Mean-field model of boomerang nematic liquid crystals with diminished coupling of molecular uniaxial and biaxial susceptibilities

Agnieszka Chrzanowska*
Institute of Physics, Kraków University of Technology, ul. Podchorążych 1, 30-084 Kraków, Poland

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The mean-field theory approach has been applied to the boomerang type particles from P. I. C. Teixeira, A. Masters, and B. Mulder [Mol. Cryst. Liq. Cryst. **323**, 167 (1998)] but with diminished strength of the interaction coefficient responsible for the coupling between molecular uniaxial and biaxial susceptibilities. For the rodlike particles, when the apex boomerang angle is larger than 107.35°, the stable uniaxial rodlike phase occurs. For smaller angles, beyond the point where the transition is of the second order (the Landau point) and for diminished parameter of molecular biaxial-uniaxial coupling, a biaxial phase is observed with the transition undergoing directly from the isotropic phase. According to the order parameters the character of this transition is of the first order. Such behavior is in accordance with the Sonnet-Durand-Virga model of the biaxial phases. The change in the type of the phase transition order is also illustrated by the changes in the equations of state and the changes in second and third derivatives of the free energy. The possibilities to tailor interaction coefficients of real molecules to obtain such a phase transition scenario are discussed.

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I. INTRODUCTION

Existence of biaxial nematic phases is an intriguing phenomenon. Finding of such substances in thermotropic media would be very fruitful for applications. This fact was the main reason for the interest in studying the subject. It has turned out, however, that biaxial nematic phases are difficult to obtain in experiment or computer simulation as well, since other phenomena, like creation of smectics or demixing, intervene [1].

First predictions about biaxial nematic liquid crystals come from the 1970s thanks to Freiser [2], who, using an approach similar to that of Maier and Saupe [3], predicted that long and flat molecules could form a biaxial nematic phase of D_{2h} symmetry, in addition to the nematic uniaxial phase. This paper was followed by the Refs. [4–6]. It was not until 10 years later that the first experimental report appeared that the biaxial phase was indeed observed. The system reported by Yu and Saupe [7] was, in fact, a lyotropic liquid crystal. For unknown reasons until now, chemical compounds that could form thermotropic biaxial phases are difficult to synthesize. It is interesting that, with exception of a polymeric material from Ref. [8], all subsequent experimental reports concern either bent-core molecules [9–13] or tetrapodes [14–17]. No experimental evidence about molecules forming more regular rectangular boxes and exhibiting biaxial phases is known up to now, although the theory indicates such possibility [18].

Contrary to the experimental outcome the theoretical achievements are still accumulating giving continuous rise to better understanding of the phenomenon of biaxiality. These achievements consist of the Landau de Gennes descriptions [19–24] and the theories of the mean-field and Onsager type [25–39]. The Monte Carlo and molecular dynamics simulations push the knowledge about biaxiality beyond limitations of the second virial or mean-field assumptions, thus giving rise to more realistic outcome [40–56]. Because of the experimental results, the banana, V-shaped molecules or tetrapod systems are of special interest [57–60]. These considerations are rooted in the above-mentioned theoretical approaches, yet identification of the appropriate potential or Landau expansion parameters is not an easy task. In order to obtain the reliable phase diagram one needs a direct reference to the bent-core-shaped interactions which can be given either by the assessment of the excluded volume [57] or Gay-Berne formulas [60] for boomerangs.

The first theoretical analysis of a bent-core system has been given by Teixeira *et al.* [57] within the mean-field approach. Using Straley's formalism [6] with the aid of the Onsager theory, Teixeira *et al.* predicted that the molecular aggregate composed of two joined at the ends hard spherocylinders and forming a sort of a boomerang can give rise to the stable biaxial phase with the transition from the uniaxial phase being a continuous transition. Only at the Landau point does the biaxial phase bifurcate directly from the isotropic phase. It has turned out, however, that the range of the apex angle of the boomerangs in the vicinity of the Landau point, where the biaxial is so close to the isotropic phase as not to enter the smectic formation, is very small. According to Luckhurst [48] it is about 2°. This can be one of the factors giving rise to difficulties in obtaining stable biaxial phases from real compounds.

This scenario—a single Landau point with a direct transition from the isotropic phase into the biaxial one and the existence in the vicinity of the Landau point of the prolate and oblate uniaxial phases that separates the isotropic phase from the biaxial one—is the most common one in the case of biaxiality and is recovered practically by all the approaches, either theoretical or simulative, that find biaxial phases. The

*achrzano@usk.pk.edu.pl

same picture, although of a different origin, occurs in the case of the rod-disk mixtures [61–65].

Another picture of the possible sequences of the phase transitions has been given by Sonnet *et al.* [29] and by Bisi *et al.* [33]. The new features they have found is the existence of the isotropic-biaxial nematic (I-NB) phase transition of the first-order and uniaxial nematic biaxial tricritical point. These models assume minimal [29] or diminished [33] coupling between uniaxial and biaxial molecular susceptibilities (given, as it will be explained in the text, by the $\tilde{\gamma}$ coefficient).

These theoretical investigations on the possible influence of the parameters give no bridge to the real systems as yet or to the factors that could lead to such modeling of the molecular parameters. Nevertheless, checking possible changes to the phase diagram scenario is fully legitimate on the mathematical grounds and has been in use in other systems, too [66]. A minimal coupling model exhibiting isotropic, uniaxial, and biaxial nematic phases was also analyzed in Ref. [31]. The possibility of the above-mentioned nematic uniaxial nematic biaxial tricritical point [29] is analyzed there as well.

According to Grzybowski and Longa [60] a credible theory should treat dispersion and dipolar interactions on an equal footing with the steric repulsion. Following this line they included additional effects by adding dipoles or considering three branches of the bent-core molecule. The molecules they used were the Gay-Berne interacting ellipsoids of uniaxial and biaxial shape and endowed with a transverse central dipoles.

Almost at the same time, Zheng and Palffy-Muhoray [35] considered inclusion of the London-Van der Waals interaction energy between polarizable molecules, yet the results provided a well-known V-shaped picture of the phase diagram with the single Landau point. Contrary to Zheng *at al.*, Grzybowski and Longa [60] not only reconstructed the typical shape of the phase diagram but also found the whole line of the Landau points. In the case of the nonpolar three-part molecules, the Landau point was found to be at the apex angle of 89°, having the tendency to be shifted to lower angles when the dipol is added. When the dipole-dipole interactions attains about 20% of the total energy, then the Landau point changes into an I-NB line that widens on further increasing dipol strength. For the biaxial ellipsoids a line of the Landau points was also observed even in the absence of the dipoles.

The above-described features are not all that can be found in the systems composed of the bent-core molecules. Very puzzling was the finding of Longa, Pająk, and Wydro [67], where a first microscopic demonstration of spontaneous chiral symmetry breaking in nonlayered bent-core liquid crystals has been presented. In this work, besides ordinary isotropic (I), uniaxial nematic (NU), and biaxial nematic (NB) phases, the obtained phase diagrams exhibit, additionally, tetrahedratic, N_T and $N*_T$ phases.

In the present paper we consider a one-component system of particles related to the boomerangs analyzed by Teixeira *et al.* [57]. In our mean-field approach, however, we will use the interaction coefficients slightly different than regarded in this work. We will be investigating, namely, an influence of diminished strength of the coupling between uniaxial and biaxial molecular susceptibilities on the orientational order parameter profiles of the system and, in particular, their characteristics near the transition points. Additionally, equations of state and specific heats will be given and discussed.

Section II presents the details of the model. Section III provides formulas for the pressure and specific heat. In Sec. IV the results are presented and, finally, Sec. V contains concluding remarks.

