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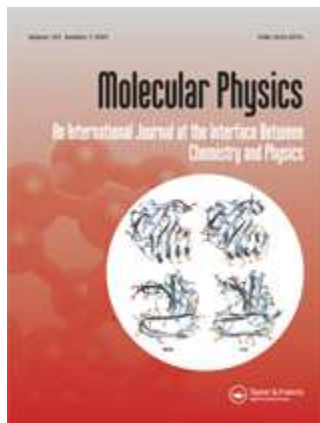
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Excluded area computations for non-convex molecules

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By using methods of computer-aided geometric design (CAGD), we compute explicitly the excluded area for a pair of non-convex molecules obtained by moving a disk of radius h on a circular arc of radius R and amplitude 2α : they are referred to as boomerangs or horseshoes, depending on the value of α . **As a result, the excluded area always attains its absolute minimum when the molecules are antiparallel, instead of parallel, a feature that makes them a good candidate to study shape polarity effects in steric interactions.** Although the excluded area is in general a rather complicated function of the relative orientation, with α and $\eta := h/R$ acting as parameters, when $\eta \ll 1$ a remarkably simple formula is obtained. In this limit, the anisotropic part of the excluded area is independent of η .

keywords: excluded area, steric interactions, convolution curve, Minkowski sum.

I. INTRODUCTION

The excluded region \mathcal{E} for a pair of molecules \mathcal{M} and \mathcal{M}' conceived as rigid bodies is the region of space that is unaccessible to one of them (*e.g.* \mathcal{M}') because of the presence of \mathcal{M} . To find \mathcal{E} one has to track the trajectory of a reference point O' rigidly connected to \mathcal{M}' when \mathcal{M}' glides on \mathcal{M} and so: *a*) it has a *fixed* orientation with respect to the (fixed) molecule \mathcal{M} and *b*) it possesses at least a point of its boundary $\partial\mathcal{M}'$ in contact with a point of the boundary $\partial\mathcal{M}$ of \mathcal{M} . The volume of the excluded region, shortly the *excluded volume*, is independent of the choice of O' since the volume measure is invariant under translations. The excluded volume has an important physical meaning since it is proportional to the second virial coefficient in the expansion of the equation of state in powers of the density, under the hypothesis that the molecules interact through the hard-core potential $V_{h.c.}$.

$$V_{h.c.}(d) = \begin{cases} 0 & \text{if } d > 0 \\ +\infty & \text{if } d = 0 \end{cases}$$

where d is the distance between \mathcal{M} and \mathcal{M}' . While tracking the excluded region and computing the excluded volume for two spherical molecules of radii R and R' is easy— \mathcal{E} is a sphere with radius $R + R'$ —and so $V(\mathcal{E}) = \frac{4\pi}{3}(R + R')^2$, things become intricate when the molecular shapes are less symmetric, as in the case of liquid-crystalline compounds.

To explain the isotropic-nematic transition in colloidal suspensions forming a lyotropic liquid crystal Onsager computed explicitly the excluded volume for a pair of cylindrical molecules in the now classical paper [1]. Although the predictions were later improved by Mayer-Saupe approach which completely neglects steric contributions in favour of dispersion interactions, Onsager's approach has been applied to more realistic nematogenic molecules. An early generalization was the analytic computation of \mathcal{E} for a pair of ellipsoids of revolution by Isihara [2] through a format that relies on classical mathematical work on convex geometry, also used by Kihara [3] who obtained the formal expression of the excluded volume for a pair of equal *convex* bodies. A step forward was moved by Tjijto-Margo and Evans [4] who obtained a closed form for the excluded volume of biaxial ellipsoids which, at variance with Isihara's case, are only endowed with D_{2h} , instead of $D_{\infty h}$, symmetry. Both Kihara's and Tjijto-Margo and Evans' computations have been simplified by Singh and Kumar [5], to which the reader is referred for a self-consistent account of convex-body coordinates. Another avenue has been followed by Mulder who computed explicitly the excluded volume for spheroplatelets [6] and spherocuboids [7]. In his computations the bodies in contact are viewed as the *Minkowski sum* of other bodies, a property that makes the powerful techniques of convex-body analysis work efficiently. **In the past decade, however, the hypothesis of convex nematogenic molecules became untenable to study compounds formed, for instance, by V-shaped molecules. To tackle the technical problem of computing the excluded volume for a pair of non convex V-shaped molecules, Mulder *et al.* [8] resorted to interpolation. Precisely, they computed the excluded volume only on a finite set of configurations and used the results to interpolate the excluded volume when the relative orientation is arbitrary.**

In [7] Mulder proved a theorem that relates the excluded region \mathcal{E} to the Minkowski sum of \mathcal{M} and $\ominus\mathcal{M}'$, where $\ominus\mathcal{M}'$ is obtained from \mathcal{M}' by a central inversion about the reference point O' . This theorem is *not* limited to convex bodies, and it was known in a totally different community, namely that of computer-aided geometric design (CAGD, in short): *see, e.g.* [9]. In fact, excluded regions have been widely studied for the past three decades [10], since they are important in problems of robot motion-planning. It should be noted that the main concern in the CAGD community is not the explicit computation of the excluded volume $V(\mathcal{E})$, but a precise identification of the boundary $\partial\mathcal{E}$ of

the excluded region. However, since the restriction to convex shapes would be too narrow for realistic applications in CAGD, several attempts have been made to extract information on \mathcal{E} when the interacting—or, in this context, colliding—bodies fail to be convex. In particular, it was realized that the boundary of the Minkowski sum $\mathcal{M} \oplus \mathcal{M}'$ of two bodies \mathcal{M} and \mathcal{M}' is a subset of the *convolution* surface $\partial\mathcal{M} * \partial\mathcal{M}'$ of their boundaries $\partial\mathcal{M}$ and $\partial\mathcal{M}'$ which is obtained by adding points on $\partial\mathcal{M}$ to points on $\partial\mathcal{M}'$ that share the same unit normal vector. When \mathcal{M} and \mathcal{M}' are convex, the boundary of $\mathcal{M} \oplus \mathcal{M}'$ coincides with $\partial\mathcal{M} * \partial\mathcal{M}'$ while, when convexity is not guaranteed, the former set is contained in the latter and can be recovered through a *trimming* procedure that, roughly speaking, amounts to remove self-intersections and/or internal contours from the convolution surface. As a matter of fact, lot of work has been done to propose numerical algorithms to handle the trimming procedure (see, e.g. [11], [12]).

In this paper we apply the CAGD techniques outlined in Sec. II to compute the excluded area for a pair of non-convex planar molecules. The choice of a two-dimensional context is twofold. First, it is easier to determine convolution curves rather than convolution surfaces: we should keep in mind that in our context we need to compute the excluded area for *any* relative orientation of \mathcal{M} and \mathcal{M}' and this in general leads to a long distinction of subcases that are more difficult to handle in three-dimensions. Moreover, in the liquid crystal literature there has been recently a surge of interest for two-dimensional systems that can be used to mimic the behaviour of liquid crystals confined between two close, parallel walls. The influence of molecular shapes upon the the orientational transition in an ensemble of two-dimensional hard rod fluids has been stressed in [13] where, using a scaled particle theory, it was proved that changing the length-to-width ratio of hard rectangles makes the isotropic-nematic transition being replaced by a transition in which the orientational order possesses a fourfold symmetry axis. The rich variety of phase transitions in two-dimensional systems has been checked recently by experiments [14] and simulations [15]. Here, in Section III, we illustrate in detail the computations of the excluded area for a family of non-convex molecules that is a direct generalization of the discorctangles studied in [16] where the excluded area was employed to build an interaction potential. Strictly speaking, we study two subfamilies: the former is formed by two-dimensional *boomerangs* obtained by moving the center of a disk of radius h along a circular arc of radius $R > 2h$ that subtends an angle of amplitude $2\alpha < \pi$ (see Fig. 1a).

The latter is formed by *horseshoes* that differ from boomerangs only because $2\alpha > \pi$ (Fig. 1b). We examine in detail the different expressions of the excluded area that emerge on varying both α and the relative orientation. Although in general the excluded area is a complicated function of the relative orientation and of the geometric parameters α and $\eta := h/R$, it boils down to a simple expression in the limit when $\eta \ll 1$.

The molecules considered in this paper also lack of central symmetry. This makes them a natural candidate to measure the *shape* polarity effect recently studied in [17]. Here it was shown that the excluded volume for a pair of equal molecules that fail to be centro-symmetric has its absolute minimum when the molecules are *anti-parallel*, instead of parallel. As remarked in [17] shape polarity survives in a three-dimensional setting, but it is stronger in two-dimensions. By computing the excluded area for horseshoes we prove that, while lack of convexity can make shape polarity effects more evident, lack of symmetry suffices to promote shape polarity in steric interactions. In fact, we explore horseshoes mainly to illustrate the relative importance that lack of central symmetry and lack of convexity have on shape polarity.

The main results of the technical computations shown in Section III are discussed in Section IV. As envisaged in [17], the existence of polar steric interactions could promote the formation of an antiferromorphic smectic phase like CP_A or SP_A phases reproduced, for instance, in computer simulations [18] where the contribution of steric interaction was recognized as crucial. The explicit formulae for the excluded area reported here, in particular those for slender molecules, could be the starting point to build a two-dimensional Onsager model in the spirit of [16]. A conclusive section and a technical appendix containing some ancillary computations close the paper.

II. EXCLUDED VOLUME, MINKOWSKI SUMS, AND CONVOLUTIONS OF GEOMETRIC OBJECTS

In this section we collect the definitions and the results employed in the paper to obtain analytic expressions for the excluded area for a pair of congruent, non-convex molecules. We start by defining the Minkowski sum of two sets A and B .

Definition II.1 *Given two sets A and B belonging to a three-dimensional vector space, their Minkowski sum is the set*

$$A \oplus B := \{\mathbf{a} + \mathbf{b} \mid \mathbf{a} \in A \text{ and } \mathbf{b} \in B\}.$$

Minkowski sums can be generalized to vector spaces of arbitrary dimension n . To visualize the Minkowski sum of A and B , the following kinematic construction can be of some help. Place the reference point O' of B on a point of the boundary ∂A of A and translate B by keeping O' along ∂A : the contour of the region spanned by B during this

1 motion is the boundary of $A \oplus B$. There is an intimate relation between the Minkowski addition of two sets and their
 2 excluded region $\mathcal{E}(A, B)$ that can be formalized by the following theorem [7]
 3

4 **Theorem II.1** *Let A and B two sets, and let*

$$5 \quad \ominus B := \{\mathbf{b} \mid -\mathbf{b} \in B\} \quad (II.1)$$

7 *be the Minkowski inverse of B with respect to its reference point O' . The set $\mathcal{E}(A, B)$ is obtained by a translation of*
 8 $A \ominus B := A \oplus (\ominus B)$ *and, in particular,*

$$10 \quad V[\mathcal{E}(A, B)] = V(A \ominus B)$$

11 *where $V(A \ominus B)$ is the volume bounded by the set $A \ominus B$, called the Minkowski difference of A and B .*

12 The importance of this theorem in excluded-volume computations was stressed only recently by Mulder in [7], to
 13 which we refer the reader for a proof. It should be noted, however, that this result has been known for a long time
 14 in the community of CAGD. In particular, a characterization of the excluded region for sets in \mathbf{R}^2 in terms of their
 15 Minkowski sum appeared in [10] and [19]. It is important to note that Theorem II.1 is *not* restricted to convex bodies.

16 However, when one of the bodies fails to be convex, the explicit determination of $\partial(A \oplus B)$ becomes rather intricate
 17 and, in fact, there is no general analytic procedure to obtain it. Despite of this, the connection between the Minkowski
 18 sum of two sets and their *convolution surface* can be exploited. Given two sets A and B , let ν_A and ν_B denote the
 19 fields of the outer unit normals of ∂A and ∂B . Then, the convolution surface $\partial A * \partial B$ of ∂A and ∂B is defined as
 20 the set [20]

$$22 \quad \partial A * \partial B := \{\mathbf{a} + \mathbf{b} \mid \mathbf{a} \in \partial A, \mathbf{b} \in \partial B, \nu_A(\mathbf{a}) = \nu_B(\mathbf{b})\}. \quad (II.2)$$

23 In two space-dimensions we can define the convolution curve of two curves A and B in a completely analogous way
 24 [9, 19]. If the sets A and B are convex, $\partial(A \oplus B)$ coincides with $\partial A * \partial B$, but in general we can only say that

$$26 \quad \partial(A \oplus B) \subseteq \partial A * \partial B \quad (II.3)$$

27 since the convolution set can have internal boundaries and self-intersections that do not appear in the Minkowski
 28 sum. Hence, as soon as the convolution set of A and B has been obtained, a *trimming* procedure is needed to remove
 29 the spurious arcs that do not enter the set $\partial(A \oplus B)$. It is precisely this trimming procedure which is difficult to
 30 implement analytically while, on the other hand, several numerical algorithms have been proposed (*see, e.g.* [11],
 31 [12]).

32 Given a point \mathbf{a} on a closed surface \mathcal{S} or on a closed curve \mathcal{C} , the map $\mathcal{N} : \mathbf{a} \mapsto \nu(\mathbf{a})$ is the Gauss map of \mathcal{S} or \mathcal{C}
 33 at \mathbf{a} and so, by equation (II.2), to obtain the convolution set we need to identify pairs of points on ∂A and ∂B at
 34 which the Gauss maps attain one and the same value. Two patches \mathcal{P}_A and \mathcal{P}_B belonging to ∂A and ∂B , respectively,
 35 are said to be *compatible* [9] if there is a bijective correspondence that assign to each point $\mathbf{a} \in \mathcal{P}_A$ a point $\mathbf{b} \in \mathcal{P}_B$
 36 such that $\mathcal{N}(\mathbf{a}) = \mathcal{N}(\mathbf{b})$. Hence, compatible patches will contribute to the set $\partial A * \partial B$. In two space dimensions, let
 37 $P \in \partial A$ and $Q \in \partial B$ be two points on compatible arcs $\mathcal{C}_i \subset \partial A$ and $\mathcal{K}_j \subset \partial B$ at which $\mathcal{N}(P) = \mathcal{N}(Q)$. If ∂A and
 38 ∂B are parameterized by t and τ , respectively, and t_0 is the value of t at P , the value of τ at Q can be written as
 39 $\tau = \tau(t_0)$. Then, the point

$$41 \quad (P * Q)(t_0) := P(t_0) - O + Q(\tau(t_0)) - O$$

42 belongs to the convolution curve $\partial A * \partial B$. Building the map $t \mapsto \tau(t)$ requires a knowledge of the curvature of both
 43 ∂A and ∂B . However, in the problem we are concerned with the compatible arcs are circles and so $\tau(t)$ is simply a
 44 shift: $\tau(t) = t + t_0$. The convolution curve has been parameterized by the same parameter t used for ∂A but, clearly,
 45 one could work with the inverse map $\tau \mapsto \tau(t)$ and parameterize the convolution curve in terms of τ . The curve
 46 that shares the same parameter with the convolution curve is called the *base curve*. The choice of the base curve is a
 47 matter of convenience, and it can vary when different pairs of compatible arcs are considered.

48 After these remarks, we outline the procedure to compute the excluded area for two-dimensional molecules \mathcal{M} and
 49 \mathcal{M}' in four steps.

- 51 1. For a given relative orientation, we identify the arcs on $\partial \mathcal{M}$ and $\partial \mathcal{M}'$ that share the same Gauss map.
- 52 2. Joining together the arcs found at step 1, we build the convolution curve $\partial \mathcal{M} * \partial \mathcal{M}'$.
- 53 3. We remove from $\partial \mathcal{M} * \partial \mathcal{M}'$ both internal contours and self-intersections to obtain the set $\partial(\mathcal{M} \oplus \mathcal{M}')$.
- 54 4. We compute the area enclosed by $\partial(\mathcal{M} \oplus \mathcal{M}')$ which, by Theorem II.1, is the excluded area of \mathcal{M} and $\ominus \mathcal{M}'$.

55 In the following sections we apply this program to a pair of two-dimensional boomerangs or horseshoes as those
 56 shown in Fig. 1.
 57
 58
 59
 60

III. BOOMERANGS AND HORSESHOES

In the $\{e_x, e_y\}$ -plane we consider a circular arc A_0B_0 of radius R , centered at a point O and subtending an angle 2α (Fig. 1). We introduce a reference molecule \mathcal{M}_0 bounded by: a) two concentric circular arcs \mathcal{C}_1^0 and \mathcal{C}_3^0 centered at O , with radius $R - h$ and $R + h$, both subtending an angle 2α and b) two semicircles \mathcal{C}_2^0 and \mathcal{C}_4^0 of radius h , centered at A_0 and B_0 , respectively: see Fig. 2.

We first determine the maximum value α_M of α compatible with the absence of self-intersections in the profile of \mathcal{M}_0 . This is easily obtained by imposing that two circles of radius h centered at $A_0 = (-R \sin \alpha, R \cos \alpha)$ and $B_0 = (R \sin \alpha, R \cos \alpha)$ are mutually tangent. A straightforward computation shows that this occurs when

$$\alpha = \alpha_M := \pi - \arcsin(\sqrt{\eta}),$$

where we have introduced the dimensionless parameter

$$\eta := \frac{h}{R} \quad (\text{III.1})$$

that ranges the interval $(0, \frac{1}{2})$. Hereafter, we rescale lengths to R .

