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Phase behavior of the thermotropic melt of asymmetric V-shaped molecules

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The phase behavior of the monodisperse melt of V-shaped molecules composed of two rigid segments of different lengths joined at their ends at an external angle α has been examined within the Landau–de Gennes approach. Each rigid segment consists of a sequence of monomer units; the anisotropic interactions in the system are assumed to be of the Maier-Saupe form. The coefficients of the Landau–de Gennes free-energy expansion have been found from a microscopic model of V-shaped molecule. A single Landau point at which the system undergoes direct continuous transition from isotropic to biaxial nematic phase is found for asymmetry parameter $\phi = 1/3$ or $\phi = 2/3$, where ϕ is the number fraction of monomer units in one of the segments. Two Landau points are found in a range $1/3 < \phi < 2/3$. Only isotropic and nematic states are found to be stable for $0 \leqslant \phi < 1/3$ and $2/3 < \phi \leqslant 1$. Regions of stability of isotropic, prolate uniaxial, and biaxial nematic phases are found for $\phi = 1/3$ and $\phi = 2/3$. In addition, a stable oblate uniaxial phase is revealed if asymmetry parameter falls in the range $1/3 < \phi < 2/3$. The region of stability of the biaxial nematic phase becomes smaller as parameter ϕ increases from $1/3$ to $1/2$ (or decreases from $2/3$ to $1/2$). Coefficients of the gradient terms have been found; for certain values of asymmetry parameter these coefficients can become negative in some ranges of angles.

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I. INTRODUCTION

The systems of V-shaped (bent-core, banana-like) compounds [1–3] have recently attracted considerable attention because they exhibit a number of diverse phenomena, including ferroelectric liquid crystalline phases [4], giant flexoelectric effect [5], strong Cotton–Mouton effect [6]. Furthermore, there are experimental evidences of formation of thermotropic biaxial nematic phase [7–11] in systems of such molecules, although some studies [12–14] indicate that the macroscopic biaxial nematic phase still remains elusive. The biaxial nematic phase, predicted by Freiser [15] in 1970, is of significant interest, in particular, for development of electro-optical devices [16–18].

The phase behavior of thermotropic melts of V-shaped molecules has been extensively studied both by theoretical methods [1,19–27] and simulations [20,28–34]. Teixeira *et al.* [19] were apparently the first to consider the phase behavior of V-shaped molecules composed of two hard spherocylinders of length L and diameter D joined at an external angle α by their ends. Having found the approximate analytical expression for a second virial coefficient, they predicted within the Onsager theory the stability of prolate uniaxial (N_U^+), oblate uniaxial (N_U^-), and biaxial (N_B) nematic phases as well as direct isotropic-biaxial (I-N_B) transition at the Landau point for $\pi - \alpha \approx 107.36^\circ$ for aspect ratio $L/D \to \infty$. The stable phases revealed in Ref. [19] were found to be in agreement with those established before for the biaxial particles of other types, such as spheroplatelets [35] and ellipsoids [36]. Camp *et al.* [20] calculated numerically a third-order virial coefficient for the model of Ref. [19] and reported that allowance for this coefficient results in decrease of angle value at the Landau point; however, it was found that even for $L/D = 10$ ratio more virial coefficients of higher orders are required for accurate description of the phase transition in this system since packing fraction was found to be unphysically high. Luckhurst [21] applied a molecular field theory to describe phase behavior of the symmetric V-shaped molecules and found regions of stability of isotropic, uniaxial nematic, and biaxial nematic phases. The value of angle between arms of V-shaped molecule at the Landau point has been found to be equal to $\psi = \arccos(-1/3) \approx 109.47^\circ$. Mettout *et al.* [23] have used an expansion of the orientational distribution function by the Wigner rotational matrices to describe the phase behavior of the molecules of C_s symmetry; the coefficients of this expansion are the components of order parameter tensors. Based on the phenomenological Landau theory they have predicted the formation of a polar uniaxial nematic phase of $C_{\infty v}$ symmetry as well as polar biaxial nematic phase with C_s symmetry. Lubensky and Radzihovsky [24] indicated that vector and third-rank traceless symmetric tensor-order parameters are required in addition to the traditional nematic tensor-order parameter [37] to distinguish between various liquid crystal phases that could be formed by V-shaped molecules, including uniaxial and biaxial polar nematics as well as phases with tetrahedratic symmetry. The additional order parameters proposed in Ref. [24] are essential for the description of the ordered chiral phases with point group symmetries D_2 and C_2. The approach proposed in Ref. [23] has been extended by Mettout [25] to construct a phenomenological theory of V-shaped molecules based on use of two second-rank order parameter tensor; the formation of the biaxial nematic phase with C_{2h} point group symmetry has been predicted.

No stable biaxial nematic phase was found in extensive off-lattice Monte Carlo simulations of systems of V-shaped particles that modeled by the hard spherocylinders [20,30], Gay-Berne particles with fixed [28,29] and fluctuating [38]

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angle between particles, soft spheres [22], and rigidly connected Lennard–Jones spheres [31]. Later, the isotropic, uniaxial nematic, biaxial nematic, and biaxial antiferroelectric hexagonal crystal phases have been revealed by Józefowicz and Longa [39] in MC study of the model of V-shaped particles with rigid and with fluctuating angle between the sufficiently long Gay-Berne arms.

Bates and Luckhurst [32] extended the Lebwohl-Lasher (LL) model [40] to study by Monte Carlo simulations on the lattice the phase behavior of V-shaped molecules composed of two distinct rods of type A and B joined at a fixed angle. For the symmetric V-shaped molecules, the anisotropic interactions ϵ_{ab} $(a,b = A,B)$ for each rod was considered to be the same $(\epsilon_{AA} = \epsilon_{AB} = \epsilon_{BB})$, in the asymmetric case the anisotropic interactions for a pair of rods of one type was assumed to be different from the rods of another type $(\epsilon_{AA} \neq \epsilon_{BB}, \epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}})$. In the symmetric case the direct isotropic-biaxial nematic transition was found at angle $\psi \approx 109.47^\circ$ between rods. Two Landau points were observed in MC simulations of asymmetric V-shaped molecules at increasing of difference in magnitude ϵ_{ab} $(a,b = A,B)$ of anisotropic interactions of rods of distinct types at fixed values of the interarm angle. The model proposed in Ref. [32] has been further extended by Bates [33] to consider the influence of flexibility of molecules on the stability of nematic phases by including the bending potential between rods in V-shaped molecule. It was found that increase in flexibility of molecules leads to destabilization of the biaxial nematic phase in favor of prolate nematic uniaxial phase.

The molecular dynamics simulation with use of full atomistic potential was performed by Peláez and Wilson [41] for ODBP-Ph-C_7 molecules; these compounds were earlier used in experimental studies [7,8] in which N_B phase has been observed. The biaxial nematic phase containing local ferroelectric domains was found [41], although degree of biaxiality was small; the omission of electrostatic charges from the model led to a stable smectic phase instead of biaxial nematic phase.

