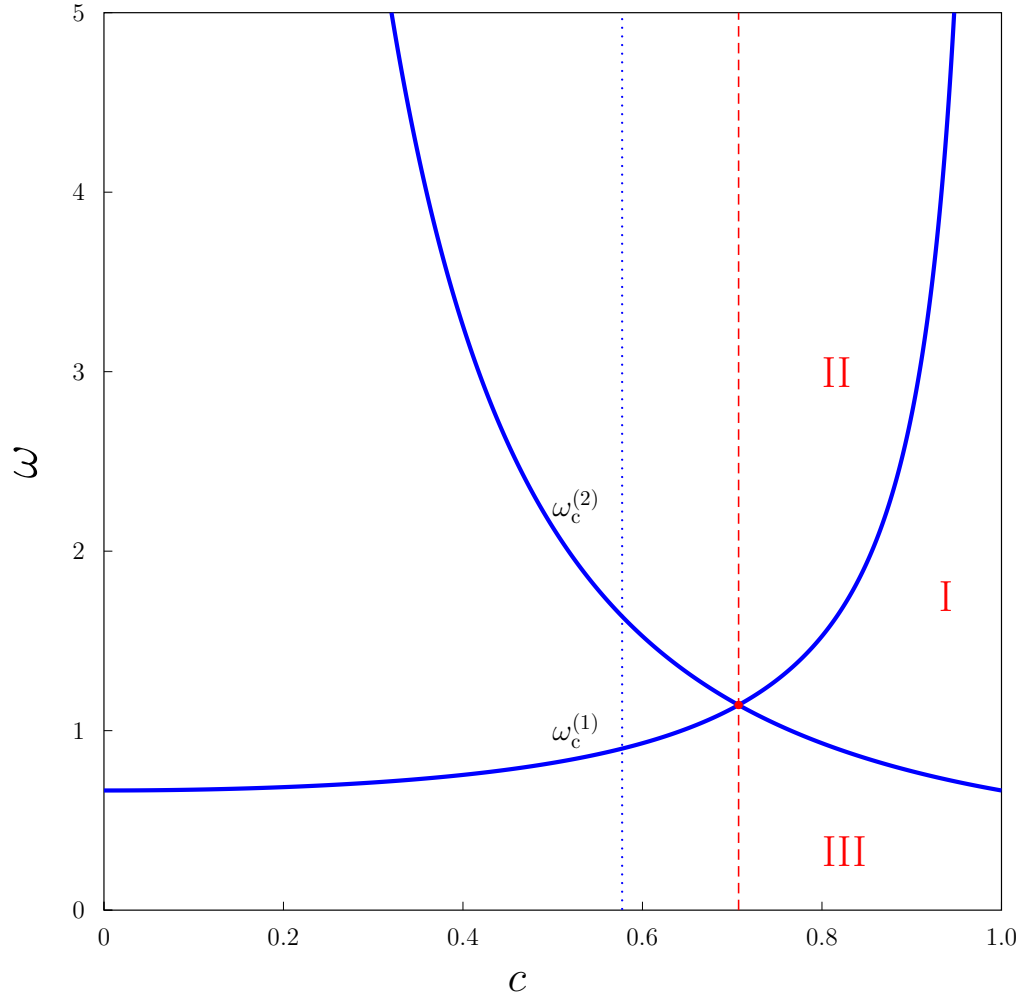
$$\omega \geqq \omega_{\mathrm{c}}^{(2)}(c) := \frac{2}{c^2(4-c^2)}$$

$$\alpha = 2\arccos\sqrt{\frac{1}{3}\left(c^2 + 2 - \sqrt{4(1-c^2)^2 + \frac{6}{\omega}}\right)}$$