To exploit the symmetry with respect to molecules' exchange, it is expedient to consider \mathcal{M} and \mathcal{M}' as images of \mathcal{M}_0 under two rotations $\mathbf{Q}(e_z, \chi)$ by suitable angles χ about the $e_z := e_x \times e_y$ axis passing through O : precisely, \mathcal{M} is the image of \mathcal{M}_0 under $\mathbf{Q}(e_z, -\vartheta/2)$ and \mathcal{M}' is the image of \mathcal{M}_0 under $\mathbf{Q}(e_z, \vartheta/2)$. Hence, $\vartheta \in [0, \pi]$ is the relative angle between the molecules \mathcal{M} and \mathcal{M}' . By orienting \mathcal{M} counterclockwise, its arcs \mathcal{C}_i can be parameterized as

$$\mathcal{C}_1 : \quad (P - O)(t) = (1 + \eta) \left[-\sin\left(t - \alpha - \frac{\vartheta}{2}\right) e_x + \cos\left(t - \alpha - \frac{\vartheta}{2}\right) e_y \right], \quad t \in [0, 2\alpha] \quad (\text{III.2})$$

$$\mathcal{C}_2 : \quad (P - A)(t) = \eta \left[-\sin\left(t + \alpha - \frac{\vartheta}{2}\right) e_x + \cos\left(t + \alpha - \frac{\vartheta}{2}\right) e_y \right], \quad t \in [0, \pi] \quad (\text{III.3})$$

$$\mathcal{C}_3 : \quad (P - O)(t) = (1 - \eta) \left[-\sin\left(-t + \alpha - \frac{\vartheta}{2}\right) e_x + \cos\left(-t + \alpha - \frac{\vartheta}{2}\right) e_y \right], \quad t \in [0, 2\alpha] \quad (\text{III.4})$$

$$\mathcal{C}_4 : \quad (P - B)(t) = \eta \left[-\sin\left(\pi + t - \alpha - \frac{\vartheta}{2}\right) e_x + \cos\left(\pi + t - \alpha - \frac{\vartheta}{2}\right) e_y \right], \quad t \in [0, \pi], \quad (\text{III.5})$$

where $A - O$, $B - O$, and the arcs \mathcal{C}_i are the images of $A_0 - O$, $B_0 - O$ and the arcs \mathcal{C}_i^0 under $\mathbf{Q}(e_z, -\frac{\vartheta}{2})$. We note that when \mathcal{M}_0 is oriented counterclockwise, the outer unit normal vectors of \mathcal{C}_i^0 rotate counterclockwise along the convex arcs but clockwise along the concave arc (see Fig. 3).

The arguments of the trigonometric functions in equations (III.2-III.5) might look awkward. We chose the keep one and the same format $-\sin(\cdot)e_x + \cos(\cdot)e_y$ to make comparisons between the Gauss maps of different arcs easier. Similarly, we parameterize the arcs forming the molecule \mathcal{M}' as

$$\mathcal{K}_1 : \quad (P - O)(t) = (1 + \eta) \left[-\sin\left(t - \alpha + \frac{\vartheta}{2}\right) e_x + \cos\left(t - \alpha + \frac{\vartheta}{2}\right) e_y \right], \quad t \in [0, 2\alpha] \quad (\text{III.6})$$

$$\mathcal{K}_2 : \quad (P - A')(t) = \eta \left[-\sin\left(t + \alpha + \frac{\vartheta}{2}\right) e_x + \cos\left(t + \alpha + \frac{\vartheta}{2}\right) e_y \right], \quad t \in [0, \pi] \quad (\text{III.7})$$

$$\mathcal{K}_3 : \quad (P - O)(t) = (1 - \eta) \left[-\sin\left(-t + \alpha + \frac{\vartheta}{2}\right) e_x + \cos\left(-t + \alpha + \frac{\vartheta}{2}\right) e_y \right], \quad t \in [0, 2\alpha] \quad (\text{III.8})$$

$$\mathcal{K}_4 : \quad (P - B')(t) = \eta \left[-\sin\left(\pi + t - \alpha + \frac{\vartheta}{2}\right) e_x + \cos\left(\pi + t - \alpha + \frac{\vartheta}{2}\right) e_y \right], \quad t \in [0, \pi], \quad (\text{III.9})$$

where $A' - O$, $B' - O$, and the arcs \mathcal{K}_i are the images of $A_0 - O$, $B_0 - O$ and the arcs \mathcal{C}_i^0 under $\mathbf{Q}(e_z, \frac{\vartheta}{2})$. Clearly,

$$\begin{aligned} A - O &= \left[-\sin\left(\alpha - \frac{\vartheta}{2}\right) e_x + \cos\left(\alpha - \frac{\vartheta}{2}\right) e_y \right] & B - O &= \left[\sin\left(\alpha + \frac{\vartheta}{2}\right) e_x + \cos\left(\alpha + \frac{\vartheta}{2}\right) e_y \right] \\ A' - O &= \left[-\sin\left(\alpha + \frac{\vartheta}{2}\right) e_x + \cos\left(\alpha + \frac{\vartheta}{2}\right) e_y \right] & B' - O &= \left[\sin\left(\alpha - \frac{\vartheta}{2}\right) e_x + \cos\left(\alpha - \frac{\vartheta}{2}\right) e_y \right]. \end{aligned} \quad (\text{III.10})$$

We now determine the convolution curve $\partial\mathcal{M} * \partial\mathcal{M}'$ of $\partial\mathcal{M} = \cup_{i=1}^4 \mathcal{C}_i$ and $\partial\mathcal{M}' = \cup_{i=1}^4 \mathcal{K}_i$ from which we will extract information on the boundary of the Minkowski sum $\partial(\mathcal{M} \oplus \mathcal{M}')$ and, then, on the excluded area between \mathcal{M} and $\ominus\mathcal{M}'$.

To understand our procedure, we focus on the case $\alpha \in [0, \frac{\pi}{4}]$ and $\vartheta \in [0, 2\alpha]$. The crosses in Fig. 4 illustrate the Gauss maps on the arcs of two molecules rotated by an angle ϑ .

The sets $\mathcal{N}(\mathcal{C}_1), \dots, \mathcal{N}(\mathcal{C}_4)$ are the angles $\angle V_1OV_2, \angle V_2OV_4, \angle V_4OV_3$, and $\angle V_1OV_3$, respectively. On the other hand, the sets $\mathcal{N}(\mathcal{K}_1), \dots, \mathcal{N}(\mathcal{K}_4)$ are the angles $\angle V'_1OV'_2, \angle V'_2OV'_4, \angle V'_4OV'_3$, and $\angle V'_1OV'_3$, respectively. When $\vartheta \in [0, 2\alpha]$ the compatible set of \mathcal{C}_1 and \mathcal{K}_1 is the arc $\angle V'_1OV_2$ of amplitude $2\alpha - \vartheta$. Using \mathcal{K}_1 as a base curve, $t \in [0, 2\alpha - \vartheta]$ along the compatible set. Similarly, the compatible set of \mathcal{C}_2 and \mathcal{K}_1 is the arc $\angle V_2OV'_2$ of amplitude ϑ along which $t \in [0, \vartheta]$, if \mathcal{C}_2 is taken as the base curve. By repeating such comparisons for all possible pairs of arcs, the convolution curve can be retraced directly.

As a fact, the sets that enter the convolution curve depend on the values of $\alpha \in [0, \alpha_M]$ and $\vartheta \in [0, \pi]$. We distinguish four cases, according to whether $\alpha \in [0, \frac{\pi}{4}]$, $\alpha \in [\frac{\pi}{4}, \frac{\pi}{2}]$, $\alpha \in [\frac{\pi}{2}, \frac{3\pi}{4}]$ and $\alpha \in [\frac{3\pi}{4}, \alpha_M]$.

A. Boomerangs I: $\alpha \in [0, \frac{\pi}{4}]$

In this case, the following regimes exist, according to the value of ϑ : $\vartheta \in [0, 2\alpha]$, $\vartheta \in [2\alpha, \pi - 2\alpha]$, $\vartheta \in [\pi - 2\alpha, \pi]$: the last interval will be split into three subintervals, as explained later.

1. $\vartheta \in [0, 2\alpha]$

We list here the arcs that contribute to the convolution curve $\partial\mathcal{M} * \partial\mathcal{M}'$, obtained through the procedure sketched in Fig. 4. We denote the compatible set $\mathcal{C}_i * \mathcal{K}_j$ of \mathcal{C}_i and \mathcal{K}_j as \mathcal{C}_{ij} : in general $\mathcal{C}_{ij} \neq \mathcal{C}_{ji}$, if $i \neq j$. Since the molecules are formed only by circular arcs, \mathcal{C}_{ij} are circular arcs too. The second and the third column in the subsequent tables contain the radii of \mathcal{C}_{ij} , scaled to R , and their centers. The fourth and the fifth columns show the values of t along \mathcal{C}_{ij} and the base curve chosen to parameterize it. The choice of the base curve was made according to the following criteria: when a concave arc is involved, the base curve always coincides with the convex segment; if no concave segment is involved in \mathcal{C}_{ij} , the base curve is the arc that allows parameterizing \mathcal{C}_{ij} with t starting from 0: this criterion has already been followed in the example of Fig. 4. The explicit representation of the arcs \mathcal{C}_{ij} is given in Appendix A.

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, 2\alpha - \vartheta]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[0, \vartheta]$	$\mathcal{C}_1(t)$
C_{21}	$1 + 2\eta$	A	$[0, \vartheta]$	$\mathcal{C}_2(t)$
C_{22}	2η	$A + A'$	$[0, \pi - \vartheta]$	$\mathcal{K}_2(t)$
C_{23}	$2\eta - 1$	A	$[\pi - 2\alpha + \vartheta, \pi]$	$\mathcal{C}_2(t)$
C_{24}	2η	$A + B'$	$[0, 2\alpha - \vartheta]$	$\mathcal{K}_4(t)$
C_{32}	$2\eta - 1$	A'	$[0, 2\alpha]$	$\mathcal{K}_2(t)$
C_{34}	$2\eta - 1$	B'	$[0, 2\alpha - \vartheta]$	$\mathcal{K}_4(t)$
C_{42}	2η	$B + A'$	$[0, 2\alpha + \vartheta]$	$\mathcal{C}_4(t)$
C_{43}	$2\eta - 1$	B	$[\vartheta, 2\alpha + \vartheta]$	$\mathcal{C}_4(t)$
C_{44}	2η	$B + B'$	$[0, \pi - \vartheta]$	$\mathcal{K}_4(t)$

Arcs like C_{13} , C_{31} and C_{33} are excluded because either the concave segment has larger curvature than the convex one (C_{13} , C_{31}) or both the segments are concave (C_{33}). Hence, as proved in [9], they cannot contribute to the boundary of the Minkowski sum $\partial(\mathcal{M} \oplus \mathcal{M}')$. We note that this property is peculiar of the two-dimensional setting and cannot be extended to three-dimensional problems. In the present case, the segments C_{23} , C_{24} and C_{34} should be trimmed since they are inner contours of the convolution curve and so cannot contribute to $\partial(\mathcal{M} \oplus \mathcal{M}')$. Finally, to account correctly for the convexity of the arcs \mathcal{C}_{3j} and \mathcal{C}_{i3} we have formally considered the radii of \mathcal{C}_3 and \mathcal{K}_3 as negative. The coordinate system we chose makes it possible to show that the pairs (C_{11}, C_{42}) , (C_{14}, C_{21}) , (C_{44}, C_{22}) , and (C_{43}, C_{32}) are symmetric with respect to the y -axis. This is indeed a general property that does not depend on the specific values of α or ϑ and that permits focussing attention on the *reduced* boundary \mathcal{R}_\oplus defined as the subset of $\partial(\mathcal{M} \oplus \mathcal{M}')$ where $x \geq 0$. Clearly, to obtain $\partial(\mathcal{M} \oplus \mathcal{M}')$ we paste \mathcal{R}_\oplus and its symmetric image with respect to the y -axis.

The area A enclosed by the set $\partial(\mathcal{M} \oplus \mathcal{M}')$ is a function $A = A(\alpha, \vartheta, R, h)$ and we compute its dimensionless counterpart $A(\alpha, \vartheta, \eta) := A(\alpha, \vartheta, R, h)/R^2$. By Theorem II.1, $A(\alpha, \vartheta, \eta)$ is the excluded area for \mathcal{M} and \mathcal{M}' when their relative orientation is $\pi - \vartheta$. To compute $A(\alpha, \vartheta, \eta)$, we decompose the reduced boundary \mathcal{R}_{\oplus} as shown in Figure 5.

Since the area bounded by a circular segment of radius r subtending an angle β is

$$\text{Sett}(r, \beta) = \frac{r^2}{2}[\beta - \sin \beta] \quad (\text{III.11})$$

and the area of a trapezium of height h_i and bases b_i, b_{i+1} is

$$\mathcal{T}(h_i, b_i, b_{i+1}) = \frac{h_i}{2}(b_i + b_{i+1}) \quad (\text{III.12})$$

we conclude that

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(\eta + 1), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta) + \text{Sett}(2\eta, \pi - \vartheta) - \text{Sett}(2\eta - 1, 2\alpha) + \frac{1}{2}\text{Sett}(2\eta, 2\alpha + \vartheta) + \mathcal{T}(h_1, b_1, b_2) + \mathcal{T}(h_2, b_2, b_3) + \mathcal{T}(h_3, b_3, b_4)], \quad (\text{III.13})$$

where the minus sign in front of $\text{Sett}(2\eta - 1, 2\alpha)$ accounts for the concavity of the segment C_{43} . Finally, by setting $x_{ij} := (C_{ij} - O) \cdot \mathbf{e}_x$ and $y_{ij} := (C_{ij} - O) \cdot \mathbf{e}_y$ we also have

$$b_1 = x_{14}(\vartheta) \quad b_2 = x_{14}(0) \quad b_3 = x_{44}(0) \quad b_4 = x_{43}(\vartheta + 2\alpha) \quad (\text{III.14})$$

and

$$h_1 = y_{14}(\vartheta) - y_{14}(0) \quad h_2 = y_{44}(\pi - \vartheta) - y_{44}(0) \quad h_3 = y_{43}(\vartheta) - y_{43}(\vartheta + 2\alpha) \quad (\text{III.15})$$

that can be computed by using the results of Appendix A. Then, it is not difficult to prove that

$$A(\alpha, \vartheta, \eta) = 2\alpha - \vartheta + 2 \sin \vartheta - \sin(2\alpha + \vartheta) + 16\alpha\eta + 4\pi\eta^2. \quad (\text{III.16})$$

$$2. \quad \vartheta \in [2\alpha, \pi - 2\alpha]$$

Figure 5b) shows the set \mathcal{R}_{\oplus} when ϑ ranges in $[2\alpha, \pi - 2\alpha]$. In the following table, we list the basic properties of the arcs that enter \mathcal{R}_{\oplus} (see also Appendix A for details)

arc	radius	center	t	base curve
C_{24}	2η	$A + B'$	$[0, \vartheta/2 - \alpha]$	$C_2(t)$
C_{14}	$1 + 2\eta$	B'	$[0, 2\alpha]$	$C_1(t)$
C_{44}	2η	$B + B'$	$[0, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{43}	$2\eta - 1$	B	$[\vartheta, \vartheta + 2\alpha]$	$C_4(t)$
C_{42}	2η	$B + A'$	$[\alpha + \vartheta/2, 2\alpha + \vartheta]$	$C_4(t)$

The area bounded by the set $\partial(\mathcal{M} \oplus \mathcal{M}')$ is

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2\eta, \vartheta - 2\alpha) + \text{Sett}(1 + 2\eta, 2\alpha) + \text{Sett}(2\eta, \pi - \vartheta) - \text{Sett}(2\eta - 1, 2\alpha) + \frac{1}{2}\text{Sett}(2\eta, 2\alpha + \vartheta) + \mathcal{T}(h'_1, b'_1, b_2) + \mathcal{T}(h_2, b_2, b_3) + \mathcal{T}(h_3, b_3, b_4)] \quad (\text{III.17})$$

where now

$$b'_1 = x_{14}(2\alpha) \quad h'_1 = y_{14}(2\alpha) - y_{14}(0) \quad (\text{III.18})$$

while b_2, b_3, b_4 and h_2, h_3 are still given by equations (III.14) and (III.15). With the results shown in Appendix A we obtain

$$A(\alpha, \vartheta, \eta) = 4 \sin \vartheta \sin^2 \alpha + 16\alpha\eta + 4\pi\eta^2. \quad (\text{III.19})$$

In the limit where $R \rightarrow \infty$ and $\alpha \rightarrow 0$ in such a way that $\alpha R \rightarrow L/2$, the molecules considered here approach a pair of equal discorectangles studied in Ref. [16]. In this limit, (III.19) is the only expression of the excluded area and, in dimensional units, it tends to

$$4 \sin \vartheta (R \sin \alpha)^2 + 16\alpha h R + 4\pi h^2 = 8hL + 4\pi h^2 + L^2 \sin \vartheta$$

which is precisely equation (4) of [16] when we set $2h = \sigma = \sigma_s$ and $L = L_s$.