It was suggested in Refs. [1,8] that local dipole moment of V-shaped mesogens may play an important role in the formation of the biaxial nematic state. Bates [34] extended the model proposed in Ref. [32] to include dipole-dipole interactions for symmetric V-shaped molecules, although only in a simple approximation based on the relative orientation of the two dipoles in neighboring sites of a lattice. By lattice MC simulation it was found that the strong dipolar interaction has widened the range of angles for which the I-N_B transition is observed so that the Landau point transforms to a line of the Landau points. Grzybowski and Longa [26] have studied within low-density approximation of the density functional theory models of bent-core molecules composed of two and three ellipsoids interacting via Gay-Berne interactions; the dipole-dipole interactions with the dipoles chosen parallel to C_2 symmetry axis of molecule have been also taken into account. In the absence of dipole-dipole interactions the single Landau point is determined at angles $\approx 107^\circ$ and $\approx 89^\circ$ for two- and three-part model of bent-core molecule, respectively. The Landau point is found to shift toward lower angles with increasing dipole-dipole interaction strength for both models. For three-part model bicritical point changes to a line of Landau points if the dipole-dipole interaction is strong enough; contrary to the MC simulation of LL model [34] no line of direct I-N_B transitions has been found in the two-part model of V-shaped mesogen. Within molecular field theory for polar biaxial nematics formed by V-shaped particles To *et al.* [42] found that increase in dipole strength results in increase of stability of nematic biaxial phase; for a sufficiently high dipole strength the line of the first-order I-N_B transitions appears instead of the Landau point.

Starting from the microscopic model of a symmetric V-shaped molecule of C_{2v} symmetry the authors of Ref. [27] have found within the Landau–de Gennes approach the phase diagram of the melt composed of such molecules. Only anisotropic interactions of the Maier-Saupe form have been taken into account. The phase diagram contains the regions of stability of isotropic, prolate uniaxial, oblate uniaxial nematic, and biaxial nematic phases; regions of stability of the biaxial nematic states are found to be located in the vicinities of two Landau points that correspond to the following values of an external angle α between arms of V-shaped molecules: $\alpha_1^* \approx 0.39\pi \approx 70.53^\circ$ and $\alpha_2^* \approx 0.61\pi \approx 109.47^\circ$.

Most of the papers cited above have studied the systems of symmetric V-shaped molecules: the exceptions are the works by Bates and Luckhurst [32], who introduced asymmetry via an anisotropy in interactions of arms of different types and Mettout *et al.* [23] who considered a model of the thermotropic liquid crystal polymer composed of hydroxybenzoic acid and hydroxynaphthoic acid. The objective of this paper is to consider the phase behavior of V-shaped molecules with asymmetry in architecture. For this purpose the model of symmetric V-shaped molecule proposed earlier [27] is extended to include rigid arms of different lengths; as distinct from the symmetric case this model of V-shaped molecule is characterized by C_s symmetry. The phase behavior of the thermotropic melt of asymmetric V-shaped molecules will be considered within the Landau theory of phase transitions [43] that is widely applied for description of systems composed of biaxial particles [35,44–52]. A peculiarity of the present work is that the coefficients of the Landau–de Gennes free-energy expansion are found explicitly from a microscopic model of V-shaped molecules. The possibility to calculate explicitly the coefficients of the Landau–de Gennes free-energy expansion for a specific model enables one to avoid difficulties of dealing with a great number of topologically distinct phase diagrams that can be derived from the coefficients that appear in phenomenological Landau theories of biaxial nematics [45–51,53]. For instance, the expansion of the Landau free energy in powers of single nematic tensor order parameter up to the sixth order for a system of biaxial molecules may contain six phenomenological coefficients [47,49], while expansion in powers of two tensor-order parameters up to the fourth order depends on 14 phenomenological coefficients [50,51].

The additional advantage of using a specific model of liquid crystalline molecule is that it enables one to find within the Landau–de Gennes approach the coefficients of gradient terms [37]. The latter are related to the elastic constants of molecule which, in turn, are of special interest due to recent observation of nematic twist bend (N_{TB}) phase in systems of achiral liquid crystal dimers [54–56] and rigid bent-core molecules [57]; the molecules in this phase are arranged on a conical helix so that director precesses on this helix and forms a fixed cone angle with the helix axis. The existence of this phase was predicted

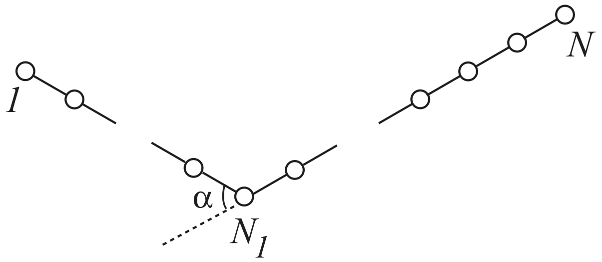

FIG. 1. Sketch of V-shaped molecule composed of two rigid rods joined at an external angle α. Rods consist of N_1 and $N_2 = N - N_1$ numbers of monomer units.

by Meyer [58]; it was found by Memmer [28] in computer simulation of Gay-Berne bent-core particles. To date, a number of approaches based on different physical mechanisms have been proposed to describe the formation of $\mathrm{N_{TB}}$ phase [58–67]. One of these approaches [60] rests on the assumption that the bend elastic constant of V-shaped molecule could become negative, which leads to the formation of a modulated phase of a system. Our calculations, although restricted by the gradient terms of the lowest orders, indicate that for the model under consideration the coefficients of gradient terms and related elastic constants can indeed be negative for some range of angles between arms of V-shaped molecule.

The paper is organized as follows. Section II contains the description of the model. The phase diagram of the melt and discussion of results are presented in the Sec. III. Section IV contains the calculation of the coefficients of the lowest-order gradient terms in the Landau–de Gennes free-energy expansion for the model of V-shaped particles. The summary of the main results is given in Sec. V; some mathematical details are presented in the Appendix.

II. MODEL

We consider a melt of Π monodisperse V-shaped molecules in a volume V. Each molecule consist of two rod-like segments joined at their ends at an external angle α as shown in Fig. 1. Rigid segments are assumed to be composed of N_1 and N_2 monomer units; the bond that connects two successive monomer units in any segment is of fixed length b.

The conformation of a molecule is specified by the positions of the monomer units $\{\mathbf{r}_j\}$, $j = 1, \dots, N$, where N is the total number of units in molecule ($N_1 + N_2 = N$). The statistical weight of the conformation $\{\mathbf{r}_j\}$ of molecule is given by [27]

$$W\big(\{\mathbf{r}_j\};\alpha\big) = \frac{1}{V}\left\{\prod_{j=2}^{N_1-1}\delta(\mathbf{u}_{j+1}-\mathbf{u}_j)\right\}\frac{\delta(|\mathbf{u}_{N_1}|-b)}{4\pi b^2} \times \delta\left[\cos(\alpha) - \frac{(\mathbf{u}_{N_1+1}\mathbf{u}_{N_1})}{b^2}\right]\frac{\delta(|\mathbf{u}_{N_1+1}|-b)}{4\pi b^2} \times \left\{\prod_{j=N_1+1}^{N_1+N_2-1}\delta(\mathbf{u}_{j+1}-\mathbf{u}_j)\right\}, \tag{1}$$

where the vector $\mathbf{u}_j$ Eq. (1), directed along the bond between the $j-1$th and jth monomers, is defined by expression: $\mathbf{u}_j = (\mathbf{r}_j - \mathbf{r}_{j-1})$. To characterize the asymmetry in lengths of arms of V-shaped molecule we introduce parameter $\phi = N_1/N = 1 - N_2/N$, which is a number fraction of monomer units in the one of rigid segments. For the values of asymmetry parameter $\phi = 0$ or $\phi = 1$ as well as for angle values $\alpha = 0$ or $\alpha = \pi$ the molecule assumes rod-like conformation characterized by $D_{\infty h}$ symmetry; if $\phi = 1/2$ and $\alpha \neq 0,\pi$, the symmetry of molecule is C_{2v}, while if $\phi \neq 1/2$ and $\alpha \neq 0,\pi$, the molecule possesses C_s symmetry.