symmetry properties

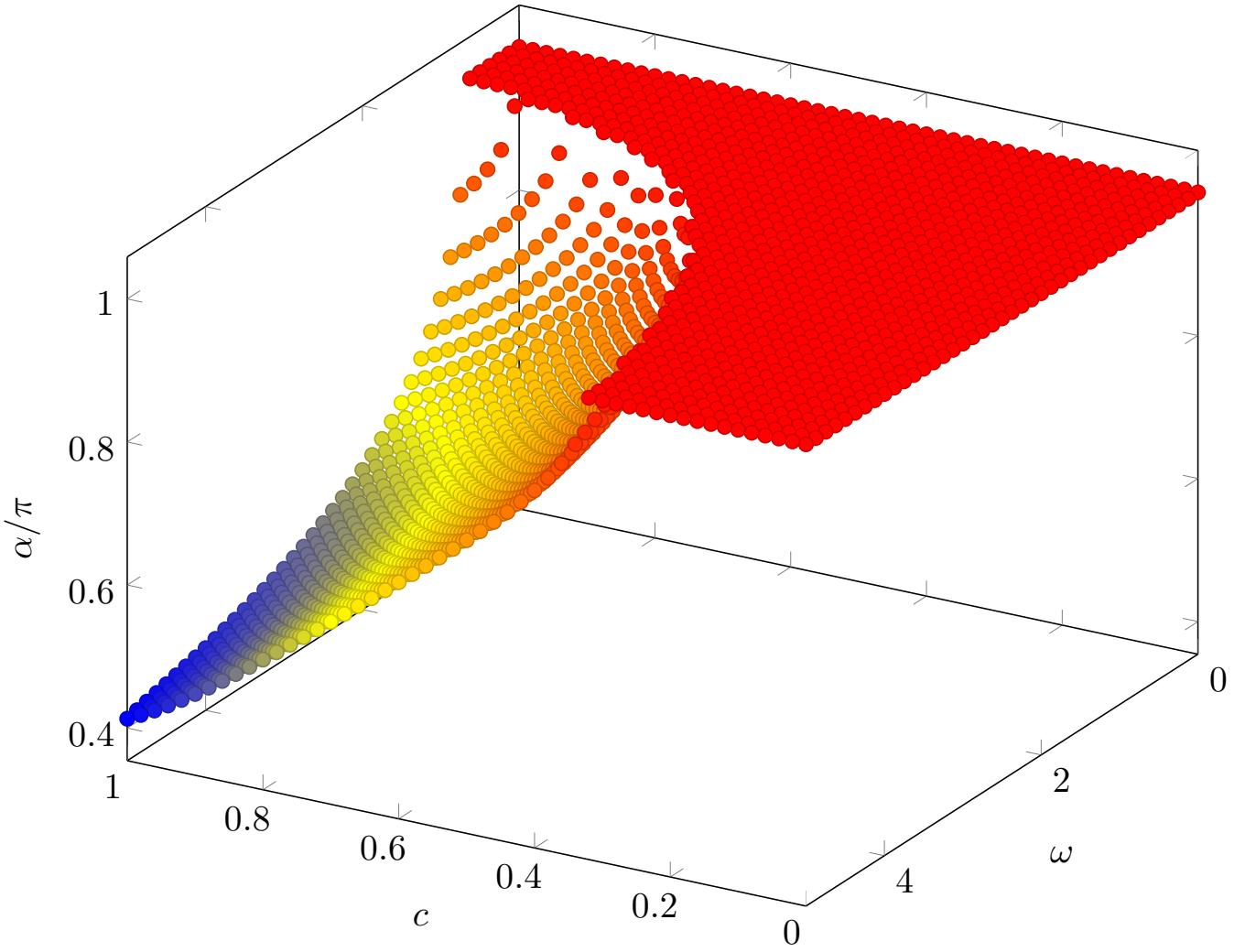
$$\omega_{\mathrm{c}}^{(2)}(c) = \omega_{\mathrm{c}}^{(1)}\left(\sqrt{1-c^2}\right) \qquad \beta(c,\omega) = \alpha\left(\sqrt{1-c^2},\omega\right)$$

phase diagram



I: x-corners II: x- and y-corners III: no corners TP: $\left(\frac{1}{\sqrt{2}}, \frac{8}{7}\right)$