$$3. \quad \vartheta \in [\pi - 2\alpha, \vartheta_{4312}]$$

When $\vartheta > \pi - 2\alpha$, computations are more intricate since the end-points of some admissible arcs C_{ij} of \mathcal{R}_\oplus lie in the interior of $\partial(\mathcal{M} \oplus \mathcal{M}')$, and so the intersections between different arcs C_{ij} are to be computed. It turns out that the set $\vartheta \in [\pi - 2\alpha, \pi]$ has to be split into three subsets according to whether $\vartheta \in [\pi - 2\alpha, \vartheta_{1243}]$, $\vartheta \in [\vartheta_{1243}, \vartheta_{1244}]$ or $\vartheta \in [\vartheta_{1244}, \pi]$, where the values ϑ_{1243} and ϑ_{1244} are defined as follows. By using the procedure sketched in Fig. 4 the arc C_{12} could contribute to \mathcal{R}_\oplus when $t \in [0, \vartheta - \pi + 2\alpha]$. However, (see Fig. 6) C_{12} intersects C_{43} at a value t_{1243} of $t \in (0, \vartheta - \pi + 2\alpha)$ until the critical value $\vartheta_{1243}(\alpha, \eta)$ of ϑ is attained, at which the arc C_{43} lies completely in the interior of \mathcal{R}_\oplus . From this value, C_{12} intersects the arc C_{44} until ϑ attains the value $\vartheta_{1244}(\alpha, \eta) > \vartheta_{1243}(\alpha, \eta)$. When $\vartheta \in [\vartheta_{1244}, \pi]$, also C_{44} lies in the interior of \mathcal{R}_\oplus and C_{12} intersects the arc C_{14} . In the following three tables we summarize the structure of \mathcal{R}_\oplus when $\vartheta \in [\pi - 2\alpha, \vartheta_{1243}]$, $\vartheta \in [\vartheta_{1243}, \vartheta_{1244}]$, and $\vartheta \in [\vartheta_{1244}, \pi]$, respectively. The explicit computations of these critical values of ϑ as well as of the limits t_{1243} , t_{4312} , t_{1244} , t_{4412} , t_{1214} , t_{1412} are shown in Appendix A: see equations (A.5), (A.6), (A.11), (A.12), (A.15), and (A.16).

arc	radius	center	t	base curve
C_{24}	2η	$A + B'$	$[0, \vartheta/2 - \alpha]$	$\mathcal{C}_2(t)$
C_{14}	$1 + 2\eta$	B'	$[0, 2\alpha]$	$\mathcal{C}_1(t)$
C_{44}	2η	$B + B'$	$[0, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{43}	$2\eta - 1$	B	$[\vartheta, t_{4312}]$	$\mathcal{C}_4(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1243}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$A' + B$	$[\pi - \frac{1}{2}(\vartheta + 2\alpha), 2\pi - (\vartheta + 2\alpha)]$	$\mathcal{K}_2(t)$

The area enclosed by the set $\partial(\mathcal{M} \oplus \mathcal{M}')$ is given by

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2\eta, \vartheta - 2\alpha) + \text{Sett}(1 + 2\eta, 2\alpha) + \text{Sett}(2\eta, \pi - \vartheta) - \text{Sett}(2\eta - 1, t_{4312} - \vartheta) + \text{Sett}(1 + 2\eta, t_{1243}) + \frac{1}{2}\text{Sett}(2\eta, 2\pi - (2\alpha + \vartheta))] + \mathcal{T}(h'_1, b'_1, b_2) + \mathcal{T}(h_2, b_2, b_3) + \mathcal{T}(h'_3, b_3, b'_4) + \mathcal{T}(h_4, b'_4, b_5) \quad (\text{III.20})$$

where now

$$b'_4 = x_{43}(t_{4312}) \quad b_5 = x_{12}(0) \quad h'_3 = y_{43}(\vartheta) - y_{43}(t_{4312}) \quad h_4 = y_{12}(t_{1243}) - y_{12}(0). \quad (\text{III.21})$$

The explicit expression of the excluded area could be written but it would not be very telling. When attention is restricted to the case $\eta \ll 1$, the approximate excluded area takes the form

$$A(\alpha, \vartheta, \eta) = 2(\vartheta + 2\alpha - \pi) + 2 \sin \vartheta + 2 \cos \vartheta \sin 2\alpha + 16\alpha\eta + O(\eta^2). \quad (\text{III.22})$$

$$4. \quad \vartheta \in [\vartheta_{4312}, \vartheta_{4412}]$$

When ϑ exceeds the value ϑ_{4312} , the arc C_{43} lies completely in the interior of \mathcal{R}_\oplus and the arc C_{12} intersects the arc C_{44} as shown in Fig. 7a).

The admissible values of t along C_{44} range the interval $[0, \pi - \vartheta - t_{4412}]$ while along C_{12} t ranges the interval $[0, t_{1244}]$, where the values of t_{1244} and t_{4412} are given in equations (A.11) and (A.12) of Appendix A. The excluded area is now given by

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2\eta, \vartheta - 2\alpha) + \text{Sett}(1 + 2\eta, 2\alpha) + \text{Sett}(2\eta, \pi - \vartheta - t_{4412}) + \text{Sett}(1 + 2\eta, t_{1244}) + \frac{1}{2}\text{Sett}(2\eta, 2\pi - (2\alpha + \vartheta))] + \mathcal{T}(h'_1, b'_1, b_2) + \mathcal{T}(h'_2, b_2, b'_3) + \mathcal{T}(h'_3, b'_3, b_5) \quad (\text{III.23})$$

where

$$b'_3 = x_{44}(t_{4412}) \quad h'_2 = y_{44}(\pi - \vartheta) - y_{44}(t_{4412}) \quad h'_3 = y_{12}(t_{1244}) - y_{12}(0). \quad (\text{III.24})$$

As discussed in the Appendix, when $\eta \rightarrow 0$ and $\alpha < \frac{\pi}{2}$, then

$$\vartheta_{4312} \simeq \pi - 2\eta \tan \alpha + O(\eta^2) \quad \vartheta_{4412} \simeq \pi - 2\eta \tan \alpha + O(\eta^2)$$

so that, if we keep only the linear terms in η , ϑ_{4312} and ϑ_{4412} coincide and this interval can be skipped. For future use, we define the angle

$$\vartheta_a(\alpha, \eta) := \pi - 2\eta \tan \alpha. \quad (\text{III.25})$$

Clearly this analysis is valid only if α is not close to $\frac{\pi}{2}$. In fact, when $\alpha > \frac{\pi}{2}$ and $\eta \rightarrow 0$ the angles ϑ_{4312} and ϑ_{4412} approach the limit value $2(\pi - \alpha)$ and so at $\alpha = \frac{\pi}{2}$ ϑ_{4312} and ϑ_{4412} have a knee where they depart from π like $\sqrt{\eta}$.

5. $\vartheta \in [\vartheta_{4412}, \pi]$

Finally, when $\vartheta \geq \vartheta_{4412}$ as given by equation (A.14), also the arc C_{44} lies completely in the interior of \mathcal{R}_\oplus and we need the intersection between C_{12} and C_{14} (Fig. 7b). On C_{12} , $t \in [0, t_{1214}]$ and on C_{14} , $t \in [t_{1412}, 2\alpha]$ (see equations (A.15) and (A.16)).

In this case the excluded area is given by

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2\eta, \vartheta - 2\alpha) + \text{Sett}(1 + 2\eta, 2\alpha - t_{1412}) + \text{Sett}(1 + 2\eta, t_{1214}) + \frac{1}{2}\text{Sett}(2\eta, 2\pi - 2\alpha - \vartheta) + \mathcal{T}(h'_1, b'_1, b'_2) + \mathcal{T}(h''_2, b'_2, b_5)] \tag{III.26}$$

where

$$b'_2 = x_{14}(t_{1412}) \quad h''_1 = y_{14}(2\alpha) - y_{14}(t_{1412}) \quad h''_2 = y_{12}(t_{1214}) - y_{12}(0). \tag{III.27}$$

When values $\eta \ll 1$ are considered, then

$$A(\alpha, \vartheta, \eta) = 4\alpha + 2 \sin 2\alpha \cos \vartheta + 16\alpha\eta + O(\eta^2). \tag{III.28}$$

Finally, by collecting together equations (III.16), (III.19), (III.22), and (III.28) and neglecting powers in η higher than one, we obtain a simple approximation A_0 for the excluded area:

$$A_0(\eta, \alpha, \theta) := \begin{cases} 2\alpha - \vartheta + 2 \sin \vartheta - \sin(2\alpha + \vartheta) + 16\alpha\eta & \vartheta \in [0, 2\alpha] \\ 4 \sin \vartheta \sin^2 \alpha + 16\alpha\eta & \vartheta \in [2\alpha, \pi - 2\alpha] \\ 2(\vartheta + 2\alpha - \pi) + 2 \sin \vartheta + 2 \cos \vartheta \sin 2\alpha + 16\alpha\eta & \vartheta \in [\pi - 2\alpha, \vartheta_a(\alpha, \eta)] \\ 4\alpha + 2 \sin 2\alpha \cos \vartheta + 16\alpha\eta & \vartheta \in [\vartheta_a(\alpha, \eta), \pi]. \end{cases} \tag{III.29}$$

B. Boomerangs II: $\alpha \in [\frac{\pi}{4}, \frac{\pi}{2}]$

When $\alpha \in [\frac{\pi}{4}, \frac{\pi}{2}]$ and so $\pi - 2\alpha < 2\alpha$, it can be checked that, when $\vartheta \in [0, \pi - 2\alpha]$, the reduced boundary \mathcal{R}_\oplus coincides with that obtained in Subsection III A 1. Moreover, $\vartheta_{4312} > 2\alpha$ and the results for $\vartheta \in [2\alpha, \pi]$ are the same as in Subsections III A 3-III A 5. New computations are needed only when $\vartheta \in [\pi - 2\alpha, 2\alpha]$ where the reduced boundary \mathcal{R}_\oplus is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[\alpha - \frac{\vartheta}{2}, 2\alpha - \vartheta]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[0, \vartheta]$	$\mathcal{C}_1(t)$
C_{44}	2η	$B + B'$	$[0, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{43}	$2\eta - 1$	B	$[\vartheta, t_{4312}]$	$\mathcal{C}_4(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1243}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[(\pi - \alpha) - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

where t_{1243} and t_{4312} are given by equations (A.5) and (A.6). The excluded area is then given by

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta) + \text{Sett}(2\eta, \pi - \vartheta) - \text{Sett}(2\eta - 1, t_{4312} - \vartheta) + \text{Sett}(1 + 2\eta, t_{1243}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1, b_1, b_2) + \mathcal{T}(h_2, b_2, b_3) + \mathcal{T}(h'_3, b_3, b'_4) + \mathcal{T}(h_4, b'_4, b_5)] \tag{III.30}$$

where the bases and the heights of the trapezia are given in equations (III.14), (III.15), and (III.21). In the limit when $\eta \ll 1$ it is possible to check that

$$A(\alpha, \vartheta, \eta) = 6\alpha - 2\pi + \vartheta + 2 \sin \vartheta + \sin(\vartheta + 2\alpha) + 16\alpha\eta + O(\eta^2). \tag{III.31}$$

The excluded area within this approximation is then

$$A_0(\eta, \alpha, \theta) := \begin{cases} 2\alpha - \vartheta + 2 \sin \vartheta - \sin(2\alpha + \vartheta) + 16\alpha\eta & \vartheta \in [0, \pi - 2\alpha] \\ 6\alpha - 2\pi + \vartheta + 2 \sin \vartheta + \sin(\vartheta + 2\alpha) + 16\alpha\eta & \vartheta \in [\pi - 2\alpha, 2\alpha] \\ 2(\vartheta + 2\alpha - \pi) + 2 \sin \vartheta + 2 \cos \vartheta \sin 2\alpha + 16\alpha\eta & \vartheta \in [2\alpha, \vartheta_a(\alpha, \eta)] \\ 4\alpha + 2 \sin 2\alpha \cos \vartheta + 16\alpha\eta & \vartheta \in [\vartheta_a(\alpha, \eta), \pi]. \end{cases} \tag{III.32}$$

as remarked before, this approximation does not hold if α is too close to $\frac{\pi}{2}$.

C. Horseshoes I: $\alpha \in [\frac{\pi}{2}, \alpha^{\text{cr}}(\eta)]$

When α exceeds $\pi/2$, the trimming procedure to obtain the boundary of the Minkowski sum $\mathcal{M} \oplus \mathcal{M}'$ from the convolution curve $\partial\mathcal{M} * \partial\mathcal{M}'$ becomes more delicate. It is crucial to determine the magnitude of ϑ_{4312} and ϑ_{4412} as compared to $2\alpha - \pi$ and $2(\pi - \alpha)$. To this aim, we impose that $\vartheta = 2\alpha - \pi$ or $\vartheta = 2(\pi - \alpha)$ solve equations (A.7) or (A.13), respectively. It can be checked that both ϑ_{4312} and ϑ_{4412} are less than $2(\pi - \alpha)$, for any value of α and η . On the other hand, $\vartheta_{4312} > 2\alpha - \pi$ if and only if

$$\alpha < \alpha_{\text{cr}}(\eta) := \frac{\pi}{2} + \frac{1}{2} \arccos(2\eta) \in \left[\frac{\pi}{2}, \frac{3\pi}{4}\right] \quad (\text{III.33})$$

whereas $\vartheta_{4412} > 2\alpha - \pi$ if and only if

$$\alpha < \alpha_{\text{cr}}^*(\eta) := \frac{\pi}{2} + \frac{1}{2} \arccos\left(\frac{\eta}{1+2\eta}\right) \in \left[\frac{\pi}{2}, \frac{3\pi}{4}\right], \quad (\text{III.34})$$

with $\alpha_{\text{cr}} < \alpha_{\text{cr}}^*$. A new critical value of ϑ replacing $\vartheta = \vartheta_{4312}$ has to be considered. In fact, when $\alpha > \pi/2$ it is possible (see Figure 12) that C_{12} becomes tangent to C_{44} when $\vartheta = \vartheta_{1244}^*(\alpha, \eta) < \vartheta_{4312}$: when this happens, the excluded area suffers a tiny jump, as a function of ϑ .

The angle ϑ_{1244}^* is defined as the value of ϑ at which the radicand in equation (A.12) vanishes, that is,

$$\vartheta = \vartheta_{1244}^*(\alpha, \eta) := 2 \arctan\left(\frac{\nu(\alpha) + \sqrt{\nu(\alpha)^2 + \mu(\alpha)^2 - \omega(\eta, \alpha)^2}}{\mu(\alpha) + \omega(\eta, \alpha)}\right), \quad (\text{III.35})$$

where we set

$$\mu(\alpha) := \sin^2 \alpha \quad \nu(\alpha) := \sin \alpha \cos \alpha \quad \omega(\eta, \alpha) := 2\eta(2\eta + 1) - \sin^2 \alpha.$$

However, the tangency between C_{12} and C_{44} affects the structure of the convolution curve if (see equation (A.12)) $t_{4412} := t(\vartheta_{1244}^*)$ lies in the interval $[0, \pi - \vartheta]$ where C_{44} belongs to \mathcal{R}_{\oplus} . As can be seen from Fig. 13, $\vartheta_{1244}^* \leq \vartheta_{4312}$ and the difference between the two functions is not easy to perceive for most values of α .

$$1. \quad \vartheta \in [0, \vartheta_{1244}^*]$$

The arcs that contribute to the excluded area are:

arc	radius	center	t	base curve
C_{11}	$2(\eta + 1)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[0, \vartheta]$	$\mathcal{C}_1(t)$
C_{44}	2η	$B + B'$	$[0, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{43}	$2\eta - 1$	B	$[\vartheta, t_{4312}]$	$\mathcal{C}_4(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1243}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[\pi - \alpha - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

The excluded area is then given by

$$\begin{aligned} A(\alpha, \vartheta, \eta) = & 2\left[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta) + \text{Sett}(2\eta, \pi - \vartheta) - \text{Sett}(2\eta - 1, t_{4312} - \vartheta)\right. \\ & \left. + \text{Sett}(1 + 2\eta, t_{1243}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1, b_1, b_2) + \mathcal{T}(h_2, b_2, b_3) + \mathcal{T}(h'_3, b_3, b'_4)\right] \quad (\text{III.36}) \\ & \left. + \mathcal{T}(h_4, b'_4, b_5)\right] \end{aligned}$$

where the bases and the heights of the trapezia are given by equations (III.14), (III.15), and (III.21). We note that the heights h_2 and h'_3 could be negative, as it should be to obtain the correct value of the excluded area.

$$2. \quad \vartheta \in [\vartheta_{1244}^*, \vartheta_{4412}]$$

When C_{12} and C_{44} touch at a point on the set \mathcal{R}_\oplus we need to consider values $t \in [0, t_{1244}]$ along C_{12} and values $t \in [\vartheta, t_{4412}]$ along C_{44} , while C_{43} is trapped in the interior of \mathcal{R}_\oplus . In this regime, the following arcs contribute to the reduced boundary \mathcal{R}_\oplus :

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[0, \vartheta]$	$\mathcal{C}_1(t)$
C_{44}	2η	$B + B'$	$[t_{4412}, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1244}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[(\pi - \alpha) - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

where t_{1214} and t_{1412} are given in equations (A.15) and (A.16). The excluded area is given by

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta) + \text{Sett}(2\eta, \pi - \vartheta - t_{4412}) + \text{Sett}(1 + 2\eta, t_{1244}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1, b_1, b_2) + \mathcal{T}(h_2', b_2', b_3') + \mathcal{T}(h_3'', b_3'', b_5)] \quad (\text{III.37})$$

where equations (III.14), (III.15), (III.21), and (III.24) have been employed too.

$$3. \quad \vartheta \in [\vartheta_{4412}, 2(\pi - \alpha)]$$

The arc C_{44} no longer contributes to the set $\partial(\mathcal{M} \oplus \mathcal{M}')$ and the arcs C_{12} and C_{14} intersect each other. The reduced boundary \mathcal{R}_\oplus is formed by the following arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[t_{1412}, \vartheta]$	$\mathcal{C}_1(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1214}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[(\pi - \alpha) - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