The anisotropic interactions that facilitate the liquid crystalline ordering of V-shaped molecules are of the Maier–Saupe (MS) form [68,69],

$$H_{MS}\big(\{\mathbf{r}_j^{(k)}\}\big) = -\frac{U}{2\rho_0}\sum_{k_1=1}^{\Pi}\sum_{k_2=1}^{\Pi}\sum_{j_1=1}^{N}\sum_{j_2=1}^{N}P_2\left[\frac{\mathbf{u}_{j_1}^{(k_1)}\mathbf{u}_{j_2}^{(k_2)}}{b^2}\right] = -\frac{\rho_0 U}{3}\sum_{\alpha}\sum_{\beta}\int d\mathbf{r}\hat{S}_{\alpha\beta}(\mathbf{r})\hat{S}_{\beta\alpha}(\mathbf{r}), \quad U = \omega T, \tag{2}$$

where $P_2(x)$ is the second-order Legendre polynomial and the Maier–Saupe parameter, ω, is assumed to be positive. The monomer number density is defined by $\rho_0 = M/V$, where total number of monomer units in a system is $M = \Pi N$. The microscopic nematic-order parameter density Eq. (2) is given by

$$\hat{S}_{\alpha\beta}(\mathbf{r}) = \frac{1}{\rho_0}\sum_{k=1}^{\Pi}\sum_{j=1}^{N}\delta\big[\mathbf{r} - \mathbf{r}_j^{(k)}\big]\frac{3}{2}\left[\frac{\big(\mathbf{u}_j^k\big)_\alpha}{b}\frac{\big(\mathbf{u}_j^k\big)_\beta}{b} - \frac{\delta_{\alpha\beta}}{3}\right], \tag{3}$$

where $\alpha,\beta = x,y,z$, and $\mathbf{r}_j^{(k)}$ is the position of jth unit in kth macromolecule that consist of $N = N_1 + N_2$ units.

The Landau free-energy expansion for the model defined by Eqs. (1) and (2) is written as follows:

$$\frac{\mathcal{F}}{MT} = -\frac{\omega}{3V}\sum_{\alpha}\sum_{\beta}\int d\mathbf{x}S_{\alpha\beta}(\mathbf{x})S_{\beta\alpha}(\mathbf{x}) - S(\{S_{\alpha\beta}\}), \tag{4}$$

where the components $S_{\alpha\beta}(\mathbf{x})$ of tensor nematic-order parameter are thermally averaged densities defined above [Eq. (3)] and functional $S(\{S_{\alpha\beta}\})$ is given by the following Legendre transform:

$$S(\{S_{\alpha\beta}\}) = \frac{1}{M}\sum_{\alpha}\sum_{\beta}\int d\mathbf{x}h_{\alpha\beta}(\mathbf{x})S_{\alpha\beta}(\mathbf{x}) - \frac{F(\{h_{\alpha\beta}\})}{T}, \qquad S_{\alpha\beta}(\mathbf{x}) = \frac{M}{T}\frac{\delta F(\{h_{\alpha\beta}\})}{\delta h_{\alpha\beta}(\mathbf{x})}. \tag{5}$$

Here $F(\{h_{\alpha\beta}\})$ Eq. (5) is a free energy of a single ideal molecule that is subjected to a conjugated field $h_{\alpha\beta}(\mathbf{x})$,

$$F(\{h_{\alpha\beta}\}) = -\frac{T}{N}\ln Q(\{h_{\alpha\beta}\}), \tag{6}$$

and corresponding partition function is of the form

$$Q(\{h_{\alpha\beta}\}) = \frac{1}{Q_0}\int d\mathbf{r}_1\dots d\mathbf{r}_N W(\{\mathbf{r}_j\};\alpha) \times \exp\left\{-\int d\mathbf{x}h_{\alpha\beta}(\mathbf{x})\hat{S}_{\alpha\beta}(\mathbf{x};N)\right\},$$

$$\begin{aligned}\hat{S}_{\alpha\beta}(\mathbf{x};N) &= \frac{1}{\rho_0}\sum_{j=1}^{N}\delta(\mathbf{r}-\mathbf{r}_j)\frac{3}{2}\left[\frac{(\mathbf{u}_j)_\alpha}{b}\frac{(\mathbf{u}_j)_\beta}{b}-\frac{\delta_{\alpha\beta}}{3}\right],\\ Q_0 &= Q(\{0\}).\end{aligned}\tag{7}$$

Next we assume that nematic ordering is global and can be described by space-independent-order parameter

$$S_{\alpha\beta} = \frac{1}{V}\int d\mathbf{x} S_{\alpha\beta}(\mathbf{x}).\tag{8}$$

With this in mind, the Landau–de Gennes free-energy expansion of the melt in powers of the rotational invariants, $\mathrm{tr}(\mathbf{S}^2)$ and $\mathrm{tr}(\mathbf{S}^3)$, of tensor Eq. (8) can be written as follows [47]:

$$\begin{aligned}N\frac{\mathcal{F}}{MT} &= (\gamma_2-\omega N/3)\mathrm{tr}(\mathbf{S}^2)+\gamma_3\mathrm{tr}(\mathbf{S}^3)+\gamma_4[\mathrm{tr}(\mathbf{S}^2)]^2\\ &\quad+\gamma_5\mathrm{tr}(\mathbf{S}^2)\mathrm{tr}(\mathbf{S}^3)+\gamma_6^{(1)}[\mathrm{tr}(\mathbf{S}^2)]^3+\gamma_6^{(2)}[\mathrm{tr}(\mathbf{S}^3)]^2.\end{aligned}\tag{9}$$

Coefficients of expansion Eq. (9) that depend upon angle α between arms of V-shaped molecule (Fig. 1) and asymmetry parameter ϕ, are given in Appendix A. The procedure of derivation of the expansion Eq. (9) that was given earlier in Ref. [27] is also described briefly in Appendix A. The rotational invariants, $\mathrm{tr}(\mathbf{S}^2)$ and $\mathrm{tr}(\mathbf{S}^3)$, can be written as

$$\begin{aligned}\mathrm{tr}(\mathbf{S}^2) &= (1/2)(3x^2+y^2),\\ \mathrm{tr}(\mathbf{S}^3) &= (3/4)x(x^2-y^2),\end{aligned}\tag{10}$$

where the following parametrization [47] of the eigenvalues of $\mathbf{S}$ tensor Eq. (8) has been used:

$$\lambda_1 = -(x+y)/2,\quad \lambda_2 = -(x-y)/2,\quad \lambda_3 = x.\tag{11}$$

All eigenvalues Eqs. (11) vanish if melt is in the isotropic phase so that $x=0$, $y=0$. Uniaxial nematic phase is realized if two of three eigenvalues Eqs. (11) are equal and distinct from zero. If, additionally, the eigenvalue that differs from two others is the largest one so that $\lambda_i = \lambda_j \neq 0$, $\lambda_i = \lambda_j < \lambda_k$, $(i \neq j \neq k)$, the melt is in prolate uniaxial (N_U^+) phase; conversely, if $\lambda_i = \lambda_j > \lambda_k$, the melt is in oblate uniaxial (N_U^-) nematic phase. Since $\mathrm{tr}(\mathbf{S}) = 0$ the distinct eigenvalue is positive for N_U^+ state and negative for N_U^- phase. For the nematic uniaxial state $x \neq 0$, and y can attain one of the following values: 0, $3x$, or $-3x$, where alignment along the x, y, and z axis corresponds to $y = 3x$, $y = -3x$, and $y = 0$ values, respectively. The biaxial nematic state corresponds to three different eigenvalues Eqs. (11).