II. MEAN-FIELD APPROACH TO THE MODIFIED BOOMERANG SYSTEM

A. Orientational distribution function

Within the mean-field approach the orientational distribution function describing the system with possible biaxial order is given by the mean-field formula

$$\hat{f}(\Omega) = \frac{\exp[-\mathrm{W}(\Omega)/(kT)]}{\int d\Omega \exp[-\mathrm{W}(\Omega)/(kT)]}, \tag{1}$$

in which the one particle mean-field potential $W(\Omega)$ is of the form

$$W(\Omega) = w_1 F_1(\theta) + w_2 F_2(\theta,\phi) + w_3 F_3(\theta,\chi) + w_4 F_4(\theta,\phi,\chi) \tag{2}$$

with F_1, F_2, F_3, and F_4 being the Straley symmetry adapted functions [6] and θ, ϕ, χ being the Euler angles:

$$\begin{aligned} F_1 &= \tfrac{1}{2}[3\cos^2(\theta) - 1] \\ F_2 &= \sin^2(\theta)\sin(2\phi) \\ F_3 &= \sin^2(\theta)\sin(2\chi) \\ F_4 &= \tfrac{1}{2}[1+\cos^2(\theta)]\cos(2\phi)\cos(2\chi) - \cos(\theta)\sin(2\phi) \\ &\quad \times \sin(2\chi). \end{aligned} \tag{3}$$

These functions are related to Δ functions used by Mulder [18] by the normalization factor $\sqrt{(3)}/2$ as follows: $\Delta^2_{00} = F_1$, $\Delta^2_{02} = 0.5\sqrt{3}F_2$, $\Delta^2_{20} = 0.5\sqrt{3}F_3$, and $\Delta^2_{22} = F_4$.

The related free-energy density is given as

$$\frac{f_N}{kT} = \frac{f_I}{kT} + \rho\langle \hat{f}(\Omega)\log[8\pi^2\hat{f}(\Omega)]\rangle + \frac{\rho^2}{2kT}\langle W(\Omega)\hat{f}(\Omega)\rangle + \rho\log(\rho), \tag{4}$$

where ρ is the number density, f_I is the free-energy density of the isotropic case, and $\langle ... \rangle$ denotes the average $\int d\Omega(...)$. (Note that the last term with logarithm has not been explicitly given in Ref. [57], since it does not influence orientational parameters and, in practical calculation, is joined to the Lagrange multipliers that ensures normalization. It is crucial to write it explicitly, however, in the calculation of pressure, since it leads to the linear term in density that occurs in pressure.) This can be further cast as

$$\frac{f_N}{kT} = \frac{f_I}{kT} + \rho\langle \hat{f}(\Omega)\log[8\pi^2\hat{f}(\Omega)]\rangle + \frac{\rho^2}{2kT}(s_1 w_1 + s_2 w_2 + s_3 w_3 + s_4 w_4) + \rho\log(\rho), \tag{5}$$

where the scalar order parameters are the averages:

$$\begin{aligned} s_1 &= \langle F_1(\theta)\hat{f}(\Omega)\rangle \\ s_2 &= \langle F_2(\theta,\phi)\hat{f}(\Omega)\rangle \end{aligned}$$

$$s_3 = \langle F_3(\theta, \chi)\hat{f}(\Omega)\rangle$$
$$s_4 = \langle F_4(\theta, \phi, \chi)\hat{f}(\Omega)\rangle. \quad (6)$$

This is a general scheme of the mean-field approach and (6) is the set of the so-called self-consistency equations, which can be solved iteratively with respect to unknowns s_1, s_2, s_3, and s_4. These self-consistency equations are the result of the minimization of the free energy

$$\frac{\delta f_N}{\delta \hat{f}} = \lambda, \quad (7)$$

where λ is a Lagrange multiplier that ensures normalization $\langle \hat{f} \rangle = 1$ and δ denotes here functional derivative or, equivalently,

$$\frac{\partial f_N}{\partial s_i} = \lambda, \quad (8)$$

where the partial derivative ∂ is performed with respect to the (discrete) set of s_i.

A particular model is considered when we assume the order dependence of the mean-field potential and the interaction coefficients w_1, w_2, w_3, and w_4 as, for instance,

$$w_1 = w_{11}s_1 + w_{13}s_3$$
$$w_2 = w_{22}s_2 + w_{24}s_4$$
$$w_3 = w_{31}s_1 + w_{33}s_3$$
$$w_4 = w_{42}s_2 + w_{44}s_4. \quad (9)$$

[Note the difference in the notation with respect to Ref. [57]: We do not include the density in the definition of w_i, hence the term ρ^2 in Eq. (4) and ρ^3 in Eq. (18).]

In general, the coefficients w_{ij} are not independent. In a series of papers [6,18,25,29,30,57], where the mean-field approach has been used, they are calculated on the basis that the two particle interactions which is given by the formula of the following structure (in the formulation with the Mulder functions):

$$W^{\text{int}}(\tilde{\Omega}) = \alpha + \beta\Delta^2_{00}(\tilde{\Omega}) + \frac{2\tilde{\gamma}}{\sqrt{3}}\left[\Delta^2_{02}(\tilde{\Omega}) + \Delta^2_{20}(\tilde{\Omega})\right] + \delta\Delta^2_{22}(\tilde{\Omega}), \quad (10)$$

which depends on the relative angular position of the two bodies $\tilde{\Omega}$ (or, equivalently, on the set of the Euler angles transforming one particle molecular frame to the molecular frame of the other particle).

Using notation of Mulder [18],

$$W^{\text{int}}(\tilde{\Omega}) = \sum \frac{2l+1}{8\pi^2} W_{l,mn}\Delta^l_{mn}(\tilde{\Omega}), \quad (11)$$

and the property

$$\int W^{\text{int}}(\tilde{\Omega})\Delta^l_{mn}(\Omega_2)d\Omega_2 = \sum_p W_{l,np}\Delta^l_{mp}(\Omega_1), \quad (12)$$

it can be be deduced that

$$w_{11} = \beta \quad w_{13} = \tilde{\gamma}$$
$$w_{22} = 3\beta/4 \quad w_{24} = \tilde{\gamma}$$
$$w_{31} = \tilde{\gamma} \quad w_{33} = 3\delta/4$$
$$w_{42} = \tilde{\gamma} \quad w_{44} = \delta. \quad (13)$$

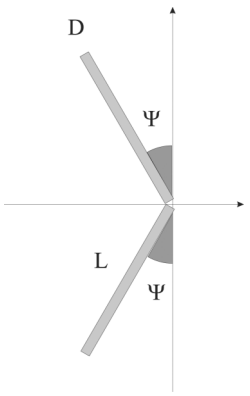

FIG. 1. Hard boomerang. The boomerang angle Ψ is defined here as the angle between the Z axis and the boomerang arms, when it is positioned symmetrically, and hence the apex angle between the boomerang arms is $\kappa = \pi - 2\Psi$. The length of the arm is L and the width is D.

Different models consider now different values of α, β, $\tilde{\gamma}$, and δ. Special attention [29,33] has been paid to the influence of the coefficient $\tilde{\gamma}$, which stands here for the strength of the coupling between molecular uniaxial and biaxial susceptibilities. These works, however, concentrate on the form of the possible phase diagram and do not focus on the orientational properties and order parameters.

B. Modified Teixeira-Masters-Mulder model

In order to study an influence of the coupling between molecular uniaxial and biaxial susceptibilities on the orientational properties of the boomerang systems, we have chosen the model from Ref. [57] as a springboard.

This model proposes coefficients α-δ with respect to the boomerangs made from two spherocylinders. For such particles the excluded volume can be obtained as the sum of two excluded volumes of constituent spherocylinders (boomerang's arms) for different relative orientations. The coefficients α-δ were deduced then by the use of the interpolation approximation.

In what follows we will be using the same coefficients as in Ref. [57], but with the γ coefficient systematically changing. It turns out that such changes have large implications.

Let us start from quoting formulas of α, β, $\tilde{\gamma}$, and δ for the boomerang system, which are our reference particles,

$$\alpha = 2DL^2\tfrac{2}{3}\left\{\left|\sin 2\Psi\right| + 4\left|\sin\left[\cos^{-1}\left(\tfrac{1}{2}\sin 2\Psi\right)\right]\right|\right\}$$
$$\beta = 2DL^2\left(\tfrac{4}{3}\left\{\left|\sin 2\Psi\right| + \left|\sin\left[\cos^{-1}\left(\tfrac{1}{2}\sin 2\Psi\right)\right]\right| - 1 - \left|\cos 2\Psi\right| - 2\left|\sin[\cos^{-1}(\sin^2\Psi)]\right|\right)$$
$$\tilde{\gamma} = 2DL^2\left\{\tfrac{1}{2} + \tfrac{1}{2}\left|\cos 2\Psi\right| - \left|\sin[\cos^{-1}(\sin^2\Psi)]\right|\right\}$$
$$\delta = 2DL^2\left\{1 + \left|\cos 2\Psi\right| + 2\left|\sin[\cos^{-1}(\sin^2\Psi)]\right| - 4\left|\sin\left[\cos^{-1}\left(\tfrac{1}{2}\sin 2\Psi\right)\right]\right|\right\}. \quad (14)$$

These coefficients are adjusted to the particles of the form given in Fig. 1. Here, the boomerang arms are of the same length L and of the width D. The angle Ψ, which is used in (14), is the angle between an arm and the vertical line. The

angle between the arms (the apex angle) is assumed as $\kappa = \pi - 2\Psi$.