α *plot*



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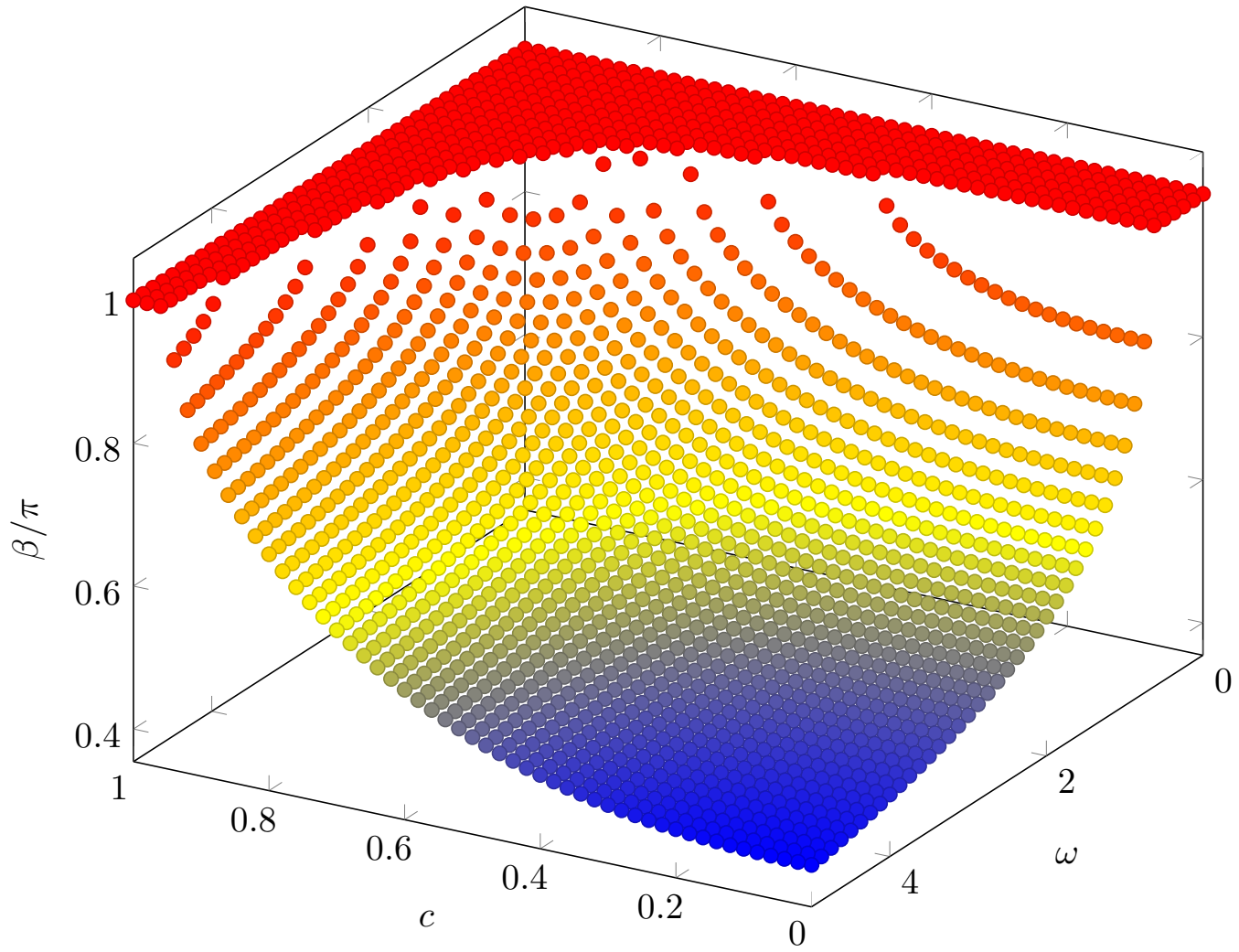
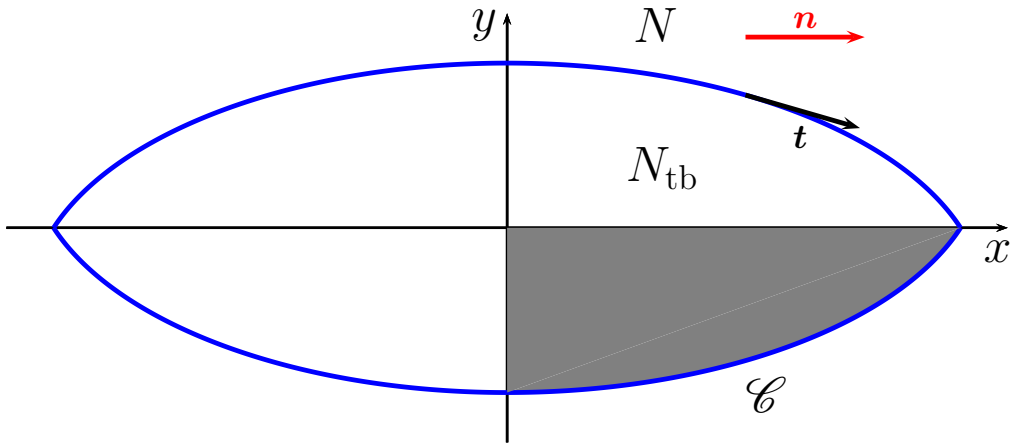