Substitutions of Eq. (10) for Eq. (9) yields

$$\begin{aligned}N\frac{\mathcal{F}}{MT} &= F(x,y,\tilde{\omega})\\ &= A(x,\tilde{\omega})+B(x,\tilde{\omega})y^2+C(x)y^4+Dy^6,\end{aligned}\tag{12}$$

where rescaled MS parameter, $\tilde{\omega}$, is given by $\tilde{\omega} = \omega N$ and the following notation has been used:

$$\begin{aligned}A(x,\tilde{\omega}) &= \frac{3}{2}\left(\gamma_2-\frac{\tilde{\omega}}{3}\right)x^2+\frac{3}{4}\gamma_3x^3+\frac{9}{4}\gamma_4x^4+\frac{9}{8}\gamma_5x^5\\ &\quad+\left(\frac{27}{8}\gamma_6^{(1)}+\frac{9}{16}\gamma_6^{(2)}\right)x^6,\end{aligned}\tag{13}$$

$$\begin{aligned}B(x,\tilde{\omega}) &= \frac{1}{2}\gamma_2-\frac{\tilde{\omega}}{6}-\frac{3}{4}\gamma_3x+\frac{3}{2}\gamma_4x^2-\frac{3}{4}\gamma_5x^3\\ &\quad+\left(\frac{27}{8}\gamma_6^{(1)}-\frac{9}{8}\gamma_6^{(2)}\right)x^4,\end{aligned}\tag{14}$$

$$C(x) = \frac{1}{4}\gamma_4-\frac{3}{8}\gamma_5x+\left(\frac{9}{8}\gamma_6^{(1)}+\frac{9}{16}\gamma_6^{(2)}\right)x^2,\tag{15}$$

$$D = \frac{1}{8}\gamma_6^{(1)}.\tag{16}$$

As found earlier [27], the phase diagram of the model of symmetric ($\phi = 1/2$) V-shaped molecules contains the regions of stability of isotropic, prolate and oblate uniaxial, and biaxial nematic phases. The biaxial nematic state is found to be stable in narrow regions located in the vicinity of two Landau points characterized by $(\alpha_1^*,\tilde{\omega}^*)$ and $(\alpha_2^*,\tilde{\omega}^*)$ in $\alpha - \tilde{\omega}$ plane. Here $\tilde{\omega}^* = 15$, $\alpha_1^* \approx 1.23096 \approx 0.39\pi \approx 70.53^\circ$, and $\alpha_2^* \approx 1.91063 \approx 0.61\pi \approx 109.47^\circ$. The I-$\mathrm{N}_\mathrm{U}^+$ transition takes place for $0 \leqslant \alpha < \alpha_1^*$ or $\alpha_2^* < \alpha \leqslant \pi$ while the I-N_U^- transition occurs for α values in the range $\alpha_1^* < \alpha < \alpha_2^*$. As will be shown in the next section, the phase behavior of the melt of V-shaped molecules is strongly affected by the asymmetry in the lengths of arms of molecules.

III. PHASE DIAGRAMS

Since the coefficients Eqs. (A3)–(A8) of the Landau–de Gennes expansion are not altered by change of variables $\phi \to (1-\phi)$, the phase diagrams for asymmetry parameter ϕ and $1-\phi$ are the same; hence, we will restrict our consideration to the case $0 \leqslant \phi \leqslant 1/2$ only. Moreover, because the substitution $\alpha \to \pi - \alpha$ also does not alter Eqs. (A3)–(A8), the phase diagrams are to be symmetric with respect to $\alpha = \pi/2$. The coefficients of the even orders Eqs. (A3), (A5), (A7), and (A8) are found to be positive in the range $\alpha \in [0,\pi]$ for all possible values of asymmetry parameter $\phi \in [0,1]$. The coefficients of the third Eq. (A4) and fifth Eq. (A6) orders vanish if the following condition holds true:

$$\sin^2(\alpha) = \frac{2}{9}\frac{1}{\phi(1-\phi)},\quad \alpha \in [0,\pi].\tag{17}$$

This equation has real solutions for $1/3 \leqslant \phi \leqslant 2/3$; if $\phi = 1/3$ or $\phi = 2/3$ the only solution is $\alpha = \pi/2$, while if $1/3 < \phi < 2/3$ there are two values of angle α, $\alpha_1^*(\phi)$ and $\alpha_2^*(\phi)$, at which the odd order coefficients vanish. The solutions of Eq. (17) are shown in Fig. 2 as function of asymmetry parameter ϕ. For a given value of parameter ϕ the coefficients of the third Eq. (A4) and fifth Eq. (A6) orders are negative if $0 \leqslant \alpha < \alpha_1^*(\phi)$ or $\alpha_2^*(\phi) < \alpha \leqslant \pi$, while they are positive for $\alpha_1^*(\phi) < \alpha < \alpha_2^*(\phi)$. According to Fig. 2 the odd-order coefficients are always negative if asymmetry parameter falls in $0 \leqslant \phi < 1/3$ or $2/3 < \phi \leqslant 1$ ranges. As also indicated in Fig. 2, the solutions α_1^* and α_2^* of Eq. (17) are symmetric about value $\phi = 1/2$.

To find the isotropic-nematic boundary we have to equate the free energies of isotropic and uniaxial nematic states and take into account for the stability condition

$$A(x,\tilde{\omega}) = 0,\quad \frac{\partial}{\partial x}A(x,\tilde{\omega}) = 0,\quad \frac{\partial^2 A(x,\tilde{\omega})}{\partial x^2} > 0,\tag{18}$$

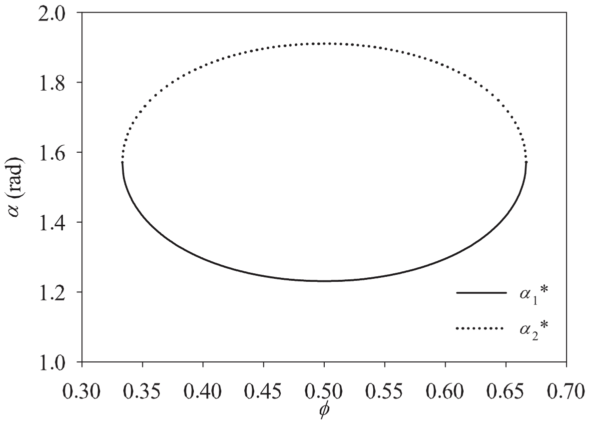

FIG. 2. Plots of values of the solutions α_1^* and α_2^* of Eq. (17) as function of asymmetry parameter.