C. Bifurcation point

By the use of the above formulas (14), one can provide an exact expression for the bifurcation point where the anisotropic solution occurs from the isotropic branch. The way how to calculate this expression has been given in detail in the already-mentioned paper of Mulder [18], where there is provided a basis of the biaxial nematic phase analysis within the density-functional approach and the corresponding bifuraction analysis. In general, bifurcation analysis is based on the free-energy functional, where the general form of the solution based on the basic symmetry adapted functions is introduced with respect to the lowest order and suitable for the expected symmetry. Such a choice is strictly valid close to the bifurcation point from the isotropic phase (or, in general, other phase from which the bifuraction occurs). The condition of the free-energy minimum provides then the equation whose solution corresponds to the bifuraction point. The benefit of the bifurcation analysis from the isotropic phase, where the distribution function is simple and known beforehand, is that the whole calculation can be done analytically and is free from any approximations. Then, once we know where the brench of anisotropic solutions can be found, a detailed analysis of the order parameters can be performed. Even if the model is of $L = 2$ interactions, the solution beyond the vicinity of the bifurcation point is of the form of exponential function with $L = 2$ terms in the exponent (1), so the analysis requires solving self-consistency equations emerging from the general condition for the free-energy minimum (8).

Using the expressions (14) and comparing it to the formalism of Mulder one can provide K interaction kernel coefficients, defined as in Ref. [18], which, subsequently, are needed to find the bifurcation point,

$$\begin{aligned} K^0_{00} &= 8\pi^2\alpha \\ K^2_{00} &= \frac{8\pi^2}{5}\beta \\ K^2_{02} = K^2_{20} &= \frac{16\pi^2}{5\sqrt{3}}\tilde{\gamma} \\ K^2_{22} &= \frac{8\pi^2}{5}\delta. \end{aligned} \tag{15}$$

In what follows we will be using the above model with possibility to change $\tilde{\gamma}$ as $\tilde{\gamma} = \gamma * \gamma_{PT}$, where γ is the fractional number and γ_{PT} is the Teixeira *et al.* model value as in (14).

The bifurcation point λ_0 (bifurcation density) due to Mulder is given due to the formulas (due to Ref. [18])

$$\kappa^* = \tfrac{1}{2}\left(K^2_{00} + K^2_{22}\right) - \sqrt{\left(K^2_{00} - K^2_{22}\right)^2 + 4K^2_{02}}, \tag{16}$$

$$\lambda_0 = -8\pi^2/\kappa^*. \tag{17}$$

D. Pressure and specific heat

In order to examine the type of the transition it can be useful to look at the behavior of the P-T equation of state, and specific heat at constant volume. The pressure can be calculated from the expression obtained on the basis of (4) and $\rho = N/V$ with V being volume:

$$\begin{aligned} \beta P &= -\frac{\partial(\beta f_N)}{\partial V} \\ &= \rho + \frac{\rho^2}{2kT}(s_1 w_1 + s_2 w_2 + s_3 w_3 + s_4 w_4), \end{aligned} \tag{18}$$

and the specific heat from the definition

$$C_V = -T\frac{\partial^2 f_N}{\partial T^2}. \tag{19}$$

III. STUDY OF BIAXIALITY IN THE BOOMERANG MEAN-FIELD SYSTEM

In this section order parameters will be presented for the boomerangs with length of the arms $L = 10.0$ and width $D = 0.00001$ (hence of the length to width ratio being of 10^6) and the density $\rho = 1.0$. We will start the discussion from the perfect boomerang system properties (as in Ref. [57]) (but with respect to *temperature changes*, not density), then we will study the cases, where the coefficient $\tilde{\gamma}$ is allowed to change.

To obtain the mentioned order parameters the self-consistency equations (7) have been solved for the model considered (1) by the use of an iterative manner with application of the 32 (2×16) point Gaussian quadratures for performing the integrals. The iteration has been stopped when the cumulative error *error* is less than 0.000001. The cumulative *error* is calculated as a sum of absolute values of differences between old and updated values of the distribution function $\hat{f}(\Omega)$ at each Gaussian point. Using absolute values is important because these differences may have different signs, just adding them may lead to spurious cancellations. Bifurcation analysis has been used prior to this calculation to find the range of the temperature, within which the anisotropic solution is present.

It should be noted that the bifurcation analysis can provide only the point (temperature) at which an anisotropic phase bifurcates from the isotropic solution for a given set of the symmetry adapted functions (like, for instance here, the Straley functions). It cannot provide the type of the solution. Since it is possible that different phases can be realized within the same set of the symmetry adapted function it is needed next to solve the above-mentioned self-consistency equations for a given type of the phase. To find a solution for a given type of the phase one has to use *any* form suitable for the desired phase as the starting point for the iteration process. After obtaining convergence the energy has to be calculated and, then, after examination of different phases and the corresponding energies, the one with the smallest value of the energy has to be chosen as the most stable solution. It can happen, however, that the same phase can have different representations according to the position of the coordinate system. For example, a truly uniaxial nematic phase, where only s_1 and s_3 are nonzero, if the coordinate system is rotated by 90°, then it can look at first glance as a biaxial solution with all $s_i's$ having nonzero values. That the phase is truly uniaxial it can be recognized due to the fact it will have the same energy as the solution with only nonzero s_1 and s_3. Also,

certain relations hold for the order parameters calculated in the coordinate systems that are rotated (see Ref. [18]).

Please note that in general the presented formalism with self-consistency equations (6) works as the mean-field theory as well as the Onsager theory of hard bodies. This is the fact that the relevant parameter here is ρ/kT. It is the matter of choice which interpretation is used. Here the inspiration of the interactions comes from the hard boomerangs, but then we allowed one of the interaction parameters to change, so, strictly speaking, the particles are not hard bodies. For this reason, in what follows we adopt the language of mean-field theory and use T as the control parameter. Using temperature as the control parameter will have, however, consequences on the behavior of energy and pressure versus this parameter. Here is the main difference between Onsager hard-body description and the mean-field approach—instead of ρ/kT as the single relevant parameter in the formulas for energy (5) and pressure (18) one needs to consider influence of the density and temperature separately.

A. Teixeira-Masters-Mulder boomerang model

In Fig. 2 a typical picture of the order parameters occurring in the mean-field approach is presented for different boomerang angles.

On diminishing temperature a first-order transition occurs at which s_1 sharply rises and increases its value on further cooling reaching the level of 1 for perfect alignment [Fig. 2(a)]. For boardlike particles (here $\Psi = 0.21\pi$ and $\Psi = 0.215\pi$) s_1 is negative and its extreme possible value is -0.5 (perfect planar alignment). Together with s_1 a nonzero value of s_3 (a parameter describing the influence of the molecular biaxiality on the uniaxial phase) occurs, yet its increase is not so severe, it reaches some maximum and then tends toward zero value [68]. On further cooling, at a certain value of s_1 and s_3 another transition takes place, which, due to the behavior of s_2 and $|s_4|$, is of the second-order type—these parameters rise continuously from the zero value. The obtained phase is of the biaxial symmetry.

The order of magnitude of values for temperature, pressure, and heat come here from the assumptions made in the considered model: the size of the objects or particles, the density, and the limitations of the second virial approach. Since the relevant parameter in the model is the ratio kT/ρ and we are interested only in the type of behavior of pressure and energy, we have used a simplified assumption of $\rho = 1$. Note also that the assumption of the second virial approach influences strongly the value of the kT/ρ at which the phase transitions occur. Usually, to improve such predictions, additional scalings, such as, for instance, Parsons Lee scaling, are used. Correspondence of the outcome of the considered model to real systems would require additional modelling and is foreseen for future research work.

In the case of s_1 (the average of the second Legendre polynomial) an interesting property has been observed within the range of the biaxial phase. The derivative of s_1 (Fig. 3) clearly exhibits a linear character which indicates that s_1 itself is the square function of the temperature. This property holds only for the rodlike system.