Correspondingly, the excluded area is given by

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta - t_{1412}) + \text{Sett}(1 + 2\eta, t_{1214}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1''', b_1, b_2) + \mathcal{T}(h_2'', b_2', b_5)] \quad (\text{III.38})$$

where use of equations (III.14), (III.21) and (III.27) has been made together with

$$h_1''' = [y_{14}(\vartheta) - y_{14}^{\text{bis}}(t_{1412})]. \quad (\text{III.39})$$

$$4. \quad \vartheta \in [2(\pi - \alpha), \pi]$$

Here the arc C_{42} is replaced by the arc C_{11}^{bis} with scaled radius $2(1 + \eta)$, centered at O , based on the curve \mathcal{C}_1 and symmetric about the y -axis. On \mathcal{R}_\oplus , $t \in [\frac{\vartheta}{2} - (\pi - \alpha), \vartheta - 2(\pi - \alpha)]$ along C_{11}^{bis} . Moreover, the arc C_{12} is replaced by C_{12}^{bis} that differs from C_{12} only for the base curve and along which $t \in [0, t_{1214}^{\text{bis}}]$. The reduced boundary is formed by the following arcs:

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[t_{1412}, \vartheta]$	$\mathcal{C}_1(t)$
C_{12}^{bis}	$1 + 2\eta$	A'	$[0, t_{1214}^{\text{bis}}]$	$\mathcal{K}_2(t)$
C_{11}^{bis}	$2(1 + \eta)$	O	$[\frac{\vartheta}{2} - (\pi - \alpha), \vartheta - 2(\pi - \alpha)]$	$\mathcal{C}_1(t)$

The value of t_{1412} is still given by (A.16), while the value t_{1214}^{bis} can be obtained in the same way as t_{1214} (see equation (A.15)) apart from the different parametrization of the arc C_{12}^{bis} as compared to C_{12} . As a result, t_{1214}^{bis} attains the value

$$t_{1214}^{\text{bis}} := \pi - \alpha + \arcsin\left(\frac{\sin \alpha}{1 + 2\eta}\right). \quad (\text{III.40})$$

Then, the excluded area is now given by

$$A(\alpha, \vartheta, \eta) = 2\left[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta - t_{1412}) + \text{Sett}(1 + 2\eta, t_{1214}^{\text{bis}}) + \frac{1}{2}\text{Sett}(2(1 + \eta), \vartheta - 2(\pi - \alpha)) + \mathcal{T}(h_1''', b_1, b_2') + \mathcal{T}(h_2''', b_2', b_3'')\right] \quad (\text{III.41})$$

where

$$b_3''' = x_{12}^{\text{bis}}(0) \quad h_2''' = y_{12}^{\text{bis}}(t_{1214}) - y_{12}^{\text{bis}}(0). \quad (\text{III.42})$$

D. Horseshoes II: $\alpha \in [\alpha^{\text{cr}}, \alpha^{\text{cr}*}]$

Here we need to distinguish the following regimes, according to whether $\vartheta \in [0, \vartheta_{1244}^*]$, $\vartheta \in [\vartheta_{1244}^*, 2\alpha - \pi]$, $\vartheta \in [2\alpha - \pi, \vartheta_{4412}]$, $\vartheta \in [\vartheta_{4412}, 2(\pi - \alpha)]$ or $\vartheta \in [2(\pi - \alpha), \pi]$.

1. $\vartheta \in [0, \vartheta_{1244}^*]$

The reduced boundary \mathcal{R}_{\oplus} is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[0, \vartheta]$	$\mathcal{C}_1(t)$
C_{44}	2η	$B + B'$	$[0, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{43}	$2\eta - 1$	B	$[\vartheta, t_{4312}]$	$\mathcal{C}_4(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1243}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[\pi - \alpha - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

and the excluded area is given by

$$A(\alpha, \vartheta, \eta) = 2\left[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta) + \text{Sett}(2\eta, \pi - \vartheta) - \text{Sett}(2\eta - 1, t_{4312} - \vartheta) + \text{Sett}(1 + 2\eta, t_{1243}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1, b_1, b_2) + \mathcal{T}(h_2, b_2, b_3) + \mathcal{T}(h_3', b_3, b_4') + \mathcal{T}(h_4, b_4', b_5)\right]. \quad (\text{III.43})$$

2. $\vartheta \in [\vartheta_{4412}^*, \vartheta_{4412}]$

The reduced boundary is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[0, \vartheta]$	$\mathcal{C}_1(t)$
C_{44}	2η	$B + B'$	$[t_{4412}, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1244}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[(\pi - \alpha) - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

and the excluded area is

$$A(\alpha, \vartheta, \eta) = 2\left[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta) + \text{Sett}(2\eta, \pi - \vartheta - t_{4412}) + \text{Sett}(1 + 2\eta, t_{1244}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1, b_1, b_2) + \mathcal{T}(h_2', b_2, b_3') + \mathcal{T}(h_3'', b_3', b_5)\right]. \quad (\text{III.44})$$

$$3. \quad \vartheta \in [\vartheta_{4412}, 2(\pi - \alpha)]$$

The essential boundary is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[t_{1412}, \vartheta]$	$\mathcal{C}_1(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1214}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[\pi - \alpha - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

and the excluded area is

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta - t_{1412}) + \text{Sett}(1 + 2\eta, t_{1214}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1''', b_1, b_2') + \mathcal{T}(h_2''', b_2', b_5)] . \quad (\text{III.45})$$

$$4. \quad \vartheta \in [2(\pi - \alpha), \pi]$$

When ϑ ranges in this interval, the excluded region coincides with that found in Section (III C 4) for ϑ ranging in the same interval, and the excluded area is given by equation (III.41).

E. Horseshoes III: $\alpha \in [\alpha^{\text{cr}*}, \alpha_0]$

The lower bound of this interval is the value $\alpha^{\text{cr}*}$ of α at which $\vartheta_{4412} = 2\alpha - \pi$ and the upper bound is the value α_0 of α at which $\vartheta_{1244}^* = 0$. By use of equation (III.35) we obtain

$$\alpha_0 := \pi - \arcsin\left(\sqrt{\eta(2\eta + 1)}\right) .$$

$$1. \quad \vartheta \in [0, \vartheta_{1244}^*]$$

The reduced boundary is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[0, \vartheta]$	$\mathcal{C}_1(t)$
C_{44}	2η	$B + B'$	$[0, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{43}	$2\eta - 1$	B	$[\vartheta, t_{4312}]$	$\mathcal{C}_4(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1243}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[\pi - \alpha - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

and the excluded area is given by

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta) + \text{Sett}(2\eta, \pi - \vartheta) - \text{Sett}(2\eta - 1, t_{4312} - \vartheta) + \text{Sett}(1 + 2\eta, t_{1243}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1, b_1, b_2) + \mathcal{T}(h_2, b_2, b_3) + \mathcal{T}(h_3', b_3, b_4') + \mathcal{T}(h_4, b_4', b_5)] \quad (\text{III.46})$$

$$2. \quad \vartheta \in [\vartheta_{1244}^*, \vartheta_{4412}]$$

The essential boundary is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[0, \vartheta]$	$\mathcal{C}_1(t)$
C_{44}	2η	$B + B'$	$[t_{4412}, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1244}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[\pi - \alpha - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

and the excluded area is

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta) + \text{Sett}(2\eta, \pi - \vartheta - t_{4412}) + \text{Sett}(1 + 2\eta, t_{1244}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1, b_1, b_2) + \mathcal{T}(h'_2, b_2, b'_3) + \mathcal{T}(h''_3, b'_3, b_5)]. \quad (\text{III.47})$$

$$3. \quad \vartheta \in [\vartheta_{4412}, 2(\pi - \alpha)]$$

The essential boundary is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[t_{1412}, \vartheta]$	$\mathcal{C}_1(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1214}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[\pi - \alpha - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

and the excluded area is

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta - t_{1412}) + \text{Sett}(1 + 2\eta, t_{1214}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h''_1, b_1, b'_2) + \mathcal{T}(h'_2, b'_2, b_5)]. \quad (\text{III.48})$$

$$4. \quad \vartheta \in [2(\pi - \alpha), \pi]$$

The essential boundary is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[t_{1412}, \vartheta]$	$\mathcal{C}_1(t)$
C_{12}^{bis}	$1 + 2\eta$	A'	$[0, t_{1214}^{\text{bis}}]$	$\mathcal{K}_2(t)$
C_{11}^{bis}	$2(1 + \eta)$	O	$[\frac{\vartheta}{2} - \pi + \alpha, \vartheta - 2(\pi - \alpha)]$	$\mathcal{C}_1(t)$

and the excluded area is

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta - t_{1412}) + \text{Sett}(1 + 2\eta, t_{1214}^{\text{bis}}) + \frac{1}{2}\text{Sett}(2(1 + \eta), \vartheta - 2(\pi - \alpha)) + \mathcal{T}(h''_1, b_1, b'_2) + \mathcal{T}(h''_2, b'_2, b''_3)]. \quad (\text{III.49})$$

F. Horseshoes IV: $\alpha \in [\alpha_0, \alpha_m]$

For these values of α , $\vartheta_{1244}^* < 0$ and so the arc C_{43} never enters the reduced boundary. As a result, only three regimes survive.

$$1. \quad \vartheta \in [0, \vartheta_{4412}]$$

The essential boundary is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[0, \vartheta]$	$\mathcal{C}_1(t)$
C_{44}	2η	$B + B'$	$[t_{4412}, \pi - \vartheta]$	$\mathcal{K}_4(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1244}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[\pi - \alpha - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

and the excluded area is

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta) + \text{Sett}(2\eta, \pi - \vartheta - t_{4412}) + \text{Sett}(1 + 2\eta, t_{1244}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h_1, b_1, b_2) + \mathcal{T}(h'_2, b_2, b'_3) + \mathcal{T}(h''_3, b'_3, b_5)]. \quad (\text{III.50})$$

$$2. \quad \vartheta \in [\vartheta_{4412}, 2(\pi - \alpha)]$$

The essential boundary is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[t_{1412}, \vartheta]$	$\mathcal{C}_1(t)$
C_{12}	$1 + 2\eta$	A'	$[0, t_{1214}]$	$\mathcal{C}_1(t)$
C_{42}	2η	$B + A'$	$[\pi - \alpha - \frac{\vartheta}{2}, 2(\pi - \alpha) - \vartheta]$	$\mathcal{K}_2(t)$

and the excluded area is

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta - t_{1412}) + \text{Sett}(1 + 2\eta, t_{1214}) + \frac{1}{2}\text{Sett}(2\eta, 2(\pi - \alpha) - \vartheta) + \mathcal{T}(h'''_1, b_1, b'_2) + \mathcal{T}(h''_2, b'_2, b_5)]. \quad (\text{III.51})$$

$$3. \quad \vartheta \in [2(\pi - \alpha), \pi]$$

The essential boundary is formed by the arcs

arc	radius	center	t	base curve
C_{11}	$2(1 + \eta)$	O	$[0, \alpha - \frac{\vartheta}{2}]$	$\mathcal{K}_1(t)$
C_{14}	$1 + 2\eta$	B'	$[t_{1412}, \vartheta]$	$\mathcal{C}_1(t)$
C_{12}^{bis}	$1 + 2\eta$	A'	$[0, t_{1214}^{\text{bis}}]$	$\mathcal{K}_2(t)$
C_{11}^{bis}	$2(1 + \eta)$	O	$[\frac{\vartheta}{2} - (\pi - \alpha), \vartheta - 2(\pi - \alpha)]$	$\mathcal{C}_1(t)$

and the excluded area is

$$A(\alpha, \vartheta, \eta) = 2[\frac{1}{2}\text{Sett}(2(1 + \eta), 2\alpha - \vartheta) + \text{Sett}(1 + 2\eta, \vartheta - t_{1412}) + \text{Sett}(1 + 2\eta, t_{1214}^{\text{bis}}) + \frac{1}{2}\text{Sett}(2(1 + \eta), \vartheta - 2(\pi - \alpha)) + \mathcal{T}(h'''_1, b_1, b'_2) + \mathcal{T}(h''_2, b'_2, b'_3)]. \quad (\text{III.52})$$

IV. RESULTS

By joining the expressions given in equations (III.16), (III.19)—or (III.30), if $\alpha \in [\frac{\pi}{4}, \frac{\pi}{2}]$ —(III.20), (III.23), and (III.26) we obtain a piecewise expression for the area $A(\alpha, \vartheta, \eta)$ enclosed by the Minkowski sum $\mathcal{M} \oplus \mathcal{M}'$. By Theorem II.1 and since we are in a planar setting, $A(\alpha, \vartheta, \eta)$ also represents the excluded area between the same molecules

when they are at a relative angle $\varphi := \pi - \vartheta$. Figure 8 illustrates the behaviour of the excluded area against φ , when $\eta = 10^{-2}$, and $\alpha = \pi/6$ and $\pi/3$, respectively. The graphs clearly indicate that the excluded area attains its absolute minimum when the molecules are antiparallel, while the configuration at which the molecules are parallel is only a local minimum. The two minima are separated by a maximum attained at $\varphi \gtrsim \frac{\pi}{2}$. Thus we can say that steric interactions are polar since they distinguish between parallel and antiparallel alignments. Moreover, the fact that the excluded area is minimized when two boomerangs are antiparallel suggests the possibility that an ensemble made of these molecules could exhibit a rich variety of phase transitions: hence, it would be interesting to use the excluded area found here to build a steric interaction potential in the spirit of [16] or [13]. In particular, if a scaled particle approach is followed, the excluded area has to be modified to account the different size of the interacting molecules.

Figure 10 shows the excluded area for a pair of horseshoes against the relative orientation $\varphi = \pi - \vartheta$, for four values of α , one for each regime considered here. At variance with boomerangs, the difference between the relative minimum at $\varphi = 0$ and the absolute maximum decreases when the opening angle approaches its upper bound α_M . This is not surprising since, when α is close to α_M , the molecular morphology hinders the exploration of the concave regions when the molecules are antiparallel. Equivalently, when $\alpha \rightarrow \alpha_M$ the molecules tend to acquire an equatorial symmetry that makes parallel and antiparallel configurations undistinguishable.

Following [17], to measure the relative magnitude of the minima of the excluded area, we introduce the *polarity index* ϱ defined according to

$$\varrho(\eta, \alpha) := 3 \frac{A(\alpha, 0, \eta) - A(\alpha, \pi, \eta)}{A(\alpha, 0, \eta) + A(\alpha, \pi, \eta)} \quad (\text{IV.1})$$

where the second argument in A is the value of φ and the factor 3 has been chosen to normalize the maximum value of ϱ at 1: in the parlance of [17], $\varrho(\eta, \alpha) = I_p(0)$.

Figure 11 shows the behaviour of ϱ as a function of $\alpha \in [0, \alpha_M]$, when $\eta = 10^{-2}$. As a result, the polarity index does not have a monotonic profile. For boomerangs ($\alpha \leq \frac{\pi}{2}$) the polarity index steadily increases from the value $\varrho(0) = 0$ attained for discorectangles that are centro-symmetric molecules. For horseshoes ϱ fails to be a monotone function of α but decreases as α approaches α_M , attaining the asymptotic value $\varrho(\alpha_M) = 0$ in the limit when $\eta \rightarrow 0$, so that a horseshoe reduces to a circle with no shape polarity. Finally, the absolute maximum of ϱ saturates at 1 in the limit when $\eta \ll 1$.

The analytic piecewise expression of the excluded area for a pair of boomerangs or horseshoes could be difficult to handle. However, the function A_0 defined in equation (III.29) represents a good approximation in the limit when $\eta \ll 1$ and so the molecules are slender bodies. Figure 9 shows the graphs of both $A(0.1, \varphi, \frac{\pi}{6})$ and $A_0(0.1, \varphi, \frac{\pi}{6})$. Although η is not exceedingly small, A_0 is still able to capture the essential behaviour of the excluded area. When $\eta = 10^{-2}$, the two graphs are practically identical. We also note that, at this level of approximation, η and φ are weakly coupled through the angle $\vartheta_a(\alpha, \eta)$. In particular, a pair of thin boomerangs and a pair of genuine arcs with $\eta \equiv 0$ have excluded areas with the same anisotropic part.

V. CONCLUSIONS

We computed analytically the excluded area for a pair of planar, identical molecules that are a generalization of the discorectangles considered in [16]. The molecules, named boomerangs or horseshoes, depending on the value of an angular parameter, have two important geometric properties. They are not convex and they lack a center of symmetry. The former feature makes the explicit computation of the excluded area a non-trivial task that was overcome by resorting to techniques employed in CAGD that relate the Minkowski sum of two bodies to their convolution curve. Obtaining the convolution curve requires tracking the behaviour of the Gauss map of the two bodies while extracting information on the Minkowski boundary from the profile of the convolution curve requires a trimming procedure for which at the moment there is no analytic general procedure. We managed to succeed by using a molecular profile formed by piecewise circular arcs.

Lack of central symmetry in the molecules makes it possible to explore shape polarity effects on the excluded area. Precisely, it turns out that the absolute minimum of the excluded area as a function of the relative orientation between the two molecules is attained when the molecules are antiparallel, instead of parallel. Following [17], we introduced a polarity index to measure the magnitude of this effect. It turned out that the polarity index attains its absolute maximum when $2\alpha \gtrsim \pi$ while its absolute minimum 0 is always attained at $\alpha = 0$ and also at $\alpha = \alpha_M$, when $\eta \rightarrow 0$. This behaviour can be explained by noting that large values of the opening angle mask the concave region bounded by an horseshoe, that cannot be explored by the other molecule. As a result, though the molecules are not centro-symmetric, their asymmetry is hidden.