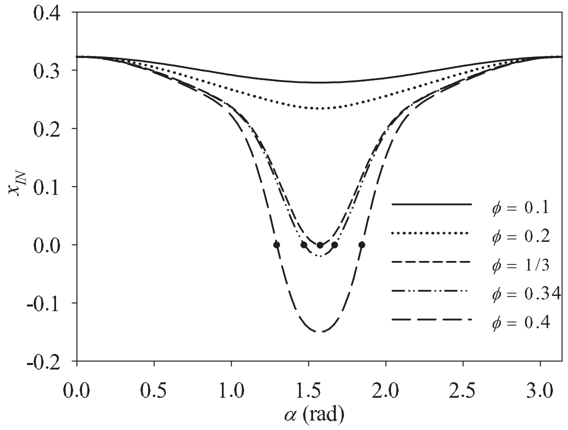

FIG. 3. Order parameter jump at I-N transition. The positions of points α_1^* and α_2^* are indicated by filled circles for each curve that contains such points. There is only one point $\alpha_1^* = \alpha_2^*$ for curve with $\phi = 1/3$.

where function $A(x,\tilde{\omega})$ is defined above [Eq. (13)]. In turn, the boundaries of the isotropic-biaxial nematic transition can be found from the following set of equations:

$$\frac{\partial F(x,y,\tilde{\omega})}{\partial x} = 0, \quad \frac{\partial F(x,y,\tilde{\omega})}{\partial y} = 0,$$
$$F(x,y,\tilde{\omega}) = 0, \tag{19}$$

provided that the matrix of second derivatives of function $F(x,y,\tilde{\omega})$ with respect to x and y variables is positive definite. The boundaries of the uniaxial nematic-biaxial nematic transition can be found from solution of equations

$$\frac{\partial F(x,y,\tilde{\omega})}{\partial x} = 0, \quad \frac{\partial F(x,y,\tilde{\omega})}{\partial y} = 0,$$
$$\frac{\partial}{\partial u}A(u,\tilde{\omega}) = 0, \quad F(x,y,\tilde{\omega}) = A(u,\tilde{\omega}), \tag{20}$$

provided that the stability conditions are fulfilled.

The behavior of order parameter jump at isotropic-nematic transition, x_{IN}, is described by the following equation:

$$\left(\tfrac{9}{4}\gamma_6^{(2)} + \tfrac{27}{2}\gamma_6^{(1)}\right)x^3 + \tfrac{27}{8}\gamma_5 x^2 + \tfrac{9}{2}\gamma_4 x + \tfrac{3}{4}\gamma_3 = 0, \tag{21}$$

which can be derived from Eqs. (18). The solutions of Eq. (21) are shown in Fig. 3 for a number of different values of asymmetry parameter. As it follows from Fig. 3, the value x_{IN} is positive while asymmetry parameter remains in range $\phi < 1/3$ ($\phi > 2/3$). For $\phi = 1/3$ ($\phi = 2/3$) the order parameter jump vanishes at single point $\alpha = \pi/2$; if asymmetry parameter falls within $1/3 < \phi \leqslant 1/2$ or $1/2 \leqslant \phi < 2/3$ ranges this happens at two points $\alpha_1^*(\phi)$ and $\alpha_2^*(\phi)$. The value of x_{IN} becomes negative in interval $\alpha_1^*(\phi) < \alpha < \alpha_2^*(\phi)$ if ϕ belongs to $1/3 < \phi \leqslant 1/2$ or $1/2 \leqslant \phi < 2/3$ ranges.

The phase diagram of melt under consideration is shown in Fig. 4(a) for several ϕ values from interval $0 \leqslant \phi < 1/3$. At these values of asymmetry parameter the V-shaped chain is effectively of rodlike shape (regardless of the angle α value) so there is only isotopic-prolate uniaxial nematic (I-$\mathrm{N_U^+}$) transition. However, the temperature of the I-$\mathrm{N_U^+}$ transition decreases ($\tilde{\omega} \sim 1/T$) and the region of stability of isotropic phase becomes larger for $0 < \alpha < \pi$ as asymmetry parameter grows in range $0 \leqslant \phi < 1/3$. As indicated in Fig. 4(b) all eigenvalues Eqs. (11) plotted for $\phi = 0.3$ value and special value of rescaled MS parameter $\tilde{\omega} = 10$ vanish in isotropic phase while in $\mathrm{N_U^+}$ phase the eigenvalue that is distinct from two other is the largest one.

Phase diagrams of melt of V-shaped molecules for a number of values of asymmetry parameter ϕ that belong to the range $1/3 \leqslant \phi < 1/2$ are shown in Fig. 5. The phase diagram for case $\phi = 1/3$ [Fig. 5(a)] contains the regions of stability of isotropic, prolate uniaxial nematic, and biaxial nematic phases. The single Landau point (defined by conditions $\gamma_2 - \tilde{\omega}/3 = 0$ and $\gamma_3 = 0$) at which the direct continuous transition takes place from isotropic state to biaxial nematic state is located in $(\alpha,\tilde{\omega})$ plane at $\alpha = \alpha_1^* = \alpha_2^* = \pi/2$, $\tilde{\omega} = 15$. For the value of asymmetry parameter $\phi = 0.335$, the phase diagram changes qualitatively: the region of stability of oblate nematic uniaxial phase ($\mathrm{N_U^-}$) appears [Fig. 5(b)]. As shown in this figure the $\mathrm{N_U^-}$ phase is bounded from above by nematic biaxial phase. As far as we know this kind of topology of phase diagram for systems constituted by biaxial molecules was first conjectured by Mulder [70], who considered within the Onsager approach the phase behavior of spheroplatelet particles (see Fig. 6 in Ref. [70]). Upon further increase of asymmetry parameter, the region of stability of $\mathrm{N_U^-}$ phase becomes larger as is shown in Fig. 5(c). At the same time the regions of stability of biaxial nematic phase located above α_1^* and α_2^* Landau points become smaller. The increase of ϕ parameter up to $\phi = 0.4$ [Fig. 5(d)] results in further separating of $\alpha_1^*(\phi)$ and $\alpha_2^*(\phi)$ Landau points; the regions occupied by the biaxial nematic phase are greatly reduced while stability region of oblate uniaxial nematic phase $\mathrm{N_U^-}$ increases sharply. The temperature of I-$\mathrm{N_U^-}$ transition that takes place between the Landau points increases as ϕ varies in the range $1/3 < \phi \leqslant 1/2$ and decreases if ϕ increases within range $1/2 \leqslant \phi < 2/3$. In turn, the temperature of I-$\mathrm{N_U^+}$ transition decreases as parameter α grows in the range $0 \leqslant \alpha < \alpha_1^*(\phi)$ and increases if parameter α grows in the range $\alpha_2^*(\phi) < \alpha \leqslant \pi$. The comparison of phase diagrams presented in Figs. 5(a)–5(d) leads to the conclusion that stability region of the biaxial nematic phase is markedly larger for asymmetric V-shaped molecules (in particular, for $\phi = 1/3$ or $\phi = 2/3$) than for more symmetric V-shaped molecules (as ϕ tends to 1/2).

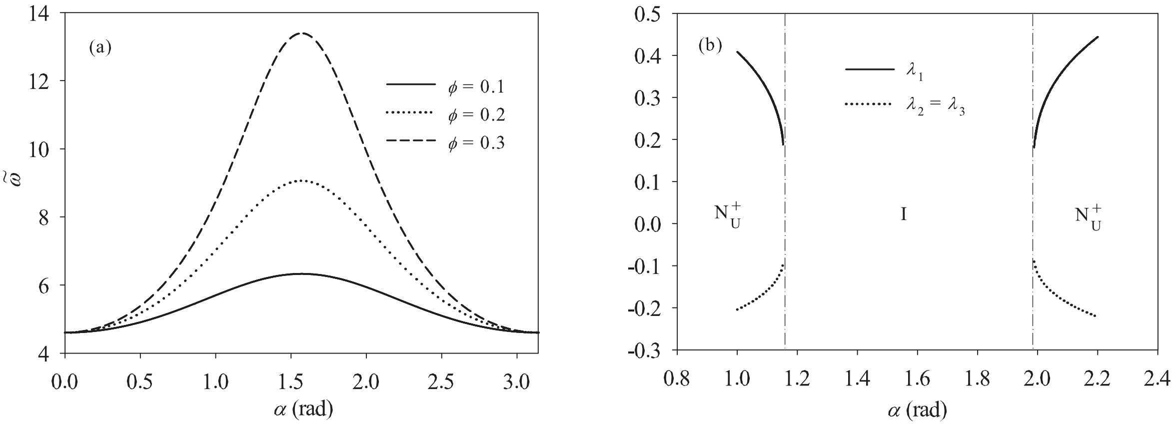

FIG. 4. (a) Lines of the first order I-N_U^+ phase transitions for $\phi < 1/3$. The isotropic (I) and prolate uniaxial nematic (N_U^+) phases are stable below and above of each curve, respectively. (b) Plots of eigenvalues Eqs. (11) for $\phi = 0.3$ and $\tilde{\omega} = 10$ with $\lambda_1 > \lambda_2 = \lambda_3$. The vertical dash-dot lines correspond to the boundaries of isotropic phase where all eigenvalues vanish.