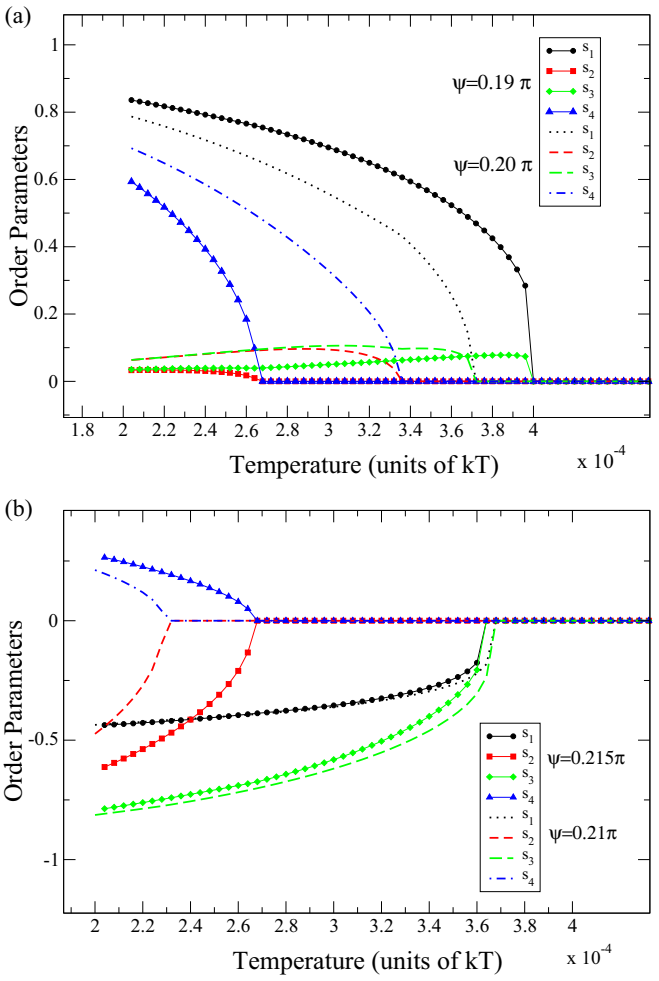

FIG. 2. Order parameters s_1, s_2, s_3, and s_4 for the phases of the boomerang particles of different boomerang angle Ψ, where the transition to the uniaxial phase is of the first order. The closest to the Landau point ($\Psi = 0.2017835\pi$) results, where the transition to the uniaxial phase becomes of the second order, are for ($\Psi = 0.20\pi$). Panel (a) shows rodlike boomerangs case and panel (b) shows boardlike case.

The equation of state (βP versus temperature) is presented in Fig. 4. The apparent changes at the uniaxial-biaxial transitions are well visible—the curves change their slopes, with the change the more pronounced the further system is from the Landau point. At the isotropic phase βP is equal to ρ [according to (18)]; in our case it is assumed $\rho = 1$.

It is important to discuss the fact that the excess pressure obtained for the Teixeira-Masters-Mulder model and its modifications at some temperatures attains negative values. For the density $\rho = 1.0$ in most cases this happens already within the uniaxial phase. The transition to the biaxial phase only in the vicinity of the Landau point occurs with the positive values of the pressure. This scenario can completely change if the isotropic contribution f_I is concerned. Modeling this contribution is, however, beyond the scope of the discussed Teixeira-Masters-Mulder model and its modifications. Putting smaller values of ρ will shift pressure values to the region of positive values but still some parts of the pressure will be negative. It has been checked that this situation is a peculiarity

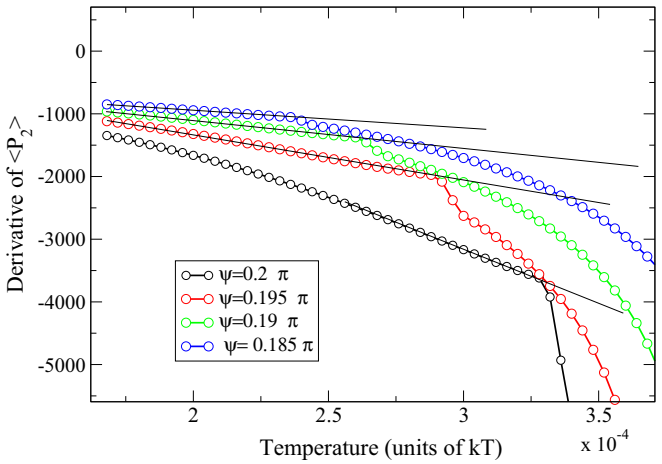

FIG. 3. Derivative of the order parameter $s_1 = \langle P_2 \rangle$ versus temperature. In the biaxial phase its linear character shows that s_1 is of the square type for any boomerang angle in the case when the particles are rodlike.

of the assumed banana model and occurs in the formulation of the mean-field type representation as well as in the Onsager hard-body representation.

More details are available from the analysis of the specific heats. Two major features can be distinguished here: At the uniaxial-biaxial transition one observes a jump in the values whereas at the isotropic-uniaxial transition these properties at first sight can be judged as divergent (within the limits of the accuracy of performing numerical derivatives). To prove exactly that these values are divergent requires, however, a separate mathematical consideration. What is apparent from the present results is an increase of the specific heat with increasing temperature and then at the nematic-isotropic transition a sudden jump. Another possible scenario (and maybe more convincing) is that the above-mentioned increase is finite, ending at the discontinuous maximum, which lowers

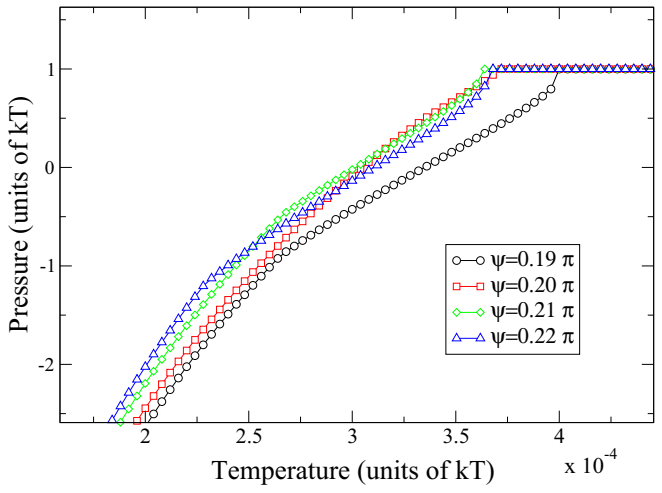

FIG. 4. P-T equation of state. (The excess pressure βP versus temperature.) The curve with squares is the closest to the Landau point, which occurs for $\Psi = 0.2017835\pi$. Note the smoothness of this curve in the mesogenic region in comparison to the other profiles. The negative values come here from the fact that the presented results are for the excess pressure relative to the isotropic phase.

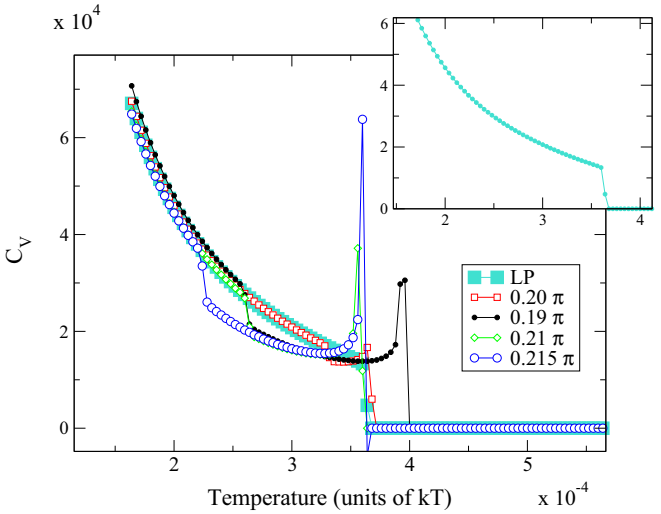

FIG. 5. The specific heat according to (19) for the standard boomerang case. LP denotes the boomerang angle corresponding to the Landau point, for which the specific heat is given also in the inset.

the more close the system geometry is to the Landau point. On approaching the Landau point this effect weakens (see the curves for $\Psi = 0.2\pi$), and at the Landau point no increase is observed (in detail it is given in the inset of Fig. 5.

Based on these specific heat characteristics, one obtains information about how they behave at the first and at the second-order transitions: In the case of the second-order transition one deals with a discontinuous jumps on the monotonically changing profiles. In the case of the first-order transition one gets, besides discontinuous changes, a local maximum—the higher the stronger character of the first order. Within the biaxial phase all the profiles of the equations of state are very similar, regardless the shape of the boomerang, remaining at the same level. A jump at the uniaxial biaxial transition indicates also that it belongs to the weak second-order transition types. The larger values of the specific heat in the biaxial phase with respect to the uniaxial phase are connected to the fact that in the biaxial phase an additional degree of orientational order consumes an additional part of energy.