Clearly this paper opens the ways to several studies. First, it would be interesting to use the analytic expression of the excluded area for a pair of boomerangs or even its approximation (III.29) to explore phase transition by building

a density-functional theory, in the spirit of [16]. Then, it raises a natural question. Do the techniques employed here work in three space dimensions? By looking again at the CAGD literature ([12], [21]) we gain the impression that, if the molecular shapes are modelled as union of simple patches on which the Gauss map is easily computable, then the task could be successfully pursued, maybe numerically. Another three-dimensional extension that dwells on a different method has been studied in [22] where, by resorting to a mixed approach, both analytical and numerical, we are able to obtain the excluded volume for molecules conceived as aggregates of spheres, generalizing the results of [23] and [24] to different molecular morphologies.

However, also remaining in two space dimensions could be of interest. The unusual behaviour of the excluded area as a function of the relative orientation suggests that a study of an ensemble formed by boomerangs could lead to a rich spectrum of phase transitions, especially when the polarity index is high. A density-functional or a scaled particle theory approach could benefit from the knowledge of the explicit formula for the excluded area as provided in the present paper.

APPENDIX A: ARCS FORMING A BOOMERANG

We give here the explicit parameterization of the arcs C_{ij} whose properties were listed concisely in the Tables of Sec. III.

$$C_{11} - O = 2(\eta + 1)\left[-\sin\left(t - \alpha + \frac{\vartheta}{2}\right)\mathbf{e}_x + \cos\left(t - \alpha + \frac{\vartheta}{2}\right)\mathbf{e}_y\right];$$

in some cases a different base curve was required, leading to the arc

$$C_{11}^{\text{bis}} - O = 2(\eta + 1)\left[-\sin\left(t - \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_x + \cos\left(t - \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_y\right].$$

$$C_{14} - O = B' - O + (1 + 2\eta)\left[-\sin\left(t - \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_x + \cos\left(t - \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_y\right] \quad (\text{A.1})$$

$$C_{44} - O = (B - O) + (B' - O) + 2\eta\left[-\sin\left(\pi + t - \alpha + \frac{\vartheta}{2}\right)\mathbf{e}_x + \cos\left(\pi + t - \alpha + \frac{\vartheta}{2}\right)\mathbf{e}_y\right] \quad (\text{A.2})$$

$$C_{43} - O = (B - O) + (2\eta - 1)\left[-\sin\left(\pi + t - \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_x + \cos\left(\pi + t - \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_y\right] \quad (\text{A.3})$$

$$C_{42} - O = (B - O) + (A' - O) + 2\eta\left[-\sin\left(t + \alpha + \frac{\vartheta}{2}\right)\mathbf{e}_x + \cos\left(t + \alpha + \frac{\vartheta}{2}\right)\mathbf{e}_y\right],$$

where the vectors $A - O$, $A' - O$, $B - O$, and $B' - O$ are given by equations (III.10).

When $\alpha < \pi/4$, but $\vartheta \in [2\alpha, \pi - 2\alpha]$, the arc C_{11} is replaced by the arc C_{24} given by

$$C_{24} - O = (A - O) + (B' - O) + 2\eta\left[-\sin\left(t + \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_x + \cos\left(t + \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_y\right],$$

with base curve given by C_2 .

When ϑ exceeds $\pi - 2\alpha$, the arc C_{12} contributes the set $\partial(\mathcal{M} \oplus \mathcal{M}')$. We take C_1 as its base curve, so that

$$C_{12} - O = (A' - O) + (1 + 2\eta)\left[-\sin\left(t - \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_x + \cos\left(t - \alpha - \frac{\vartheta}{2}\right)\mathbf{e}_y\right]. \quad (\text{A.4})$$

When \mathcal{K}_2 was needed as a base curve, we had to consider the arc

$$C_{12}^{\text{bis}} - O = (A' - O) + (1 + 2\eta)\left[-\sin\left(t + \alpha + \frac{\vartheta}{2}\right)\mathbf{e}_x + \cos\left(t + \alpha + \frac{\vartheta}{2}\right)\mathbf{e}_y\right].$$

While at $t = 0$ $C_{12}(0)$ coincides with $C_{42}(2\pi - 2\alpha - \vartheta)$, the largest value of t for which C_{12} belongs to $\partial(\mathcal{M}_1 \oplus \mathcal{M}_2)$ depends on ϑ . In fact, C_{12} intersects C_{43} at a point where $t = t_{1243}$. Correspondingly, $t \in [\vartheta, t_{4312}] \subseteq [\vartheta, \pi]$ along the portion of the arc C_{43} that contributes to $\partial(\mathcal{M} \oplus \mathcal{M}')$. When $\vartheta = \vartheta_{1243}$, the whole arc C_{43} lies inside $\partial(\mathcal{M} \oplus \mathcal{M}')$

and C_{12} now crosses the portion of C_{44} belonging to $\partial(\mathcal{M} \oplus \mathcal{M}')$ at a point where $t = t_{1244}$. Correspondingly, C_{44} belongs to $\partial(\mathcal{M} \oplus \mathcal{M}')$ only when $t \in [t_{4412}, \pi - \vartheta]$, for a suitable value $t_{4412} > 0$ of t . When $\vartheta = \vartheta_{1244}$, the arc C_{44} lies completely in the interior of $\mathcal{M} \oplus \mathcal{M}'$. Then, C_{12} crosses C_{14} when $t = t_{1214}$, and the portion of C_{14} in $\partial(\mathcal{M} \oplus \mathcal{M}')$ satisfies $t \in [t_{1412}, 2\alpha]$. We now show how to compute the critical values of ϑ separating different regimes, together with the values of t at which the different arcs intersect. Let us determine $C_{12} \cap C_{43}$. The values of t at which a point on C_{12} also belongs to C_{43} satisfy the equation

$$|C_{12}(t) - (B - O)|^2 = (2\eta - 1)^2$$

and a straightforward computation based on equations (A.4) and (III.10) shows that the acceptable value of t is

$$t_{1243}(\eta, \alpha, \vartheta) = \frac{\vartheta}{2} + \alpha - \arcsin \left[\frac{2\eta + \sin^2 \left(\alpha + \frac{\vartheta}{2} \right)}{(1 + 2\eta) \sin \left(\alpha + \frac{\vartheta}{2} \right)} \right]. \quad (\text{A.5})$$

Similarly, by imposing $|C_{43}(t) - (A' - O)|^2 = (2\eta + 1)^2$ and using equations (A.3) and (III.10) we arrive at

$$t_{4312}(\eta, \alpha, \vartheta) = \frac{\vartheta}{2} + \alpha + \arcsin \left[\frac{2\eta - \sin^2 \left(\alpha + \frac{\vartheta}{2} \right)}{(2\eta - 1) \sin \left(\alpha + \frac{\vartheta}{2} \right)} \right]. \quad (\text{A.6})$$

Since $t = \vartheta$ is the smallest admissible value of t on C_{43} , to determine the value of ϑ_{4312} we simply solve the equation $|C_{43}(\vartheta) - (A' - O)|^2 = (2\eta + 1)^2$ in terms of ϑ . After use of elementary trigonometric identities this requirement is recast as

$$\frac{2\eta - 1}{2} (\cos 2\alpha - \cos \vartheta) = 2\eta - \frac{1}{2} [1 - \cos(2\alpha + \vartheta)]$$

which, after little labour, can be reduced to the form

$$c_{43} \sin \vartheta + b_{43} \cos \vartheta - a_{43} = 0 \quad (\text{A.7})$$

where

$$a_{43}(\eta, \alpha) := \frac{1}{2}(2\eta - 1) \cos 2\alpha + \frac{1}{2} - 2\eta \quad b_{43}(\eta, \alpha) := \frac{1}{2} \cos 2\alpha + \eta - \frac{1}{2} \quad c_{43}(\alpha) = -\frac{1}{2} \sin 2\alpha.$$

and that can be solved by setting $x := \tan \frac{\vartheta}{2}$ and using the identities

$$\sin \vartheta = \frac{2x}{1 + x^2} \quad \cos \vartheta = \frac{1 - x^2}{1 + x^2}. \quad (\text{A.8})$$

As a result, the acceptable root is

$$\vartheta_{4312}(\eta, \alpha) = 2 \arctan \left(\frac{c_{43} - \sqrt{c_{43}^2 + b_{43}^2 - a_{43}^2}}{\eta(\cos 2\alpha - 1)} \right). \quad (\text{A.9})$$

When $\vartheta > \vartheta_{4312}$, the arc C_{43} no longer contributes to $\partial(\mathcal{M} \oplus \mathcal{M}')$, and we have to look for $C_{12} \cap C_{44}$. Thus, we first solve

$$|C_{12}(t) - (B - O) - (B' - O)|^2 = 4\eta^2$$

by finding (see equations (A.4) and (III.10)) the values of $u := t - \alpha - \frac{\vartheta}{2}$ that obey

$$a_{44} \sin u - b_{44} \cos u + k_{44} = 0 \quad (\text{A.10})$$

where

$$a_{44}(\alpha, \vartheta) := 2 \sin \left(\alpha + \frac{\vartheta}{2} \right) + \sin \left(\alpha - \frac{\vartheta}{2} \right), \quad b_{44}(\alpha, \vartheta) := \cos \left(\alpha - \frac{\vartheta}{2} \right), \quad k_{44}(\eta, \alpha, \vartheta) := 1 + \frac{2c_{44}(\alpha, \vartheta)}{1 + 2\eta}$$

with

$$c_{44}(\alpha, \vartheta) := 2 \sin \left(\alpha + \frac{\vartheta}{2} \right) \sin \alpha \cos \frac{\vartheta}{2}.$$

It is not difficult to verify that the admissible solution of equation (A.10) in terms of t is

$$t_{1244}(\eta, \alpha, \vartheta) = \alpha + \frac{\vartheta}{2} + 2 \arctan \left(\frac{-a_{44} - \sqrt{a_{44}^2 + b_{44}^2 - k_{44}^2}}{k_{44} + b_{44}} \right) \quad (\text{A.11})$$

Correspondingly, by solving $|C_{44}(t) - (A' - O)|^2 = (1 + 2\eta)^2$ and using equations (A.2) and (III.10) we find

$$t_{4412}(\eta, \alpha, \vartheta) = \alpha - \frac{\vartheta}{2} + 2 \arctan \left(\frac{-a_{44} + \sqrt{a_{44}^2 + b_{44}^2 - \left(\frac{c_{44}}{\eta} - 1\right)^2}}{b_{44} + \frac{c_{44}}{\eta} - 1} \right). \quad (\text{A.12})$$

Since the largest value of t for which C_{44} is an admissible arc is $t = \pi - \vartheta$, by solving the equation $|C_{44}(\pi - \vartheta) - (A' - O)|^2 = (1 + 2\eta)^2$ in terms of ϑ we find the upper bound on the values of ϑ for which the arc C_{44} contributes to $\partial(\mathcal{M} \oplus \mathcal{M}')$. It turns out that ϑ has to satisfy the equation

$$d_{44} \cos \vartheta - e_{44} \sin \vartheta + f_{44} = 0 \quad (\text{A.13})$$

where

$$d_{44}(\eta, \alpha) := \left(1 + \frac{1}{2\eta}\right) (\cos 2\alpha - 1) \quad e_{44}(\eta, \alpha) := \sin 2\alpha \left(1 + \frac{1}{2\eta}\right) \quad f_{44}(\eta, \alpha) := \frac{1}{2\eta} (\cos 2\alpha - 1).$$

By resorting to the identities (A.8), it is possible to prove that

$$\vartheta_{4412}(\eta, \alpha) = 2 \arctan \left(\frac{e_{44} + \sqrt{e_{44}^2 + d_{44}^2 - f_{44}^2}}{f_{44} - d_{44}} \right). \quad (\text{A.14})$$

In the limit when $\eta \rightarrow 0$, both ϑ_{4312} and ϑ_{4412} tend to the continuous function

$$\vartheta_l(\alpha) := \begin{cases} \pi & \text{if } \alpha \in [0, \frac{\pi}{2}] \\ 2(\pi - \alpha) & \text{if } \alpha \in [\frac{\pi}{2}, \pi]. \end{cases}$$

To study the behaviour of ϑ_{4312} and ϑ_{4412} when $\alpha < \frac{\pi}{2}$ we set

$$\vartheta_{4312} = \pi - (\gamma_1 \eta + \gamma_2 \eta^2)$$

in equation (A.7) and

$$\vartheta_{4412} = \pi - (\lambda_1 \eta + \lambda_2 \eta^2)$$

in equation (A.10) and expand the resulting equations in powers of η . By setting the coefficients of different powers of η equal to zero we obtain

$$\gamma_1 = \lambda_1 = 2 \tan \alpha, \quad \gamma_2 = -2 \tan^3 \alpha, \quad \lambda_2 = 2 \tan \alpha (2 - \tan^2 \alpha).$$

This approach fails at $\alpha = \frac{\pi}{2}$ where both $\pi - \vartheta_{4312}$ and $\pi - \vartheta_{4412}$ behave like $\sqrt{\eta}$, instead of η like in this case. In fact, this is a consequence of the *knee* that the limit function $\vartheta_l(\alpha)$ has at $\alpha = \frac{\pi}{2}$. We limit ourselves to point out this feature, but we do not proceed in the computations.

When $\vartheta > \vartheta_{4412}$ also C_{44} lies in the interior of $\mathcal{M} \oplus \mathcal{M}'$ and we have to turn attention to $C_{12} \cap C_{14}$. We first solve

$$|C_{12}(t) - (B' - O)|^2 = (1 + 2\eta)^2$$

to determine the value t_{1214} of t at which C_{12} intersects C_{14} . It is not difficult to check that

$$t_{1214}(\eta, \alpha, \vartheta) = \alpha + \vartheta - \pi + \arcsin \left(\frac{1}{1 + 2\eta} \sin \alpha \right). \quad (\text{A.15})$$

Similarly, by use of equations (A.1) and (III.10) we determine the value t_{1412} of t at which C_{14} crosses the arc C_{12} by imposing that

$$|C_{14}(t) - (A' - O)|^2 = (1 + 2\eta)^2 :$$

it is possible to prove that the admissible root is given by

$$t_{1412}(\eta, \alpha, \vartheta) := \alpha + \vartheta - \pi - \arcsin\left(\frac{1}{1+2\eta} \sin \alpha\right). \quad (\text{A.16})$$

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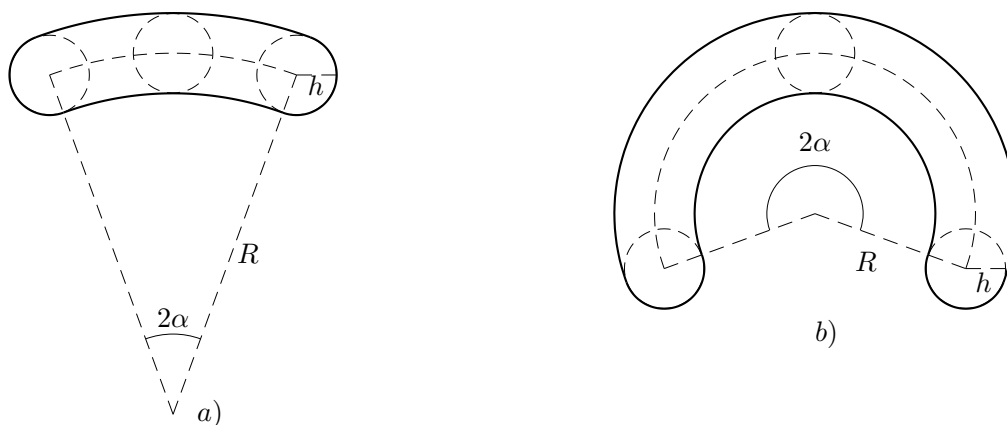


FIG. 1: Sketch of: a) a boomerang and b) a horseshoe. The molecules differ because the angle α is less than $\frac{\pi}{2}$ in the former case and larger than $\frac{\pi}{2}$ in the latter. Apart from this, both molecules can be obtained by moving the center of a disk of radius h , dashed in both figures, along the dashed circular arc of radius R .

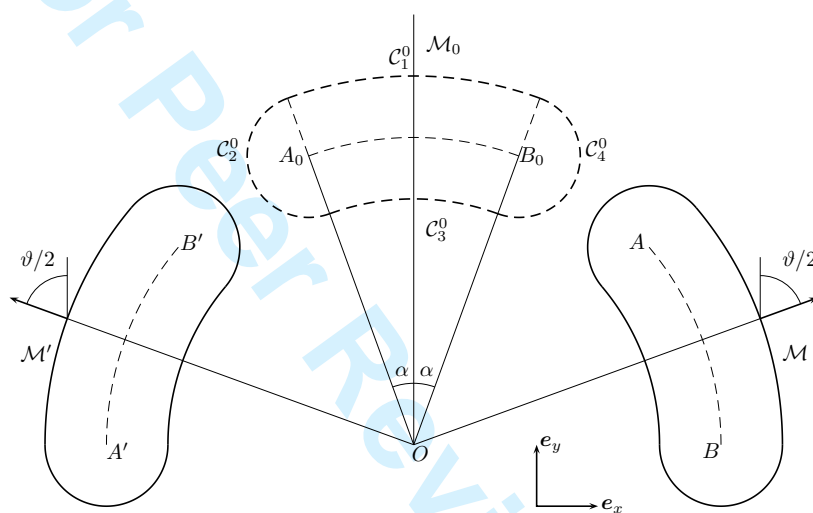


FIG. 2: The molecules \mathcal{M} and \mathcal{M}' are obtained by rotating the referential molecule \mathcal{M}_0 about the axis $e_z = e_x \times e_y$ passing through the point O by an angle $-\vartheta/2$ and $\vartheta/2$, respectively. Details of the molecular morphology are explained in the text.