The ordering of V-shaped molecules can be characterized by vectors

$$\mathbf{a} = \frac{\phi \mathbf{v}_1 - (1-\phi)\mathbf{v}_2}{\sqrt{1 - 2\phi(1-\phi)[1-\cos(\alpha)]}},$$
$$\mathbf{b} = \frac{\phi \mathbf{v}_1 + (1-\phi)\mathbf{v}_2}{\sqrt{1 - 2\phi(1-\phi)[1+\cos(\alpha)]}},$$
$$\mathbf{c} = \mathbf{a} \times \mathbf{b}, \tag{22}$$

where $\mathbf{v}_1$ and $\mathbf{v}_2$ are the unit vectors directed along the first and second arms of V-shaped molecule, respectively $[(\mathbf{v}_1\mathbf{v}_2) = -\cos(\alpha)]$. For $\phi \neq \frac{1}{2}$, the vectors Eqs. (22) correspond to a skew coordinate system, where vector $\mathbf{a}$ is parallel to the line that connects the free ends of V-shaped molecule, while vector $\mathbf{b}$ is directed along the median drawn from the vertex at the internal angle between arms. For $\phi = \frac{1}{2}$ set of vectors Eqs. (22) represent an orthogonal coordinate system used

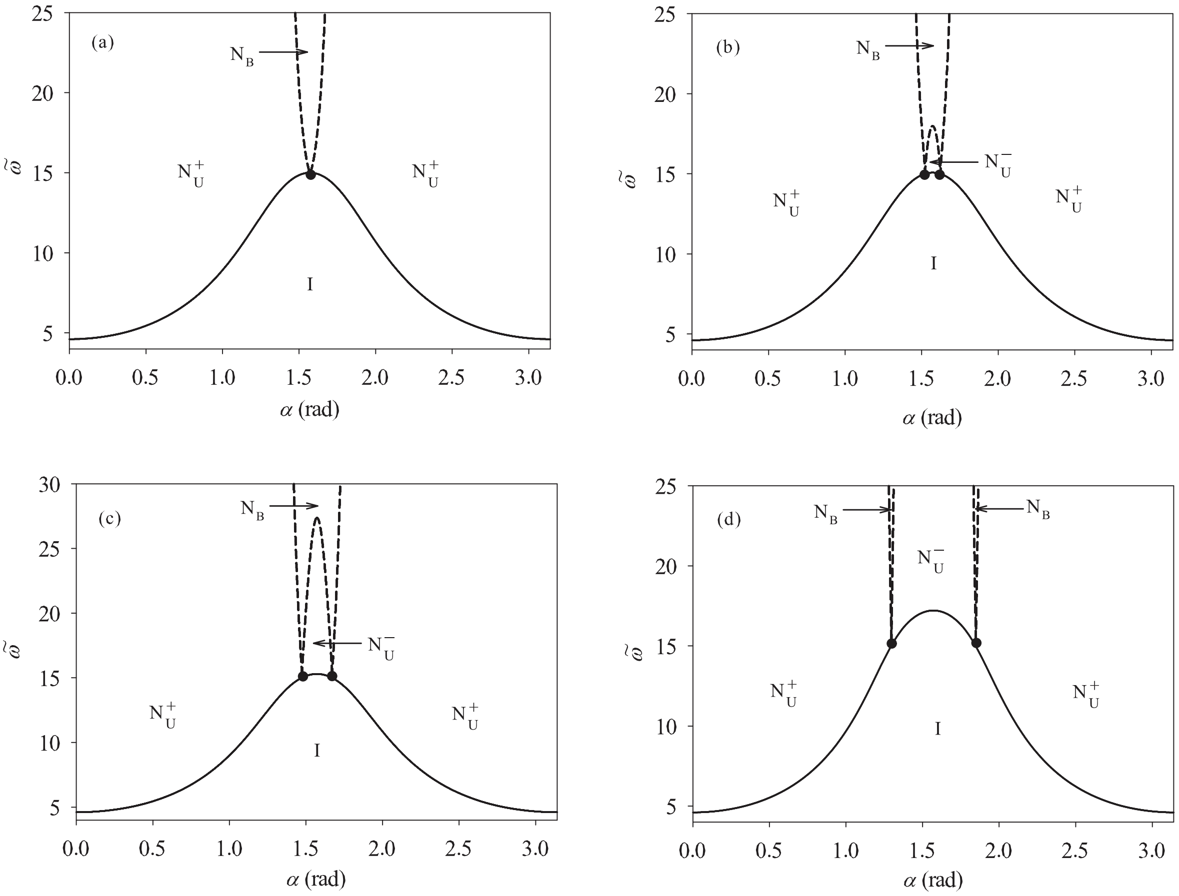

FIG. 5. Phase diagram of melt of V-shaped molecules for different values of the asymmetry parameter: $\phi = 1/3$ (a), $\phi = 0.335$ (b), $\phi = 0.34$ (c), and $\phi = 0.4$ (d). The solid line represents a first-order transition, while the dashed lines correspond to a second-order transition. The Landau points are indicated by the filled circles.

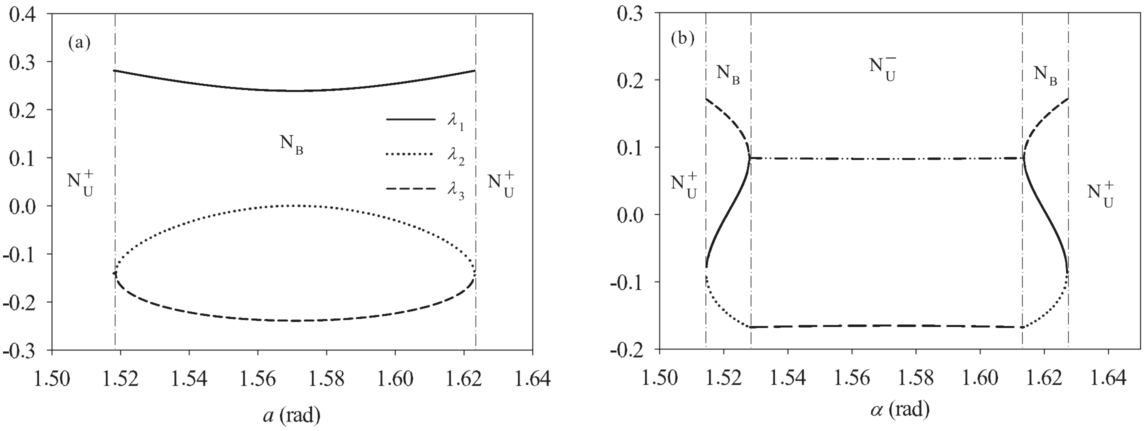

FIG. 6. (a) Plots of eigenvalues Eqs. (11) for $\phi = 1/3$ and $\tilde{\omega} = 18$ with $\lambda_1 > \lambda_2 > \lambda_3$. (b) Plots of eigenvalues Eqs. (11) for $\phi = 0.335$ and $\tilde{\omega} = 16$ in oblate uniaxial and biaxial nematic phases. For both figures the vertical dash-dot lines correspond to the boundaries of the biaxial phase where two of three eigenvalues become identical.