The above-mentioned picture has been obtained under assumption that the density is simply 1 and the transitions occur due to the changes of temperature (similarly as in the mean-field Mayer Saupe approach). This assumption holds throughout the rest of our consideration, yet one should pay attention to an unphysical effect it produces. In Fig. 4 the results obtained for pressure very quickly enter the region with negative values. It does not influence subsequent considerations on the slope of the curves and the behavior of specific heats we are interested in. This equation of state (and subsequent, too) come from the theory that is based only on the orientational contribution to the free energy. Adding a pressure part emerging from the isotropic free energy it will shift up all the pressure curves.

The positive pressure values within the region where the biaxial and uniaxial phases are encountered can be obtained also by diminishing value of the density. Smaller densities not only push the transition points to smaller temperatures but also

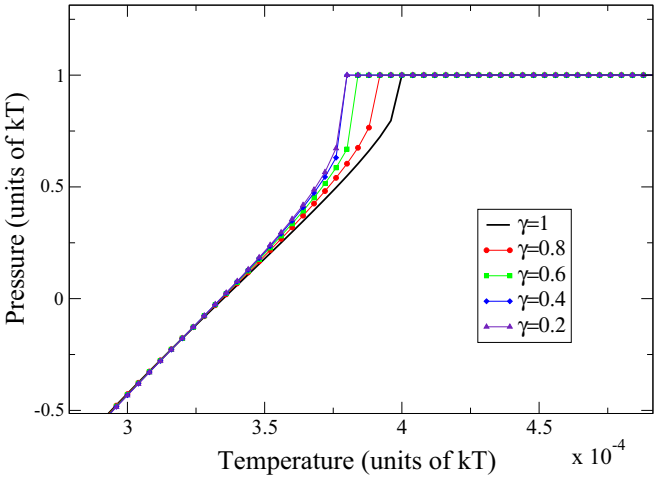

FIG. 6. *P-T* equation of state for different γ values and the boomerang angle $\Psi = 0.19\pi$.

drive the whole pressure curves in anisotropic regions to larger values.

B. The case with diminished coupling between molecular uniaxial and biaxial susceptibilities for the rodlike boomerangs

In Fig. 6 the equation of state is presented for the boomerang angle $\Psi = 0.19\pi$ and for different values of the γ coefficient, where γ is the fraction of the coefficient $\tilde{\gamma}$ from (14).

This case corresponds to the rodlike particles. Even in the uniaxial phase (the temperature range used in Fig. 6 corresponds only to this phase) the pressure profiles besides the small region close to the isotropic-uniaxial transition coincide revealing that γ has no much influence on the pressure.

Smaller values of γ push the transition temperatures toward smaller values, as well for IU as for UB transitions. Figure 7 shows also an increase of the profiles with diminishing of γ, especially on the approach of the transition points from the side of the anisotropic phases. The jump in the specific heat at UB point becomes larger with smaller γ.

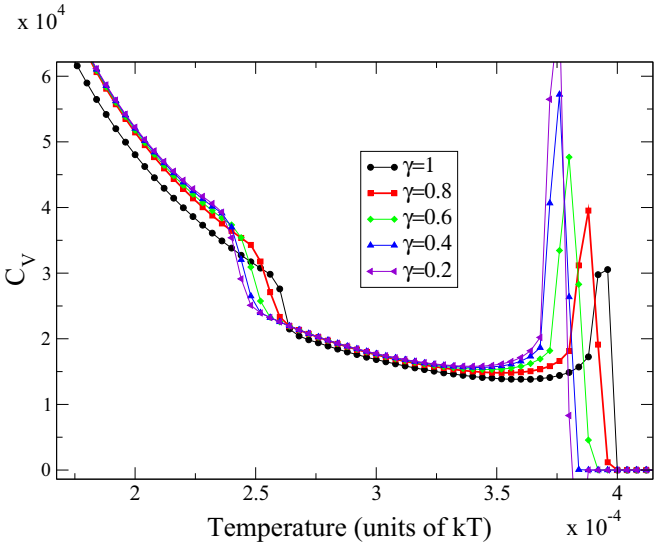

FIG. 7. The specific heat according to (19) for different γ values and the boomerang angle $\Psi = 0.19\pi$.

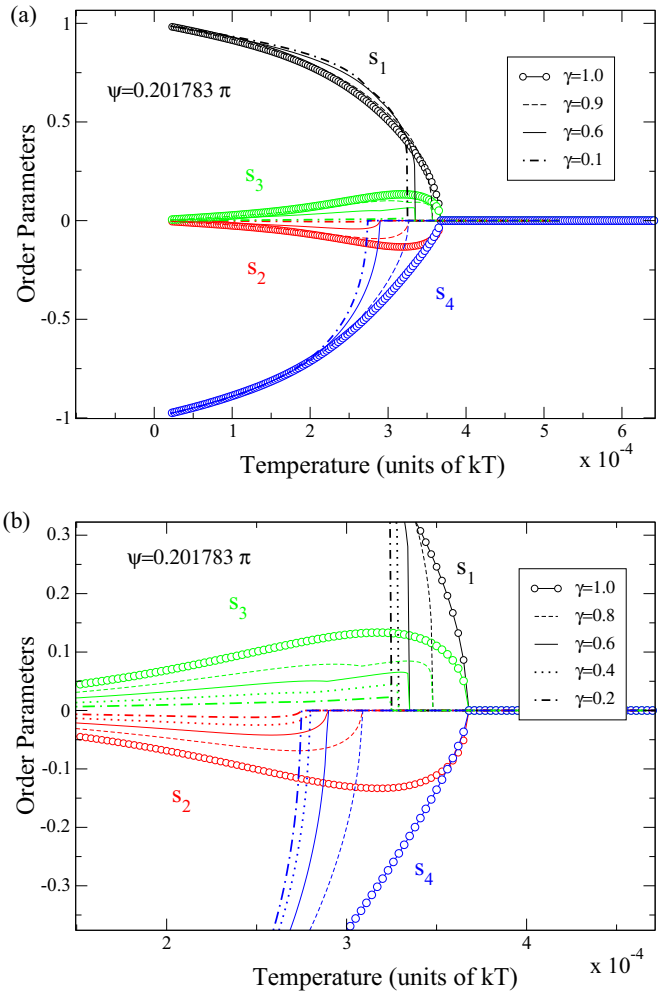

FIG. 8. Order parameters s_1, s_2, s_3, and s_4 versus the reduced temperature for the boomerang angle $\Psi = 0.201783\pi$, (the Landau point) (a) and the magnified view (b) for different values of γ.

C. The case of the diminished coupling for the boomerang angle corresponding to the Landau point.

At the Landau point (for the studied case given by the boomerang angle $\Psi = 0.201783\pi$ or by the apex angle $\kappa = 107.38^\circ$), the situation with the order parameters profiles becomes completely different from the ones presented in Fig. 2. In Fig. 8(a) the typical behavior of the Straley order parameters are shown on the chosen values of the coefficient γ obtained from the solution of the self-consistency equation. Thanks to the normalization of the Straley functions this picture is quite symmetric versus the 0 level. For $\gamma = 1$ all four order parameters rise straight at the bifurcation point with s_1 and $|s_4|$, increasing their values on cooling reaching the level of 1 for perfect alignment and s_2 and $|s_3|$, after initial rise and reaching relatively small maximum, diminishing and approaching zero [68]. Diminishing the value of γ one obtains the case with uniaxial order separating the isotropic and

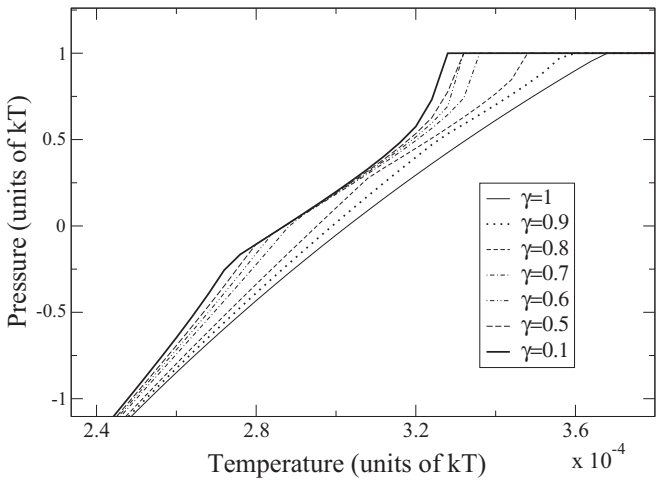

FIG. 9. *P-T* equation of state for the boomerang angle corresponding to the Landau point for perfect boomerang and by adding influence of the γ coefficient

biaxial solution with the region of uniaxiality enlarging on diminishing γ and s_2 and $|s_3|$ also diminishing their values and finally disappearing. Note that by changing the value of γ, our system is no longer at the Landau point and we use this notation only as to define the starting reference geometry.