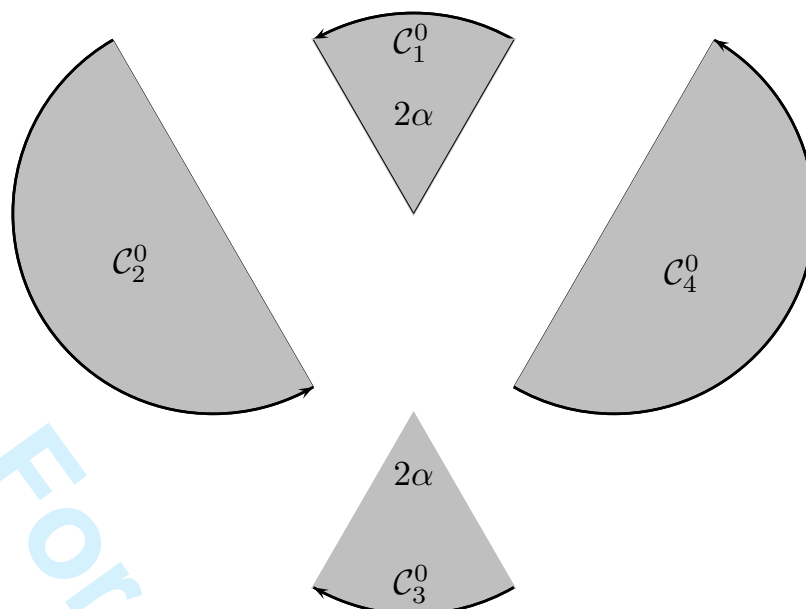


FIG. 3: We show here the images of the Gauss maps for the arcs \mathcal{C}_i^0 of the reference molecule \mathcal{M}_0 shown in Fig. 2. The arrows indicate how the unit normal rotates when \mathcal{M}_0 is described counterclockwise.

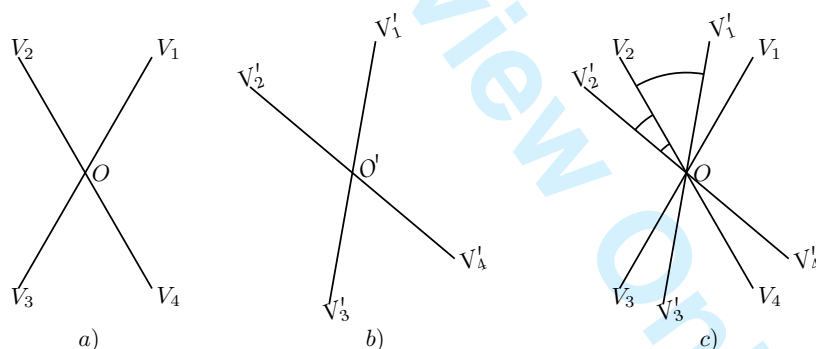


FIG. 4: The cross in *a*) schematically represents the images of the Gauss maps along the arcs of \mathcal{M} . The Gauss map $\mathcal{N}(\mathcal{C}_1)$ spans the angle $\angle V_1OV_2$; $\mathcal{N}(\mathcal{C}_2)$ spans the π -angle $\angle V_2OV_4$; $\mathcal{N}(\mathcal{C}_3)$ spans (clockwise) the angle $\angle V_4OV_3$ and $\mathcal{N}(\mathcal{C}_4)$ spans the π -angle $\angle V_1OV_3$. The cross in *b*) conveys the same information for \mathcal{M}' and so the Gauss maps $\mathcal{N}(\mathcal{K}_1), \dots, \mathcal{N}(\mathcal{K}_4)$ span, respectively, the angles $\angle V'_1O'V'_2, \angle V'_2O'V'_4, \angle V'_4O'V'_3, \angle V'_1O'V'_3$. Finally, in *c*), the two crosses are superimposed to see the arcs along which the Gauss maps coincide: this happens, for instance, along $\angle V'_1OV_2$ for the arcs \mathcal{C}_1 and \mathcal{K}_1 , and along $\angle V_2OV'_2$ for the arcs \mathcal{C}_2 and \mathcal{K}_1 . We note that this scenario holds when $\alpha \in [0, \frac{\pi}{4}]$ and $\vartheta \in [0, 2\alpha]$.

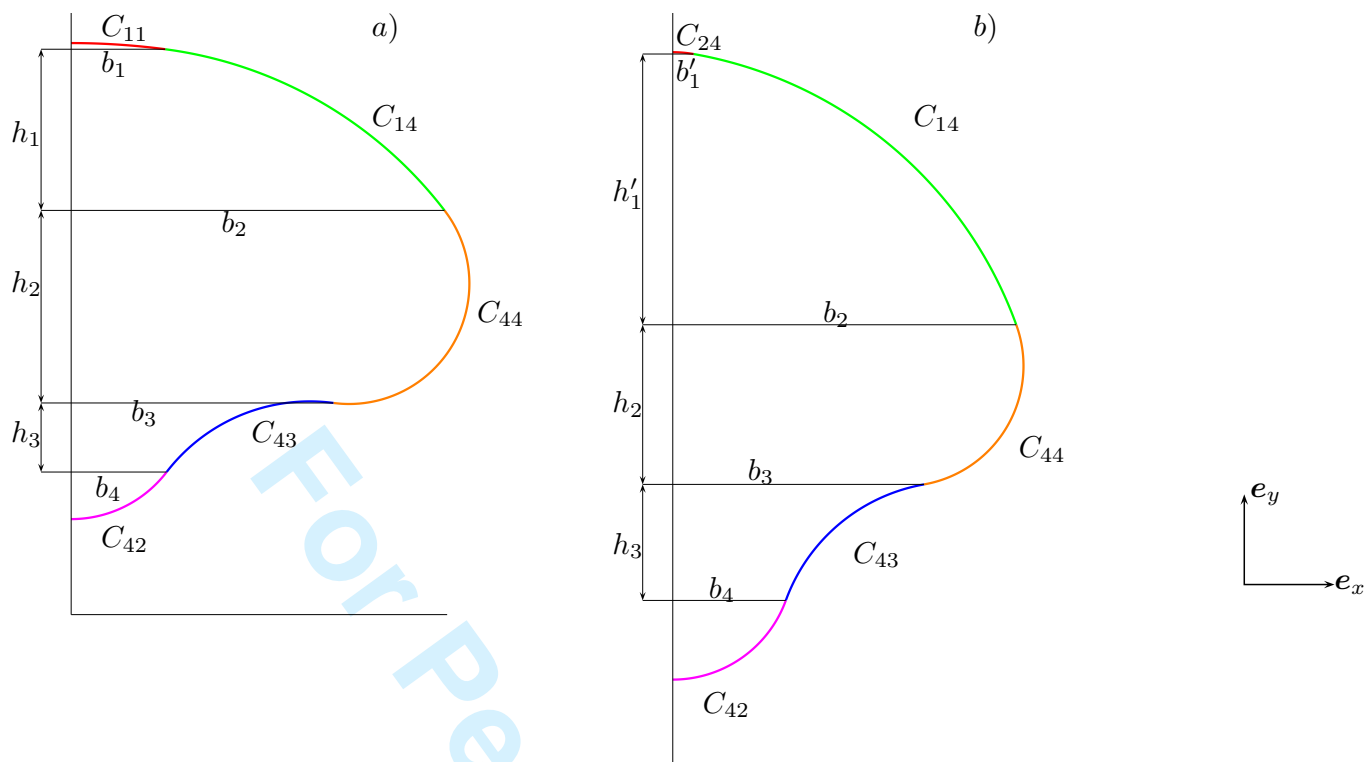


FIG. 5: a): The reduced set \mathcal{R}_\oplus corresponding to the values $\alpha = \pi/6$ and $\vartheta = \pi/4 \in [0, 2\alpha]$. The excluded region is obtained by pasting to \mathcal{R}_\oplus its symmetric set with respect to the y -axis. The excluded area is given by equations III.13 and III.16. b) The reduced set \mathcal{R}_\oplus corresponding to the values $\alpha = \pi/6$ and $\vartheta = 8\pi/18 \in [2\alpha, \pi - 2\alpha]$. Compared to a), the arc C_{11} is replaced by the arc C_{42} , while the arc C_{14} spans the interval $t \in [0, 2\alpha]$. The excluded area is now given by equations (III.17) and (III.19).

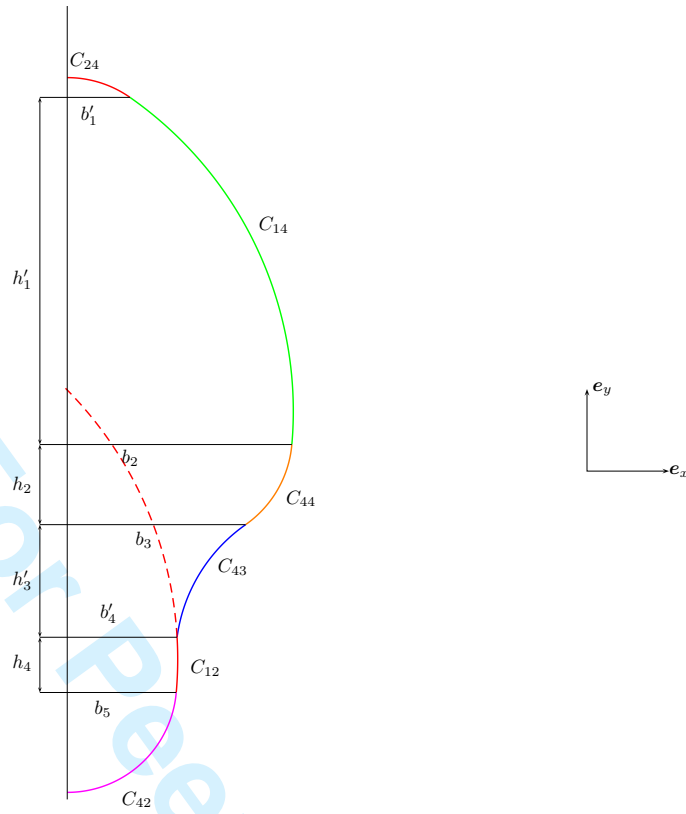


FIG. 6: The reduced set \mathcal{R}_\oplus corresponding to the values $\alpha = \pi/6$ and $\vartheta = 13\pi/18 \in [\pi - 2\alpha, \vartheta_{4312}]$. The admissible arcs \mathcal{C}_{43} and \mathcal{C}_{12} do not join at their end-points and so their intersection is needed to obtain a correct expression for the excluded area. The dashed line is the portion of \mathcal{C}_{12} that lies within the boundary of $\mathcal{M} \oplus \mathcal{M}'$. The excluded area is given by equations (III.20) and, when $\eta \ll 1$, (III.22).

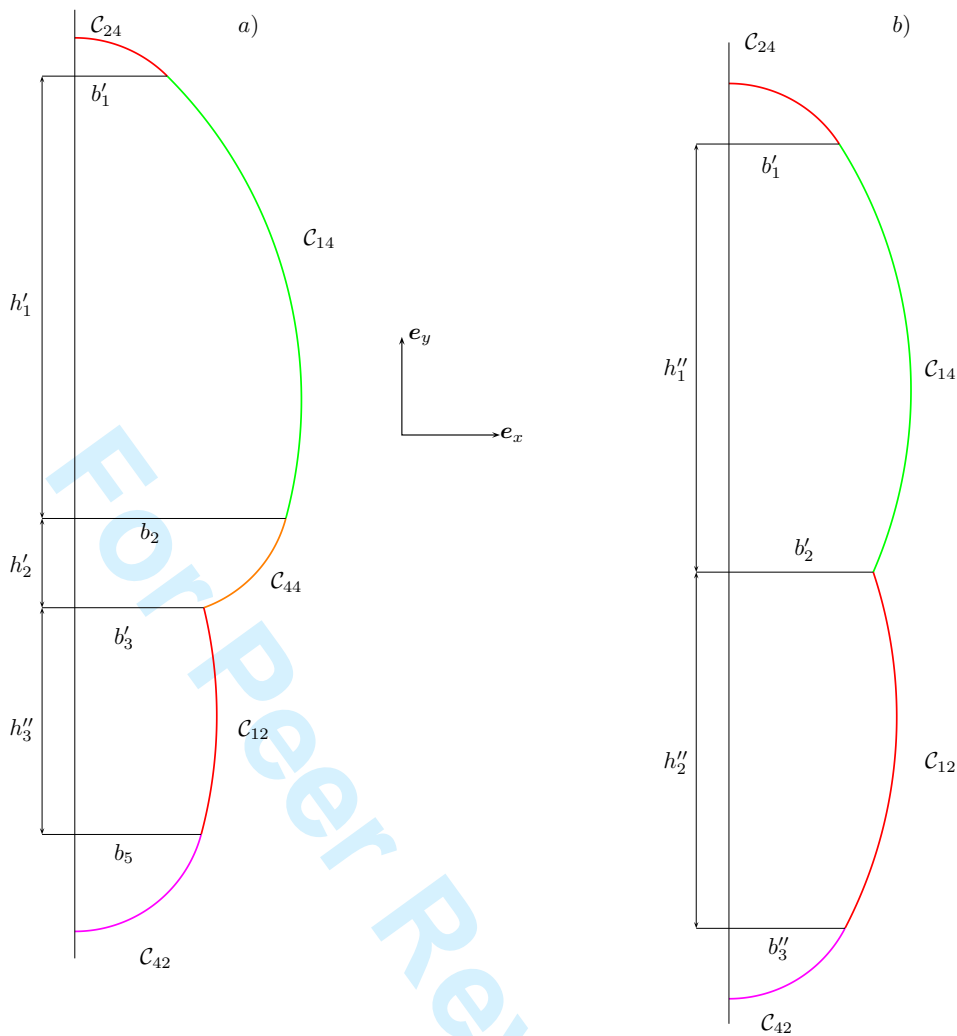


FIG. 7: *a*): The reduced set \mathcal{R}_\oplus corresponding to the values $\alpha = \pi/6$ and $\vartheta = 15\pi/18 \in [\vartheta_{4312}, \vartheta_{4412}]$. The arc \mathcal{C}_{43} lies in the interior of \mathcal{R}_\oplus and \mathcal{C}_{12} intersects \mathcal{C}_{44} . The excluded area is now given by equation (III.23). When $\eta \ll 1$ this case disappears. *b*): The reduced set \mathcal{R}_\oplus corresponding to the values $\alpha = \pi/6$ and $\vartheta = 17.5\pi/18 \in [\vartheta_{4412}, \pi]$. Also the arc \mathcal{C}_{44} lies in the interior of \mathcal{R}_\oplus and \mathcal{C}_{12} intersects \mathcal{C}_{14} . On approaching $\vartheta = \pi$ the set \mathcal{R}_\oplus also acquires an equatorial symmetry. The excluded area is given by equation (III.26) and, when $\eta \ll 1$, (III.28).

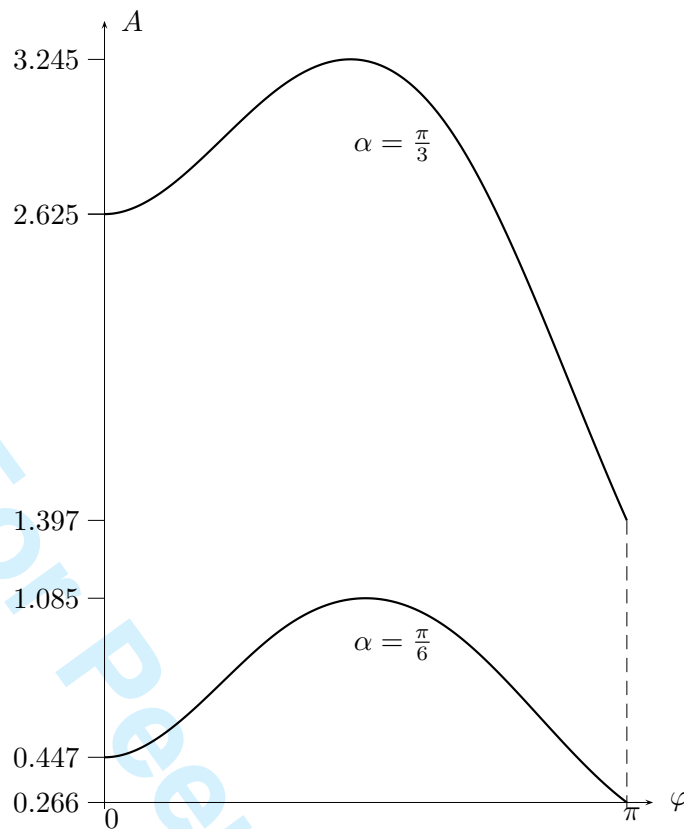


FIG. 8: The excluded area $A(\alpha, \varphi, \eta)$ between two boomerangs is plotted against their relative orientation $\varphi = \pi - \vartheta$, when $\eta = 10^{-2}$ and $\alpha = \frac{\pi}{6}$ or $\frac{\pi}{3}$. In both cases A attains its absolute minimum at $\varphi = \pi$, that is, when the molecules are antiparallel. The configuration at which molecules are parallel is still a local minimum of A . The two minima are separated by a maximum that is attained when φ is close to $\frac{\pi}{2}$.