earlier [20,27,71] to describe ordering of symmetric V-shaped molecules. It is expected that for $0 \leqslant \alpha < \alpha_1^*(\phi)$ the directions of vectors **a** are correlated in N_U^+ state in phase diagrams shown in Fig. 5, while vectors **b** become oriented in N_U^+ state if $\alpha_2^*(\phi) < \alpha \leqslant \pi$. If angle α falls in the range $\alpha_1^*(\phi) < \alpha < \alpha_2^*(\phi)$, molecules form stacks in the N_U^- phase; the symmetry plane of V-shaped molecules are orthogonal to vector **c**, while neither **a** nor **b** vectors are correlated. In the regions of stability of the biaxial nematic state all the vectors are correlated.

The plots of eigenvalues Eqs. (11) as function of angle α for several special values of asymmetry parameter are shown in Fig. 6. As indicated in Fig. 6(a) for $\phi = 1/3$ and value of rescaled MS parameter $\tilde{\omega} = 18$, there are three distinct eigenvalues in N_B phase while two of them become equal in prolate uniaxial phase. Another kind of behavior of eigenvalues in N_B phase is shown in Fig. 6(b) for $\phi = 0.335$ and $\tilde{\omega} = 16$. This is because for $\phi = 0.335$ the biaxial nematic phases are located between prolate and oblate uniaxial nematic phases [see Fig. 5(b)] as distinct from case $\phi = 1/3$ where region of stability of N_B phase is found between prolate uniaxial nematic phases. As shown in Fig. 6(b) two of three eigenvalues Eqs. (11) coincide in the uniaxial phases.

IV. COEFFICIENTS OF THE GRADIENT TERMS

In this section we calculate the coefficients of the lowest-order gradient terms for the proposed model of asymmetric V-shaped molecule and elastic constants related to these coefficients. For this purpose we have to take into account the spatial dependence of tensor field $\mathbf{S}(\mathbf{r})$ so that the Landau–de Gennes free energy is written as

$$N\frac{\mathcal{F}}{MT} = \sum_{n=2}^{\infty}\frac{1}{n!}F_n\{[\mathbf{S}(\mathbf{r})]\}, \tag{23}$$

where F_n is the nth-order contribution. To the lowest orders in $\nabla\mathbf{S}$ the second-order contribution into the Landau–de Gennes free energy assumes the form [37]

$$F_2 = \frac{1}{V}\int d\mathbf{r}\sum_{\alpha}\sum_{\beta}\Bigg\{AS_{\alpha\beta}(\mathbf{r})S_{\beta\alpha}(\mathbf{r}) + L_1\sum_{\gamma}\frac{\partial S_{\beta\gamma}(\mathbf{r})}{\partial\mathbf{r}_{\alpha}} \times \frac{\partial S_{\beta\gamma}(\mathbf{r})}{\partial\mathbf{r}_{\alpha}} + L_2\sum_{\gamma}\frac{\partial S_{\alpha\gamma}(\mathbf{r})}{\partial\mathbf{r}_{\alpha}}\frac{\partial S_{\beta\gamma}(\mathbf{r})}{\partial\mathbf{r}_{\beta}}\Bigg\}, \tag{24}$$

where $\alpha,\beta,\gamma = x,y,z$. Using the Fourier representation,

$$\tilde{S}_{\alpha\beta}(\mathbf{q}) = \int d\mathbf{r}S_{\alpha\beta}(\mathbf{r})\exp(i\mathbf{q}\mathbf{r}),$$
$$S_{\alpha\beta}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{q}}\tilde{S}_{\alpha\beta}(\mathbf{q})\exp(-i\mathbf{q}\mathbf{r}), \tag{25}$$

the second-order contribution, Eq. (24), can be rewritten as

$$F_2 = \frac{1}{V^2}\sum_{\mathbf{q}}\sum_{\alpha}\sum_{\beta}\Bigg\{[A + L_1q^2]\tilde{S}_{\alpha\beta}(\mathbf{q})\tilde{S}_{\alpha\beta}(-\mathbf{q}) + L_2\sum_{\gamma}q_{\alpha}q_{\beta}\tilde{S}_{\alpha\gamma}(\mathbf{q})\tilde{S}_{\beta\gamma}(-\mathbf{q})\Bigg\}. \tag{26}$$

Since $\mathbf{S}(\mathbf{r})$ is a symmetric and traceless tensor, S_{xx}, S_{yy}, S_{xy}, S_{xz}, and S_{yz} can be chosen as independent components. If we also take $\mathbf{q}$ to be directed along z axis, Eq. (26) reduces to

$$F_2 = \frac{1}{V^2}\sum_{\mathbf{q}}\Bigg\{\Bigg[A + \left(L_1 + \frac{L_2}{2}\right)q^2\Bigg] \times \sum_{\alpha}\sum_{\beta}\tilde{S}_{\alpha\beta}(\mathbf{q})\tilde{S}_{\beta\alpha}(-\mathbf{q}) + \frac{L_2}{2}q^2R_1(\mathbf{q},-\mathbf{q})\Bigg\}, \tag{27}$$

where we denote

$$R_1(\mathbf{q},-\mathbf{q}) = \tilde{S}_{xx}(\mathbf{q})\tilde{S}_{yy}(-\mathbf{q}) + \tilde{S}_{xx}(-\mathbf{q})\tilde{S}_{yy}(\mathbf{q}) - 2\tilde{S}_{xy}(\mathbf{q})\tilde{S}_{xy}(-\mathbf{q}). \tag{28}$$

On the other hand, the second-order contribution to the Landau free energy derived from the microscopic model described

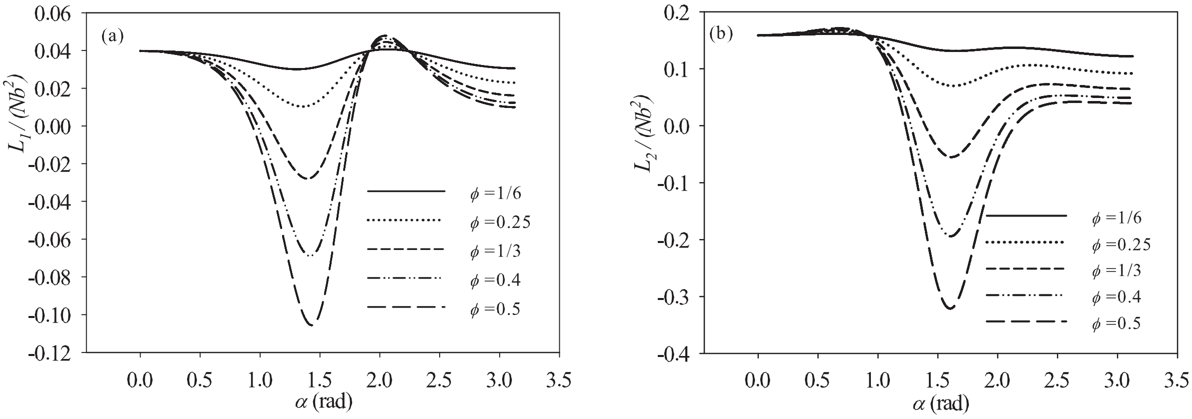

FIG. 7. Plots of rescaled elastic constants $(L_1)/(Nb)^2$ (a) and $(L_2)/(Nb)^2$ (b) as function of an external angle α of V-shaped molecule ($0 \leqslant \alpha < \pi$) for several values of asymmetry parameter.