In Fig. 8(b) the details of these order parameters profiles are given. The apparent regular and smooth behavior of s_2, whose nonzero value occurs in the biaxial phase, is connected with the second order of the phase transition from the uniaxial to biaxial phase. Contrary to this is the behavior of the parameter s_1 and the molecular biaxiality order parameter s_3. The first-order character of s_1 and s_3 at the I-NU transition is a typical feature and so is a slight discontinuity of the s_3 slope at the UN-BN transition. On diminishing γ the first-orderness of I-UN transition seems to increase. This fact suggest that the molecules may become less biaxial with diminished γ.

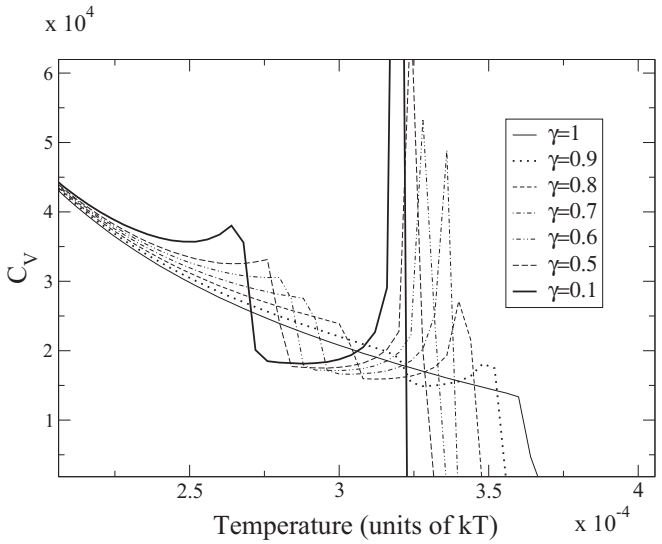

FIG. 10. The specific heat according to (19) for different γ values and the boomerang angle 0.20178π. The visible change of the slope character at NU-NB transition indicates that this phase transition becomes weakly of the first order for $\gamma < 0.8$.

This conclusion is in accordance with Tjipto-Margo *et al.* [69] findings that first-orderness of the I-UN transition is greatly reduced if the particles are made (more) biaxial.

In Fig. 9 the pressure profile versus temperature (the *P-T* equation of state) has been presented for the case where the apex angle corresponds to the Landau point and, then, subsequent changes to this profile caused by diminishing of the γ parameter. For the biaxial phase that directly enters the isotropic phase at the Landau point, the pressure profile is a monotonically decreasing function. At the point of the phase transitions the pressure profile visibly changes its character, for the isotropic-uniaxial nematic as well as for the uniaxial-biaxial nematic transition. It is also interesting to observe that within unixial regions the pressures with diminished γ quickly "coalesce" to the limiting case when $\gamma = 0$.

The evolution of temperature dependence of the specific heat over the changes of γ is given in Fig. 10. For $\gamma = 1$ the studied phase is perfectly biaxial (the Landau point where biaxial phase bifurcates from isotropic phase) and theses profiles are smooth functions bending abruptly at the IB transition. On changing values of γ a uniaxial phase comes

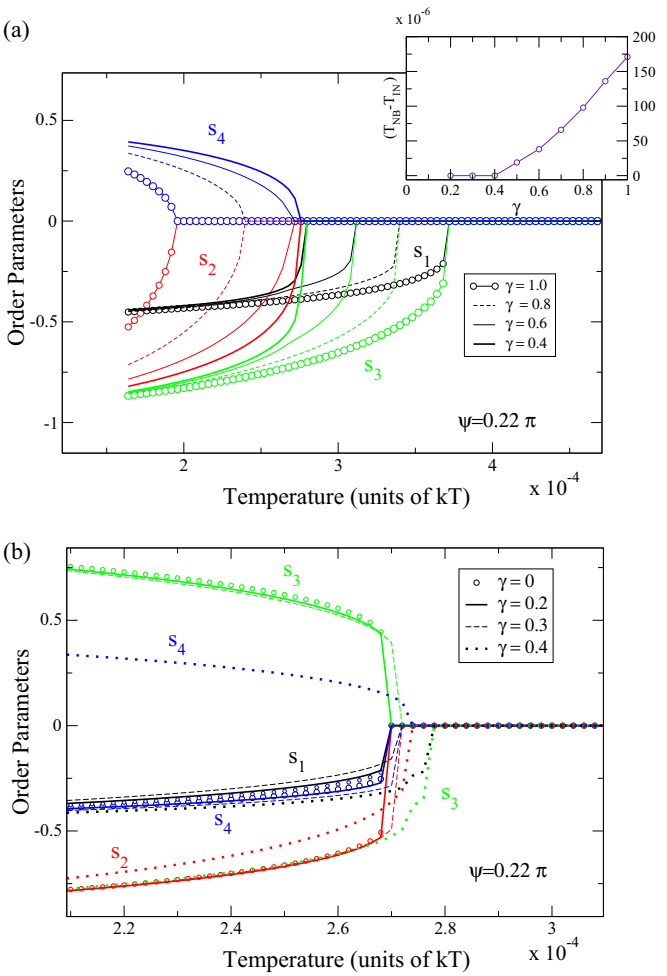

FIG. 11. Order parameters s_1, s_2, s_3, and s_4 for the boomerang angle $\Psi = 0.22\pi$ (the apex angle 100.8°). (a) order parameters for larger values of γ's where the type of ordering is like for $\gamma = 1$ (b) order parameters for smaller values of γ's with a new type of ordering for particles arrangement as proposed in Fig. 12.

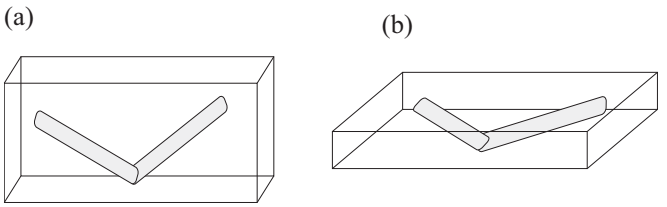

FIG. 12. An idea for the possible arrangement of boomerangs in the planar phase. Long axes are distributed in the plane, whereas the short axes can placed in two possible ways leading to the change of their order parameters sign.

to presence. Also the profiles of the specific heat exhibit characteristic changes at the point of the phase transitions. In the vicinity of the UB transition they form flat ledges while close to the IU transition they form a sharp maximum.

It is also very interesting to observe that the height of the peak close to the IU transition for $\gamma = 0.9$ is comparable to the cases with $\gamma < 0.7$ for the biaxial solutions close to the UB transition. Despite the fact that this effect is influenced by numerical calculation of derivatives, the existence of local maximum at the transition point in the mean-field models is recognized as the symptom of the transition being of the *first order*, although, here for UB, very weakly first order.

D. The diminished coupling in the system with the strong boomerang shape particles

In Figs. 11(a) and 11(b), the orientational order parameters profiles are given for the platelike system.

Figure 11(a) shows the behavior for the case when the scenario I-NU-NB holds. In uniaxial nematic s_1 and s_3 are nonzero. Since the phase is of the oblate symmetry their values are negative. On the transition to the biaxial phase the parameters s_2 and s_4 comes to play rising continuously from zero with s_2 being negative and s_4 taking on positive values. This scenario holds for $\gamma > 0.4$.

For $\gamma < 0.4$, see Fig. 11(b), the uniaxial phase is no longer present. After disappearing of the uniaxial phase one deals with a direct transition from the isotropic phase into the biaxial phase, see Fig. 11(a). The question is now what is the order of this transition. In Fig. 11(b) one observes a clear abrupt changes of the order parameters, which indicate the first orderness. For $\gamma = 0.4$ we still observe a small region of the uniaxial phase. This branch has been put here for purpose to show the change of sign in s_3 and s_4 on entering the the region where I-BN is present. Because of this sign changes, we conclude that the possible arrangement in this biaxial phase is like in Fig. 12(a). s_1 is here still negative and shows planar order with long axis of the boomerang lying in the plane, but secondary axes of the boomerang changed their position of 90°. What is the molecular mechanism of such an arrangement would be still an open question. One of the ideas would be that the arms of the boomerang may exhibit different flexibilities, also with respect to the direction of the arms possible movements. Another possibility of mechanisms is the tailored or directional interaction between arms. The boardlike character of the arms themselves may explain such an arrangement.