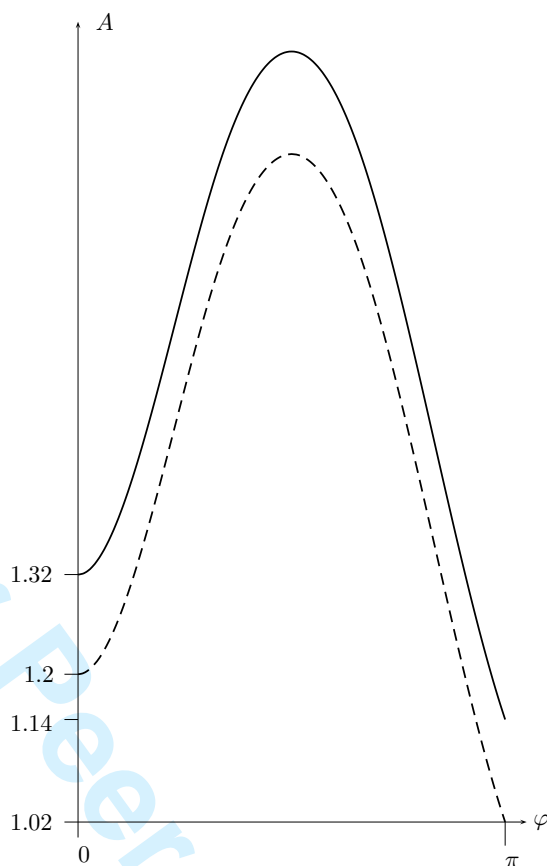


FIG. 9: The graphs of the exact excluded area $A(\alpha, \varphi, \eta)$ (solid line) and of its approximation $A_0(\alpha, \varphi, \eta)$ (dashed line) are shown for $\eta = 10^{-1}$ and $\alpha = \frac{\pi}{6}$. Although there is a quantitative discrepancy, also for such values of η A_0 follows precisely the qualitative details of A . Decreasing η makes the quantitative agreement satisfactory and when $\eta \approx 10^{-2}$ the graphs of A and A_0 practically coalesce.

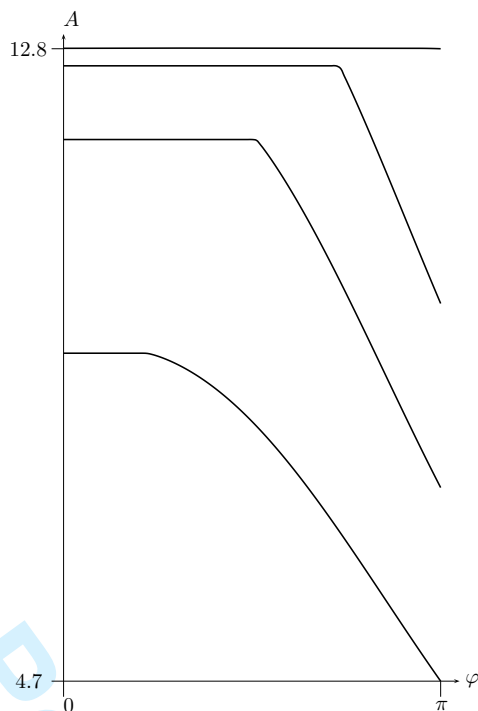


FIG. 10: The dimensionless excluded area $A(\alpha, \varphi, \eta)$ has been plotted against the relative orientation $\varphi = \pi - \vartheta$ when $\eta = 0.01$, for different values of α that, from bottom to top, bisect each of the intervals $[\frac{\pi}{2}, \alpha_{cr}]$, $[\alpha_{cr}, \alpha_{cr}^*]$, $[\alpha_{cr}^*, \alpha_0]$, and $[\alpha_0, \alpha_M]$. All profiles have the same qualitative behaviour: the excluded area has a plateau that becomes larger and larger when α increases, and then attains its absolute minimum at $\varphi = \pi$. On increasing α , the local minimum at $\varphi = 0$ becomes shallower and shallower. We note that the discontinuity at $\varphi = \pi - \vartheta_{1244}^*$ cannot be appreciated on this scale.

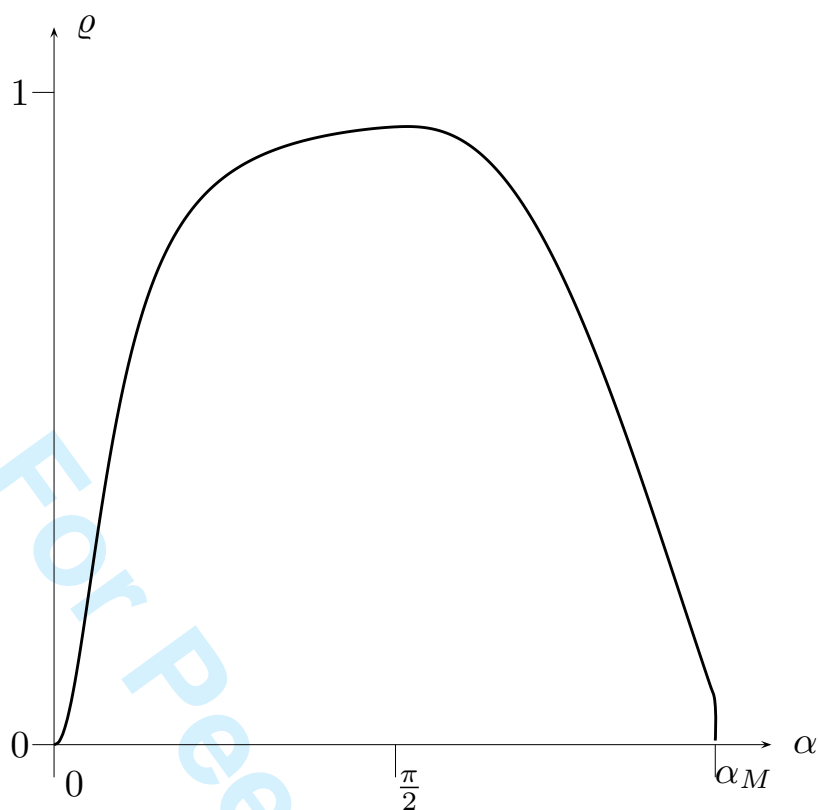


FIG. 11: The polarity index ρ defined in equation (IV.1) is plotted against $\alpha \in [0, \alpha_M]$, when and $\eta = 10^{-2}$. As a general rule, ρ attains its maximum when α is slightly larger than $\frac{\pi}{2}$. On varying η , no qualitative changes occur in the graph of ρ whose maximum saturates at 1 when $\eta \rightarrow 0$.

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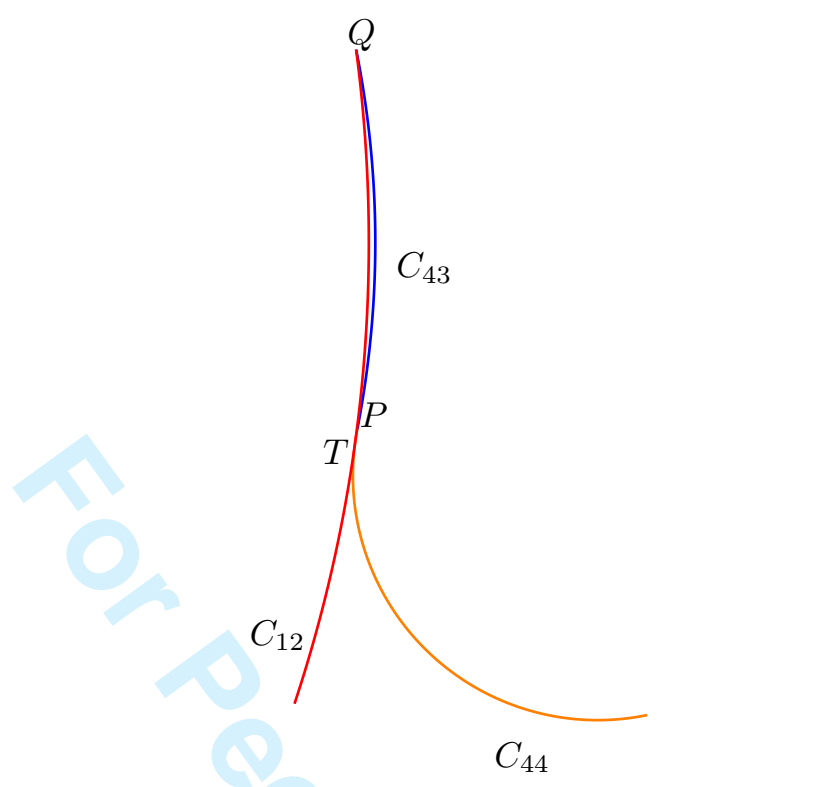


FIG. 12: When $\vartheta = \vartheta_{1244}^*$, the arcs C_{12} and C_{44} are tangent in T . The arc C_{43} , bounded by the points P and Q is trapped in the interior of \mathcal{R}_\oplus and does not contribute to its boundary. This has also an effect on the excluded area that suffers a tiny jump at $\vartheta = \vartheta_{1244}^*$ since the area bounded by the closed contour TQP is not zero.

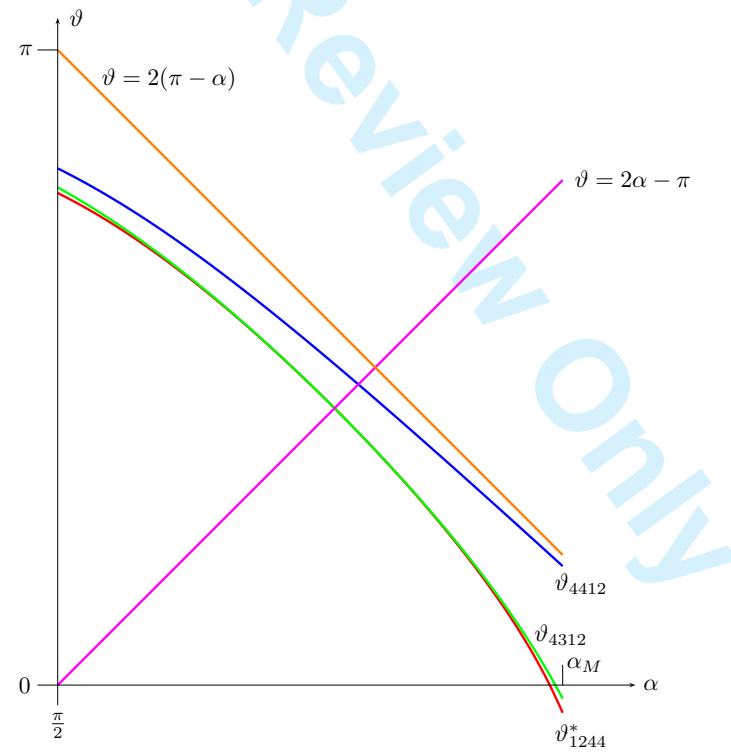
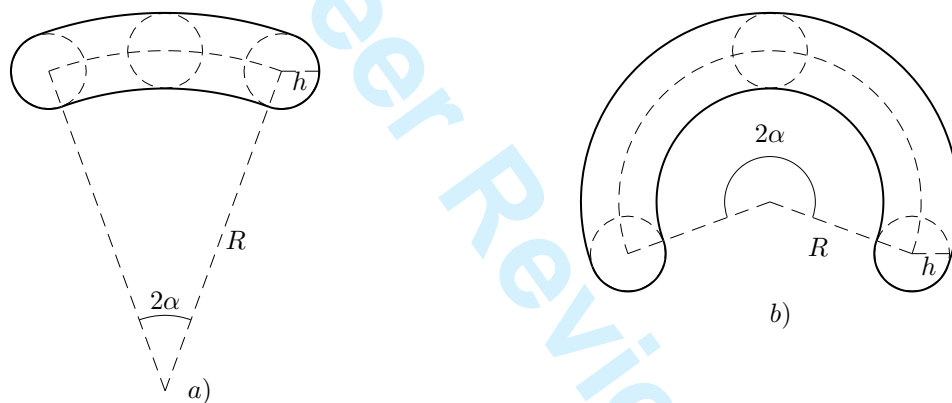
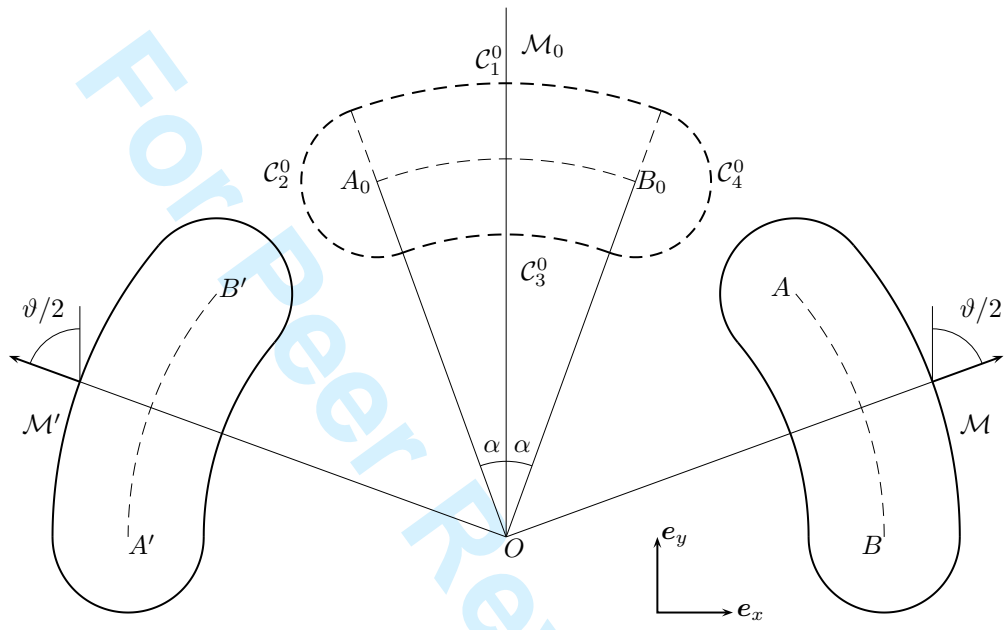
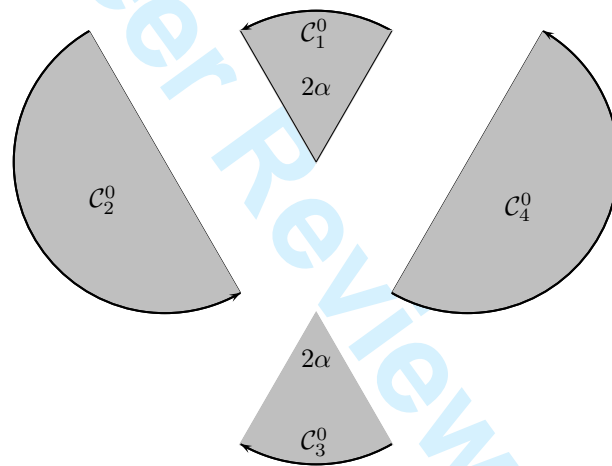


FIG. 13: The functions ϑ_{1244}^* (red curve), ϑ_{4312} (green), ϑ_{4412} (blue) are plotted against $\alpha \in [\frac{\pi}{2}, \alpha_M]$ when $\eta = 0.1$. The straight lines are $\vartheta = 2\alpha - \pi$ (magenta) and $\vartheta = 2(\pi - \alpha)$ (orange).