equilibrium regular arcs

$$F^*[y] := \int_0^a \left\{ \left[1 + \frac{1}{2}\omega \left(\frac{1}{1+y'^2} - c^2 \right)^2 \right] \sqrt{1+y'^2} + \lambda y \right\} dx$$

$y = y(x)$ Cartesian representation of a quarter of $\mathscr{C}$

$y(a) = 0$ with a to be determined



exact solution

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$$x = X(u;c,\omega) := \frac{1}{2}\frac{1}{\sqrt{(1+u^2)^5}}[2-3\omega+2\omega c^2+\omega c^4+2(2+\omega c^2+\omega c^4)u^2 + (2+\omega c^4)u^4]u$$

$$y = Y(u;c,\omega) := -\frac{1}{2}\frac{1}{\sqrt{(1+u^2)^5}}[2+\omega-2\omega c^2+\omega c^4+2(2+2\omega-3\omega c^2+\omega c^4)u^2 + (2-4\omega c^2+\omega c^4)u^4]$$

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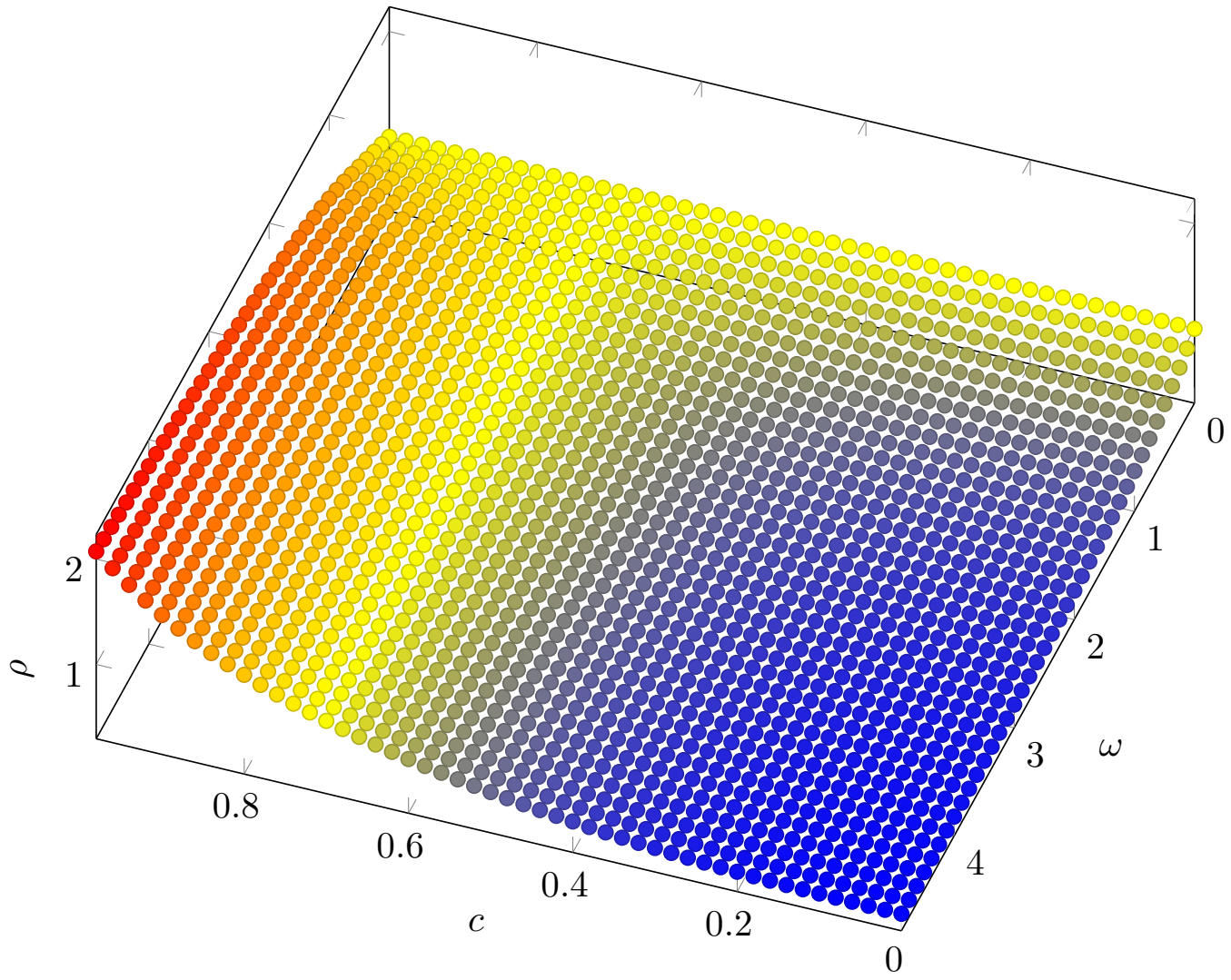
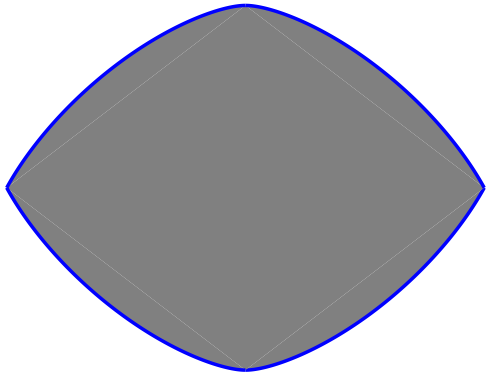
x to y aspect ratio

$$\rho := \frac{X}{Y} \qquad \rho\left(\sqrt{1-c^2},\omega\right) = \frac{1}{\rho(c,\omega)}$$