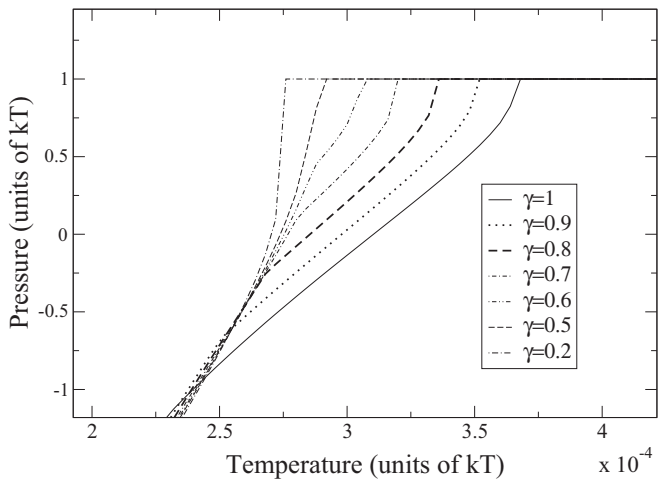

FIG. 13. *P-T* equation of state for the boomerang angle 0.215π with different γ coefficients.

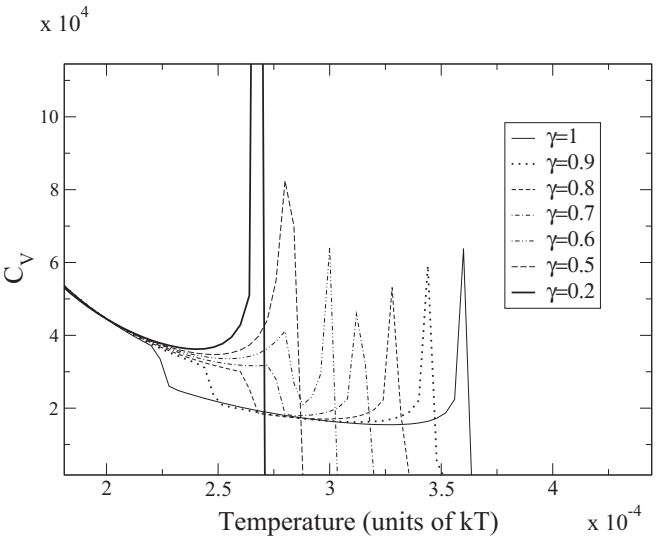

FIG. 14. The specific heat according to (19) for different γ values and the boomerang angle 0.215π.

An example of the equation of state for the considered platelike case is presented in Fig. 13. The changes are mostly visible close to the IU transition. The profiles of the pressure become steeper with diminishing of γ.

The details are revealed in Fig. 14. On diminishing γ the two transition become closer with an apparent rise of the biaxial branch in the vicinity of the transition. For $\gamma = 0.7$ the peaks seem to be at the same level. Even though this is a numerical derivation result the general conclusion emerges: The uniaxial biaxial transition is of the first type, yet very weak. For $\gamma = 0.5$ the two peaks coalesce into one very steep maximum. One deals with a direct transition from the isotropic into biaxial phase.

IV. DISCUSSION ON THE POSSIBLE REALIZATION OF THE INVESTIGATED CASE.

In order to observe a stable thermotropic biaxial phase it is crucial to create attractive molecules, which, at best, would

give rise to a direct isotropic-to-biaxial transition. One of the examples that has turned out very successful in foreseeing the biaxial phase was the proposition of making V-shaped molecules from two identical rodlike components. In Ref. [57] this result has been realized, for instance, by adjusting the Straley L2 mean-field potential to the boomerang structure, yet the formula used was general with its quadrupolar character allowing for application to a wider range of LC molecules. The considered in this paper case extends the model from Ref. [57] by allowing γ coefficient to change its values. In accordance to the results from Ref. [29], diminishing γ to zero value is a legitimate procedure. The most characteristic result obtained while investigated models with diminished γ was the transition from uniaxial (see Fig. 10) to the biaxial phase which is weakly of the first order. Such a feature has been indeed observed in the experiment, not in the case of boomerangs but instead of the tetrapode molecules. The experimentally studied tetrapodes are in principle molecules in which four mesogenic groups are tethered laterally to a single silicon atom [16,17] or to a single germanium atom [15]. In both cases, in the first by infrared spectroscopy measurements [16,17] and in the second by light scattering studies [15], it has been found that a weakly first-order NB-NU transition is possible. Moreover, in Ref. [15] also the IU transition is claimed as weakly first order. The authors conclude this on the basis of considerations performed within the framework of the Landau theory. In contrast to the conclusions from Ref. [15], in our studies the IU transition is strongly of the first order.

Microscopic approaches as compared to the so far undertaken Landau theories contain all the contributions to the uniaxial biaxial transition within the limit of $L = 2$ models, and hence they are more trustworthy. The difficulty is that the most decisive factors as far as the transition order is concerned are the order parameters and their discontinuities, whose behavior in case of weak first-order transition can be blurred by numerical errors in solving the self-consistency equation and numerical integrations. Here we provide additional feature whose observation can be helpful in distinguishing the type of the transition order. In the case of the first-order transition the second derivatives of the free energy (as, for instance, specific heats) exhibit a characteristic behavior—on approaching the transition point, where the profiles become discontinuous, they are ascending functions, whereas in the case of the second-order transition they still maintain a descending character. Hence on changing the type of the transition order the third derivative of the energy also changes the sign. Please remember that in real systems where fluctuations dictate the type of behavior the situation can be completely different (as is the case with critical exponents).

Although tetrapode molecules seem to be the closest to the considered case (because of the first-order UB transition) there is an intriguing feature that excludes them from being ideal candidates. In Ref. [38] the authors paid attention to the inversion in magnitude of order parameters that occurs while comparing experimental data to the theoretical outcome within the biaxial phase. In the uniaxial phase of rodlike systems the largest is the principal parameter $\langle P_2 \rangle$ and the molecular biaxiality parameter is very small—this observation was the same in experiment as well as in theory. The same situation occurs in the theories of the biaxial phase—the parameter bound to the molecular biaxiality is smaller. However, in the case of studied real tetrapodes in the biaxial phase there is an unexplained so far disagreement observed. In the experimental results the order parameter corresponding to the molecular biaxiality is larger. Such inversion is present if one examines boardlike particles and their order (see, for instance, the result presented in Fig. 2). In view of this one can conclude that the mentioned tertrapodes seem to behave like rods in the uniaxial phase and like boards in the biaxial phase. Such a conclusion is also in line with Teixeira and Masters's results [70]. Nevertheless, besides intriguing similarities of the current model features with the tetrapode systems properties, one should bear in mind that the genuine tetrapode molecule theory requires higher-order terms [71].

Another interesting result, besides the UB transition being of the first order, is a new arrangement like in Fig. 12(a). From this picture it is clear that such an arrangement can be induced by enhancing attractive forces when the particles are side by side. Note that coupling of the interactions strength with particles orientations is not a new idea—it naturally occurs, for instance, in the case of the Gay Berne potential, where the depth of the interaction potential depends on the mutual orientations of the particles.

At the end it is important also to repeat that the presented analysis has been done with restriction to $L = 2$ model and order parameters of the second order. Recently, it has been shown, however, that inclusion of higher-order terms may lead to a new phase occurrence [39]. In particular, the phase with fourfold rotational symmetry has been found in the system of hard colloidal boomerangs of the particular apex angle $\kappa = \pi/2$. This value, however, is far from the Landau point vicinity the current paper is focused on. In Ref. [39] the authors have also shown that the region of biaxial phase significantly reduces for the benefit of the prolate phase on introducing some flexibility of stiff arms connection. This is an example how tailoring interactions can change the system properties and how important is to understand the factors that influence biaxiality. In contrast to the results from Ref. [39], it would be more desired, however, to expand the scope of biaxial phase instead of its shrinkage. It is still an open question how to tailor interactions which could induce widening of the biaxial phase region. More work is still needed in this area.