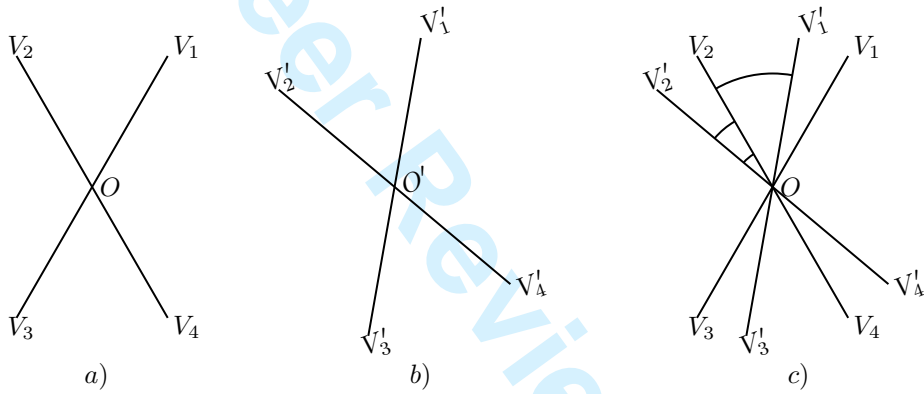


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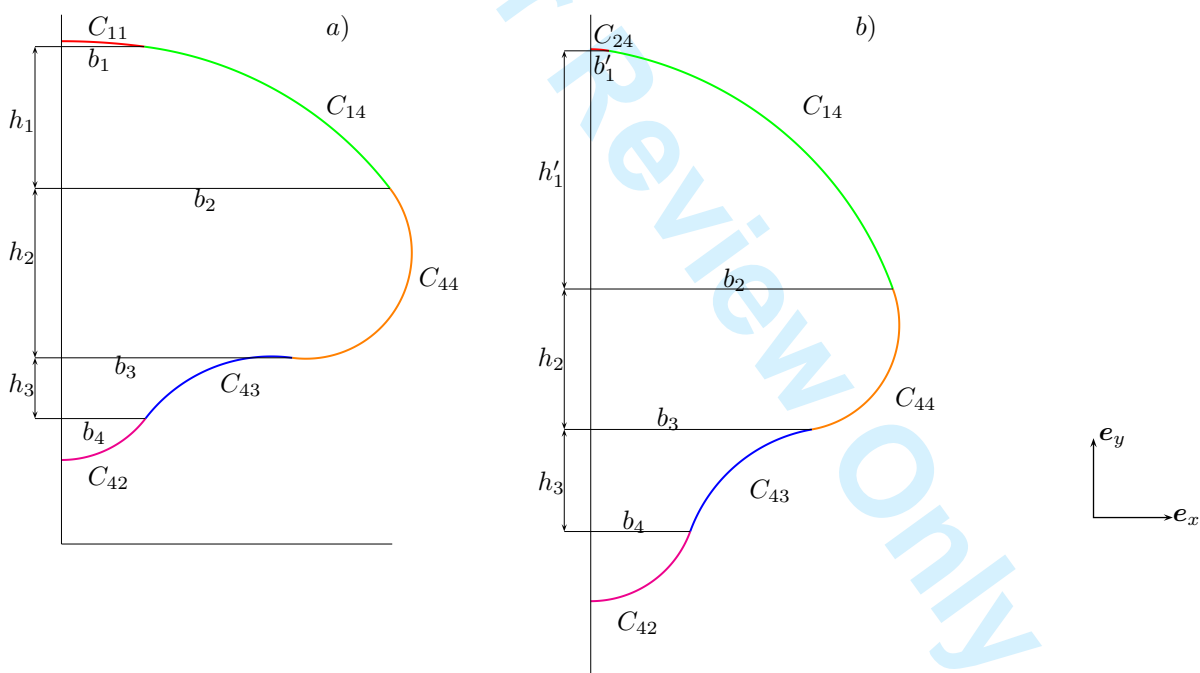


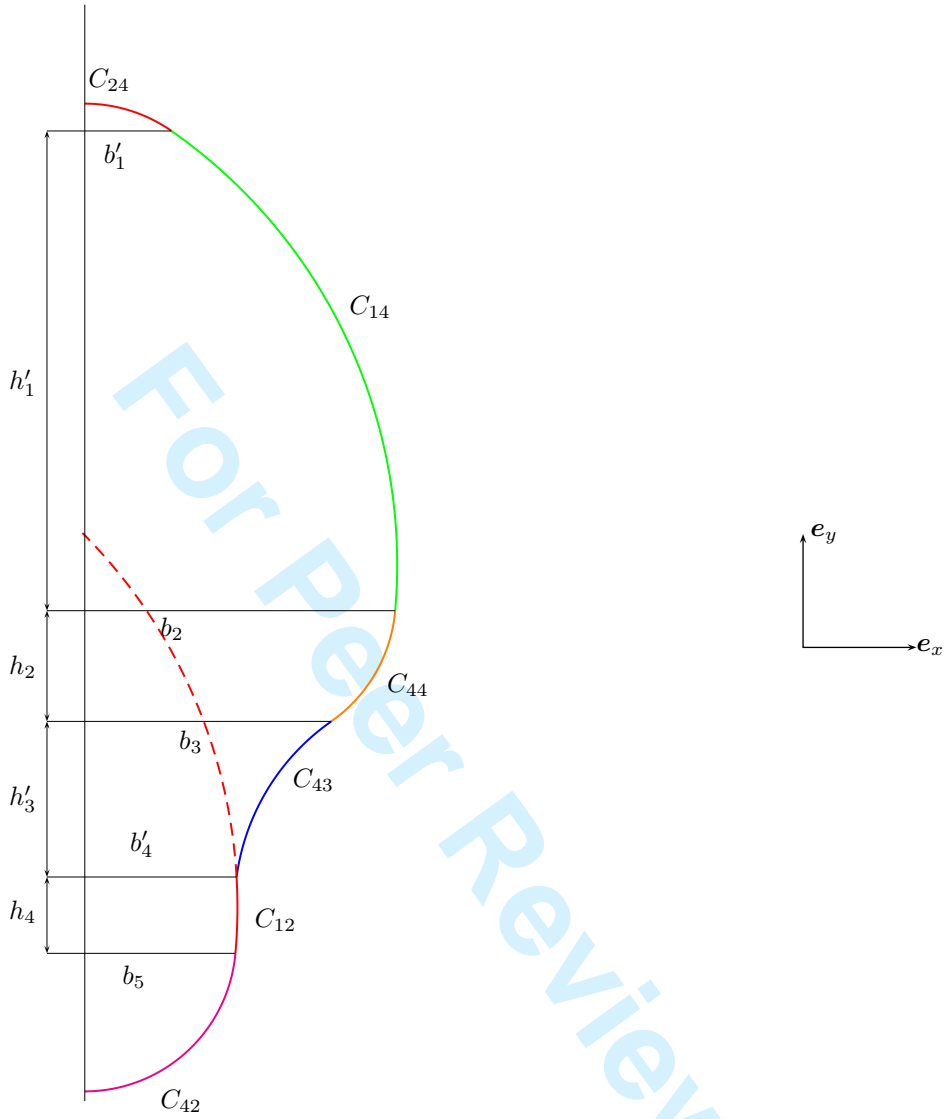


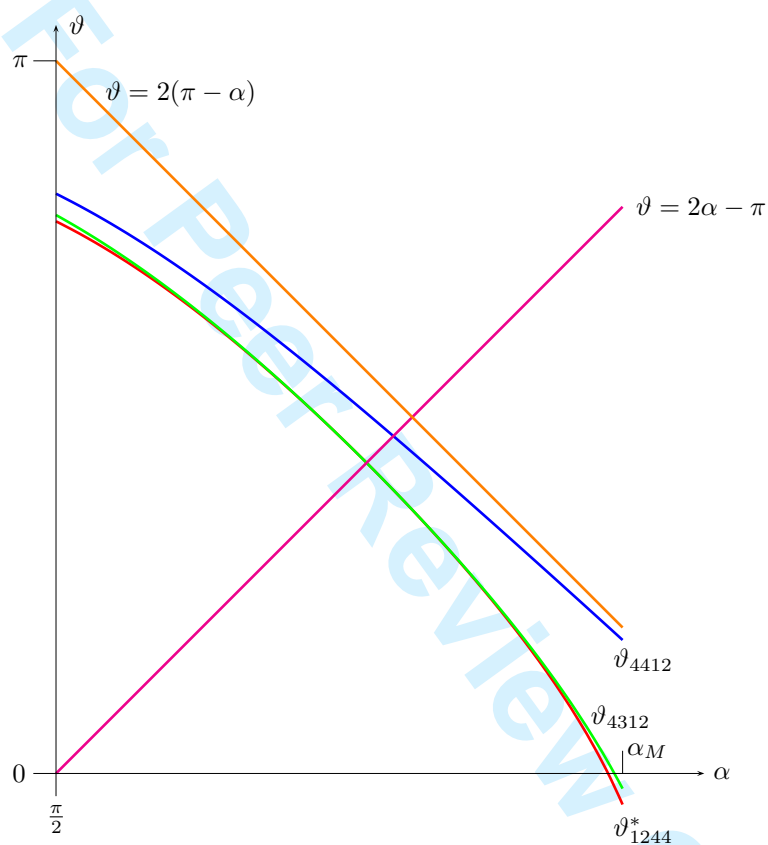
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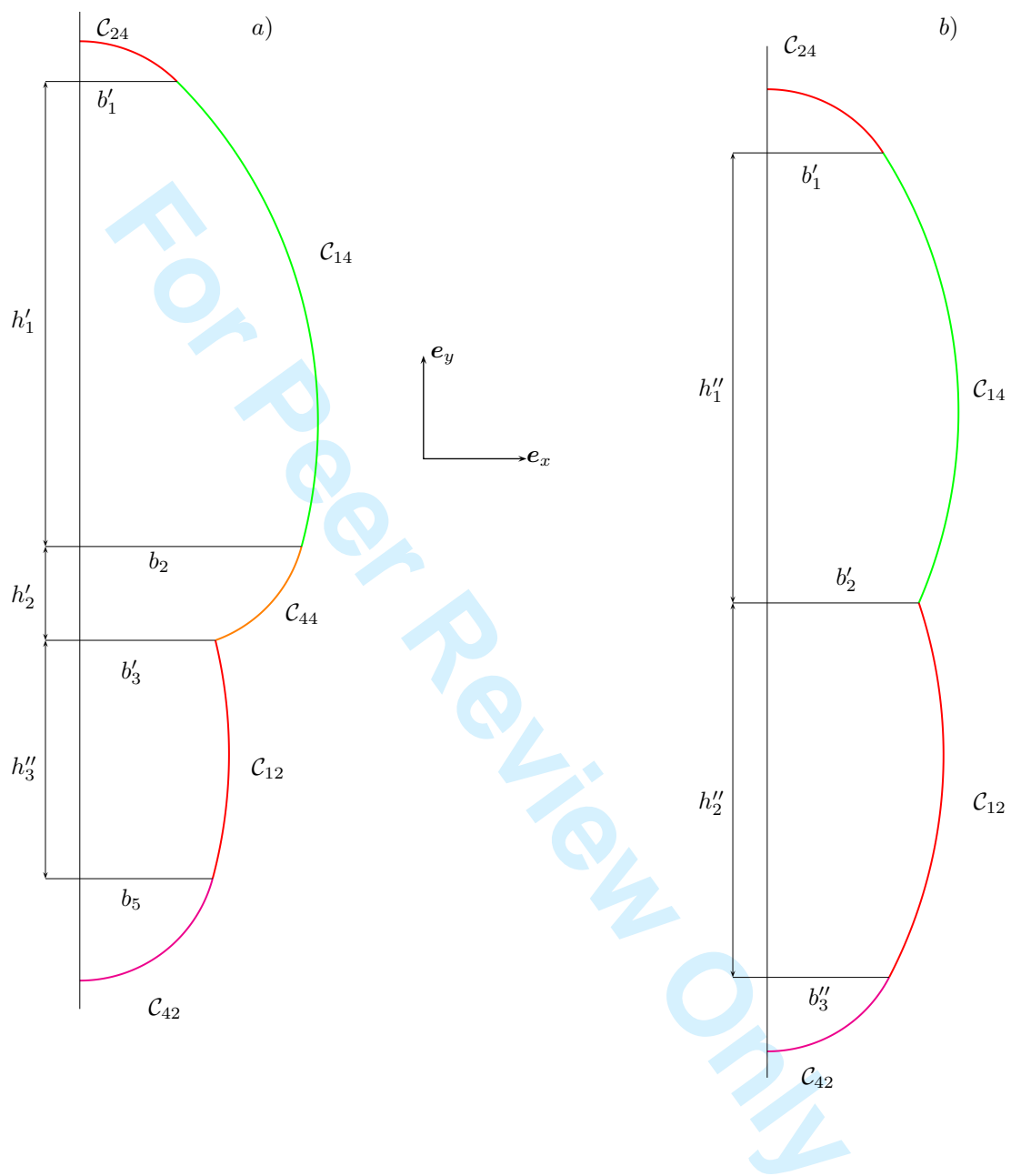
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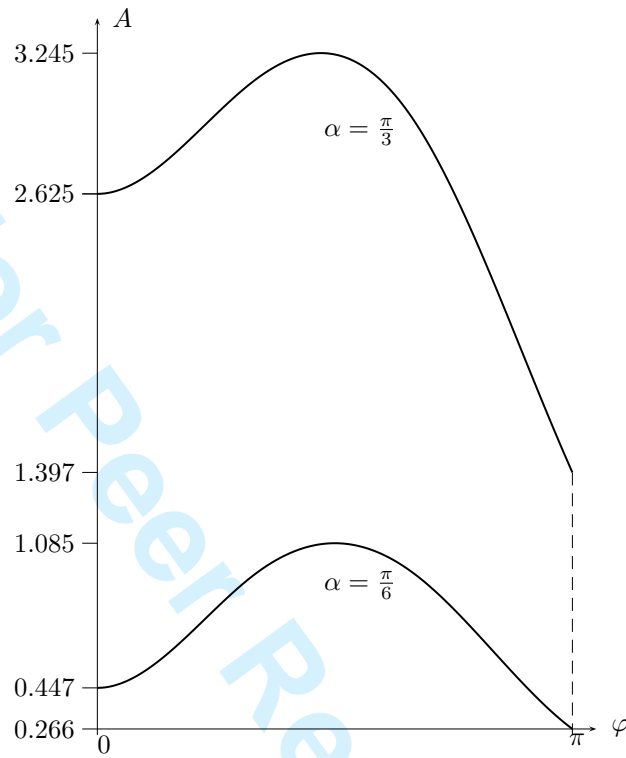


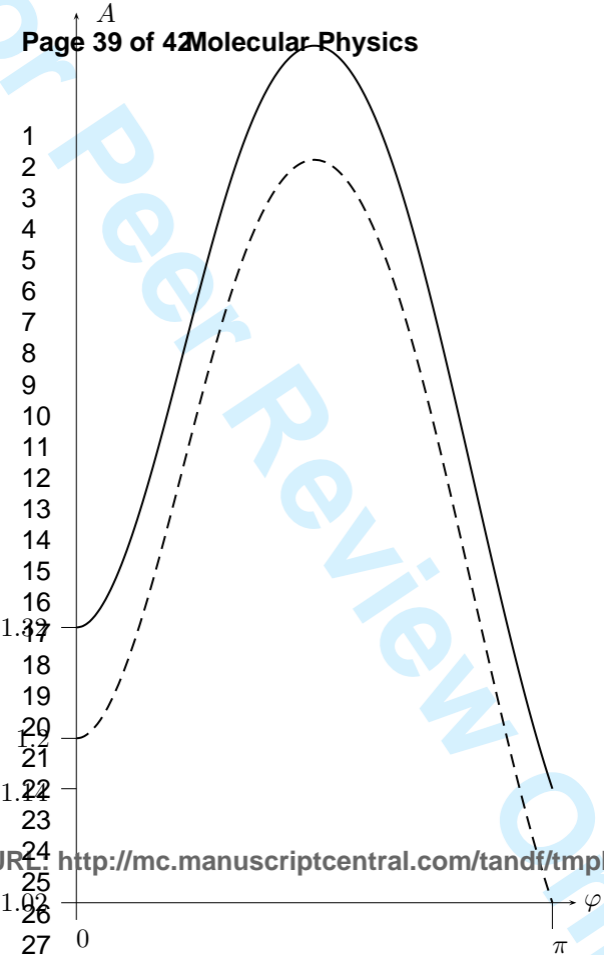


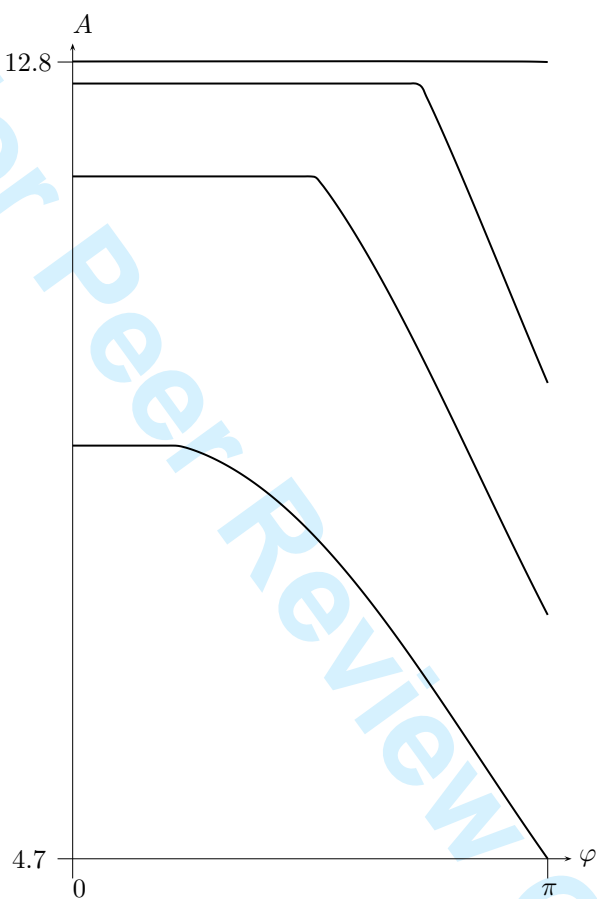


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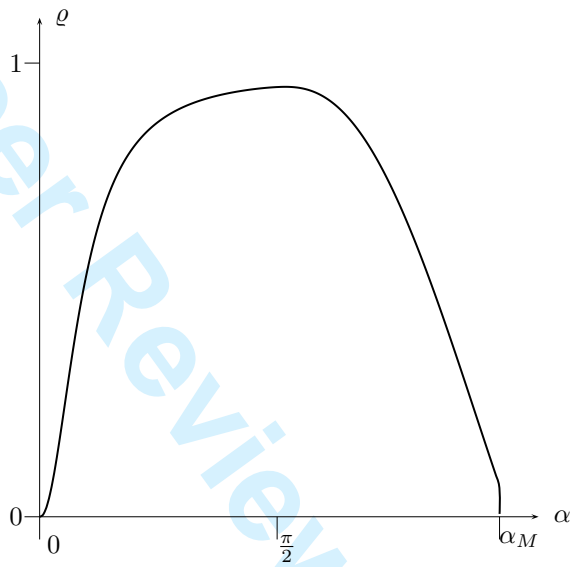


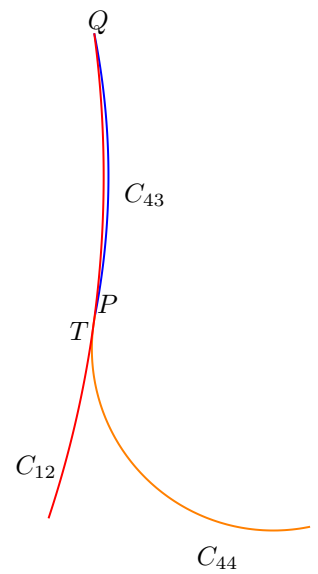




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