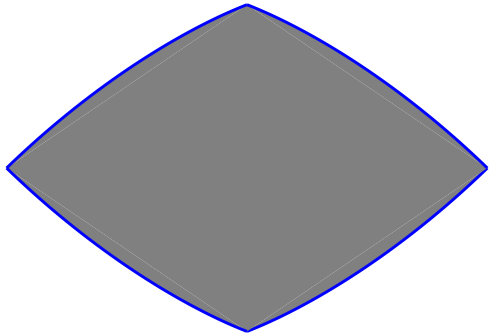
ρ *plot*



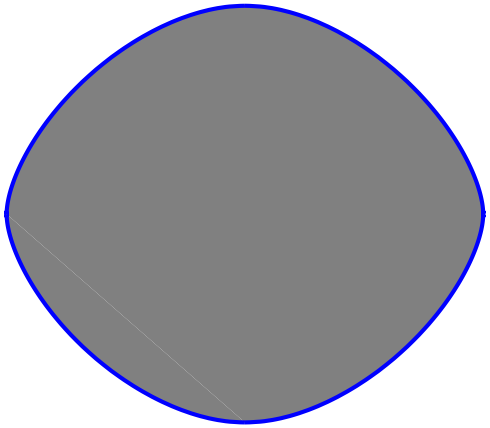
shape gallery



(a)



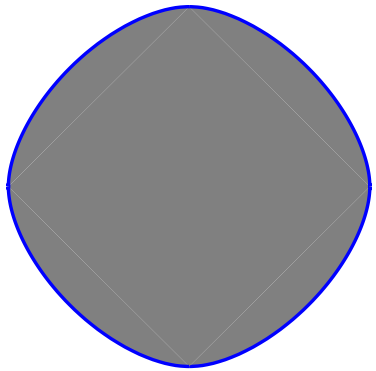
(b)



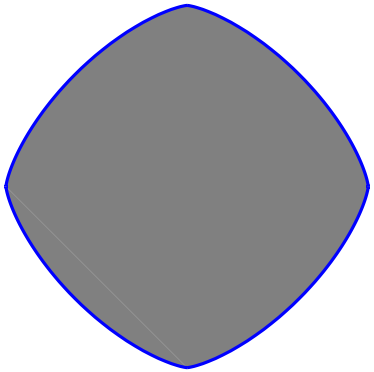
(c)

(a) I: $c = \frac{\sqrt{3}}{2}$, $\omega = \frac{3}{2}$ (b) II: $c = \frac{\sqrt{3}}{2}$, $\omega = 5$ (c) III: $c = \frac{\sqrt{3}}{2}$, $\omega = \frac{4}{7}$

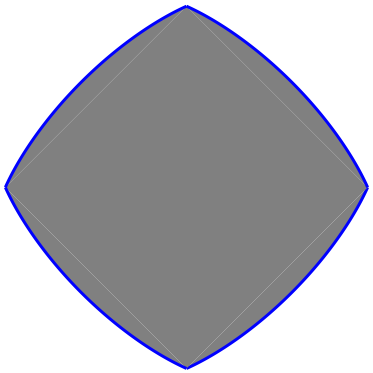
on the symmetry separatix $c = \frac{1}{\sqrt{2}}$



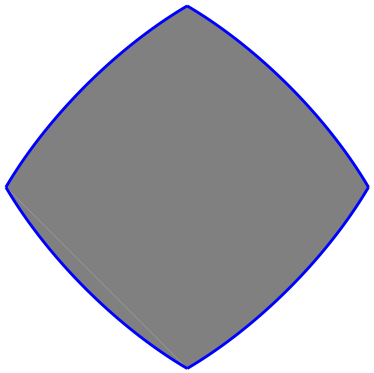
(d)



(e)