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[1] P. I. C. Teixeira, M. A. Osipov, and G. R. Luckhurst, Phys. Rev. E **73**, 061708 (2006).
[2] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
[3] W. Maier and A. Saupe, Z. Naturforsch. **13**, 564 (1958).
[4] M. J. Freiser, Mol. Cryst. Liq. Cryst. **14**, 165 (1971).
[5] R. Alben, Phys. Rev. Lett. **30**, 778 (1973).

[6] J. P. Straley, Phys. Rev. A **10**, 1881 (1974).
[7] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).
[8] K. Severing and K. Saalwachter, Phys. Rev. Lett. **92**, 125501 (2004).
[9] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett. **92**, 145505 (2004).
[10] B. R. Acharya, A. Primak, and S. Kumar, Phys. Rev. Lett. **92**, 145506 (2004).
[11] O. Francescangeli, V. Stanic, S. I. Torgova, A. Strigazzi, N. Scaramuzza, C. Ferrero, I. P. Dolbnya, T. M. Weiss, R. Berardi, L. Muccioli, S. Orlandi, and C. Zannoni, Adv. Funct. Mater. **19**, 2592 (2009).
[12] J. A. Olivares, S. Stojadinovic, T. Dingemans, S. Sprunt, and A. Jakli, Phys. Rev. E **68**, 041704 (2003).
[13] S. D. Peroukidis, P. K. Karahaliou, A. G. Vanakaras, and D. J. Photinos, Liq. Cryst. **36**, 727 (2009).
[14] M. Lehmann, S.-W. Kang, C. Köhn, S. Haseloh, U. Kolb, D. Schollmeyer, Q. Wang, and S. Kumare, J. Mater. Chem. **16**, 4326 (2006).
[15] K. Neupane, S. W. Kang, S. Sharma, D. Carney, T. Meyer, G. H. Mehl, D. W. Allender, Satyendra Kumar, and S. Sprunt, Phys. Rev. Lett. **97**, 207802 (2006).
[16] K. Merkel, A. Kocot, J. K. Vij, R. Korlacki, G. H. Mehl, and T. Meyer, Phys. Rev. Lett. **93**, 237801 (2004).
[17] J. L. Figueirinhas, C. Cruz, D. Filip, G. Feio, A. C. Ribeiro, Y. Frere, T. Meyer, and G. H. Mehl, Phys. Rev. Lett. **94**, 107802 (2005).
[18] B. Mulder, Phys. Rev. A **39**, 360 (1989); B. Groh and B. Mulder, Phys. Rev. E **59**, 5613 (1999).
[19] D. W. Allender and M. A. Lee, Mol. Cryst. Liq. Cryst. **110**, 331 (1984).
[20] M. C. J. M. Vissenberg, S. Stallinga, and G. Vertogen, Phys. Rev. E **55**, 4367 (1997).
[21] P. K. Mukherjee, Liq. Cryst. **24**, 519 (1998).
[22] P. Biscari, M. C. Calderer, and E. M. Terentjev, Phys. Rev. E **75**, 051707 (2007).
[23] G. De Matties, A. M. Sonnet, and E. G. Virga, Contin. Mech. Thermodyn. **20**, 347 (2008).
[24] D. Allender and L. Longa, Phys. Rev. E **78**, 011704 (2008).
[25] G. R. Luckhurst, C. Zannoni, P. L. Nordio, and U. Segre, Mol. Phys. **30**, 1345 (1975).
[26] B. M. Mulder, Liq. Cryst. **1**, 539 (1986).
[27] P. Palffy-Muhoray and B. Bergersen, Phys. Rev. A **35**, 2704 (1987).
[28] P. Palffy-Muhoray, Am. J. Phys. **70**, 433 (2002).
[29] A. M. Sonnet, E. G. Virga, and G. E. Durand, Phys. Rev. E **67**, 061701 (2003).
[30] L. Longa, P. Grzybowski, S. Romano, and E. G. Virga, Phys. Rev. E **71**, 051714 (2005).
[31] L. Longa, P. Grzybowski, S. Romano, and E. Virga, Phys. Rev. E **73**, 019904(E) (2006).
[32] L. Longa and G. Pajak, Liq. Cryst. **32**, 1409 (2005).
[33] F. Bisi, E. G. Virga, E. C. Gartland, Jr., G. De Matteis, A. M. Sonnet, and G. E. Durand, Phys. Rev. E **73**, 051709 (2006).
[34] A. M. Sonnet and E. G. Virga, Phys. Rev. E **77**, 031704 (2008).
[35] X. Zheng and P. Palffy-Muhoray, Discr. Contin. Dynam. Syst. B **15**, 475 (2011).
[36] A. Vaghela, P. I. C. Teixeira, and E. M. Terentjev, Phys. Rev. E **96**, 042703 (2017).
[37] P. Karbowniczek, M. Cieśla, L. Longa, and A. Chrzanowska, Liq. Cryst. **44**, 254 (2017).
[38] F. Bisi, G. R. Luckhurst, and E. G. Virga, Phys. Rev. E **78**, 021710 (2008).
[39] T. Drwenski and R. Van Roij, Mol. Phys. **116**, 2812 (2018).
[40] C. S. Shih and R. Alben, J. Chem. Phys. **57**, 3055 (1972).
[41] G. R. Luckhurst and S. Romano, Mol. Phys. **40**, 129 (1980).
[42] G. De Matteis, S. Romano, and E. G. Virga, Phys. Rev. E **72**, 041706 (2005).
[43] F. Biscarini, C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni, Phys. Rev. Lett. **75**, 1803 (1995).
[44] S. Sarman, J. Chem. Phys. **104**, 342 (1996).
[45] P. J. Camp and M. P. Allen, J. Chem. Phys. **106**, 6681 (1997).
[46] C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni, Int. J. Mod. Phys. C **10**, 469 (1999).
[47] R. Berardi and C. Zannoni, J. Chem. Phys. **113**, 5971 (2000).
[48] G. R. Luckhurst, Thin Solid Films **393**, 40 (2001).
[49] S. J. Johnston, R. J. Low, and M. P. Neal, Phys. Rev. E **66**, 061702 (2002).
[50] S. J. Johnston, R. J. Low, and M. P. Neal, Phys. Rev. E **65**, 051706 (2002).
[51] R. Memmer, Liq. Cryst. **29**, 483 (2002).
[52] S. Orlandi, R. Berardi, J. Steltzer, and C. Zannoni, J. Chem. Phys. **124**, 124907 (2006).
[53] M. A. Bates, Phys. Rev. E **74**, 061702 (2006).
[54] M. A. Bates, Chem. Phys. Lett. **437**, 189 (2007).
[55] M. A. Bates and G. R. Luckhurst, Phys. Rev. E **72**, 051702 (2005).
[56] A. G. Vanakaras, M. A. Bates, and D. J. Photinos, Phys. Chem. Chem. Phys. **5**, 3700 (2003).
[57] P. I. C. Teixeira, A. Masters, and B. Mulder, Mol. Cryst. Liq. Cryst. **323**, 167 (1998).
[58] P. J. Camp, M. P. Allen, and A. J. Masters, J. Chem. Phys. **111**, 9871 (1999).
[59] H. Takezoe and Y. Takanishi, Jpn. J. App. Phys. **45**, 597 (2006).
[60] P. Grzybowski and L. Longa, Phys. Rev. Lett. **107**, 027802 (2011).
[61] P. Palffy-Muhoray, J. J. De Bruyn, and D. A. Dunmur, Mol. Cryst. Liq. Cryst. **127**, 301 (1985).
[62] A. Chrzanowska, Phys. Rev. E **58**, 3229 (1998).
[63] A. Cuetos, A. Galindo, and G. Jackson, Phys. Rev. Lett. **101**, 237802 (2008).
[64] R. Berardi and C. Zannoni, Soft Matter **8**, 2017 (2012).
[65] E. F. Henriques and S. R. Salinas, Eur. Phys. J. E **35**, 14 (2012).
[66] A. Chrzanowska, Z. Naturforsch. A **45**, 783 (1990).
[67] L. Longa, G. Pająk, and T. Wydro, Phys. Rev. E **79**, 040701(R) (2009).
[68] M. A. Osipov, T. J. Sluckin and E. M. Terentjev, Liq. Cryst. **19**, 197 (1995).
[69] B. Tjipto-Margo and G. T. Evans, J. Chem. Phys. **94**, 4546 (1991).
[70] P. I. C. Teixeira and A. J. Masters, Phys. Rev. E **92**, 062506 (2015).
[71] R. Blaak, B. Mulder, and D. Frenkel, J. Chem. Phys. **120**, 5486 (2004).