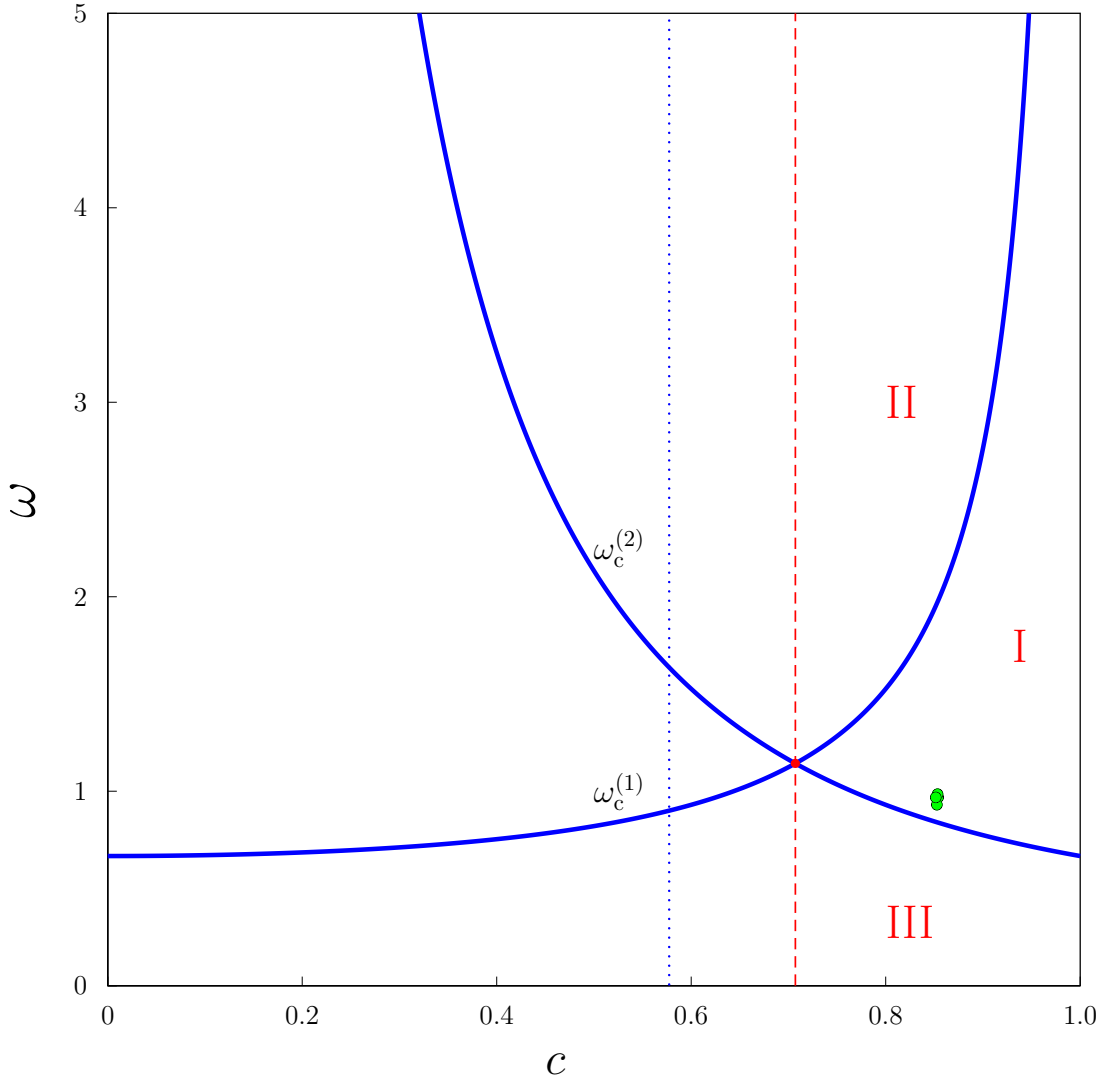
(f)



(g)

(d) $\omega = \frac{4}{7}$ (e) $\omega = \frac{8}{7}$ (f) $\omega = 2$ (g) $\omega = 3$

comparison with experiment



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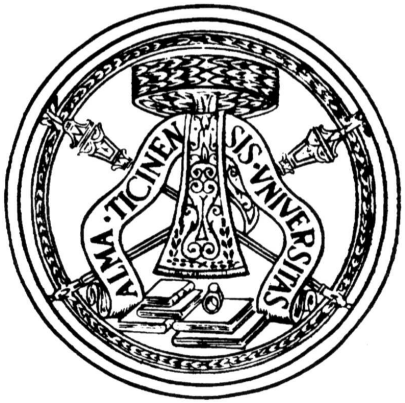

Soft Matter Mathematical Modelling

Department of Mathematics

University of Pavia, Italy