above in Sec. II reads as [27]

$$F_2 = \frac{1}{V^2}\sum_{\mathbf{q}}\sum_{(\alpha_i\beta_i)}\left\{N[\tilde{K}^{(-1)}(\mathbf{q},-\mathbf{q})]_{(\alpha_1\beta_1)(\alpha_2\beta_2)} - \frac{2\tilde{\omega}}{3}\delta_{\alpha_1\alpha_2}\delta_{\beta_1\beta_2}\right\}\tilde{S}_{\alpha_1\beta_1}(\mathbf{q})\tilde{S}_{\alpha_2\beta_2}(-\mathbf{q}), \tag{29}$$

where $(\alpha_i\beta_i)$ pairs take values (xx),(yy),(xy),(xz),(yz), and $\tilde{K}^{(-1)}(\mathbf{q},-\mathbf{q})$ is the matrix inverse to the matrix $\tilde{K}(\mathbf{q},-\mathbf{q})$. The elements of matrix $\tilde{K}(\mathbf{q},-\mathbf{q})$ are the Fourier transforms of the pair correlation functions of orientational densities of an ideal V-shaped molecule defined by Eq. (A1) at $n = 2$.

The calculation of an expansion of elements of matrices $\tilde{K}(\mathbf{q},-\mathbf{q})$ and $\tilde{K}^{(-1)}(\mathbf{q},-\mathbf{q})$ up to the q^2 order ($|\mathbf{q}| = q$) are described in Appendix B. By substituting Eqs. (B5) into Eq. (29), we find that the second-order contribution, Eq. (29), can be rewritten as

$$F_2 = \frac{1}{V^2}\sum_{\mathbf{q}}\left\{\left[2\gamma_2 + C_0^{(2)}(qbN)^2 - \frac{2\tilde{\omega}}{3}\right]\sum_{\alpha}\sum_{\beta}\tilde{S}_{\alpha\beta}(\mathbf{q})\tilde{S}_{\beta\alpha}(-\mathbf{q}) + C_1^{(2)}(qbN)^2R_1(\mathbf{q},-\mathbf{q})\right\}, \tag{30}$$

where coefficient γ_2 is given by Eq. (A3), while coefficients $C_i^{(2)} = C_i^{(2)}(\alpha)$ are as follows:

$$\begin{aligned} C_0^{(2)} &= \frac{1}{42[d(\alpha,\phi)]^2}[5(1-4\xi+2\xi^2) + 14\xi^2P_1 + 20\xi(1-2\xi)P_2 + 16P_3\xi^2], \\ C_1^{(2)} &= \frac{1}{63[d(\alpha,\phi)]^2}[5(1-4\xi+2\xi^2) + 21\xi^2P_1 + 20\xi(1-2\xi)P_2 + 9P_3\xi^2], \end{aligned} \tag{31}$$

where $P_n \equiv P_n[\cos(\alpha)]$ is the nth order Legendre polynomial, and where the following notation has been used:

$$d(\alpha,\phi) = 1 - 2\xi(1-P_2), \quad \xi = \phi(1-\phi). \tag{32}$$

Comparison of Eqs. (27) and (30) yields the following results for coefficients used in Eq. (27):

$$\begin{aligned} A &= \frac{10}{3d(\alpha,\phi)} - \frac{2\tilde{\omega}}{3}, \\ L_1 &= \frac{5}{126}\left[\frac{1-4\xi+2\xi^2+4\xi(1-2\xi)P_2+6\xi^2P_3}{[d(\alpha,\phi)]^2}\right](Nb)^2, \\ L_2 &= \frac{2}{63}\left[\frac{5(1-4\xi+2\xi^2)+21\xi^2P_1+20\xi(1-2\xi)P_2+9P_3\xi^2}{[d(\alpha,\phi)]^2}\right](Nb)^2. \end{aligned} \tag{33}$$

For rod case ($\alpha = 0$ or $\alpha = \pi$ or $\xi = 0$) we find $A = 10/3 - 2\tilde{\omega}/3$, $C_0^{(2)} = 5/42$, and $C_0^{(2)} = 10/63$, so that $L_1 = 5/126$ and $L_2 = 10/63$, which is in agreement with results of Shimada, Doi, and Okano [72] (please note that our definition of microscopic orientational order parameter Eq. (3) differs from the one used in Ref. [72] by factor 3/2).

The behavior of the rescaled coefficients $L_1/(Nb)^2$ and $L_2/(Nb)^2$ are shown in Fig. 7 as function of angle α. It follows from Fig. 7 that for small values of asymmetry parameter ($\phi = 1/6$ or $\phi = 1/4$), the functions $L_i/(Nb)^2$ ($i = 1,2$) are positive in the range $0 \leqslant \alpha < \pi$. As asymmetry parameter grows, these functions may become negative in some ranges of angle α; the more symmetric V-shaped molecule is, the wider is the range of negative values of the coefficients L_1 and L_2 (Fig. 7). Equation (27) can be written as [73]

$$F_2 = \frac{1}{V^2}\sum_{\mathbf{q}}\left\{\frac{3}{2}\left[A+\left(L_1+\frac{2L_2}{3}\right)q^2\right]\tilde{S}^{+}(\mathbf{q})\tilde{S}^{+}(-\mathbf{q})+\frac{1}{2}[A+L_1q^2][\tilde{S}^{-}(\mathbf{q})\tilde{S}^{-}(-\mathbf{q})+4\tilde{S}_{xy}(\mathbf{q})\tilde{S}_{xy}(-\mathbf{q})]\right.$$
$$\left.+2\left[A+\left(L_1+\frac{L_2}{2}\right)q^2\right][\tilde{S}_{xz}(\mathbf{q})\tilde{S}_{xz}(-\mathbf{q})+\tilde{S}_{yz}(\mathbf{q})\tilde{S}_{yz}(-\mathbf{q})]\right\}, \quad (34)$$

where $\tilde{S}^{\pm}(\mathbf{q}) = \tilde{S}_{xx}(\mathbf{q}) \pm \tilde{S}_{yy}(\mathbf{q})$. If, for example, coefficient L_1 becomes negative [Fig. 7(a)], the quadratic Eq. (34) ceases to be positive definite and the isotropic system could lose its stability at some nonzero wave vector with respect to formation of a modulated state. However, to correctly describe this case, one has to take into account the expansion of second–fourth contributions into the Landau–de Gennes free energy at least up to q^4. Since only the lowest orders of $\nabla\mathbf{S}$ terms were considered, the Frank elastic constants K_i (K_1 (splay), K_2 (twist), and K_3 (bend)) are proportional to L_1 and L_2: $K_1 = K_3 \sim (2L_1 + L_2)$, $K_2 \sim 2L_1$ [74]; hence, for this model of V-shaped molecule, the K_3 constant may become negative for some ranges of angle α.

V. CONCLUSION

The phase behavior of a thermotropic melt of asymmetric V-shaped molecules has been inspected within the Landau–de Gennes approach. The coefficients of the Landau-de Gennes free-energy expansion have been found from microscopic model of V-shaped molecule, that is assumed to be composed of two rigid segments of different lengths joined at their ends at an external angle α; each segment consists of a sequence of monomer units. The asymmetry of molecules is characterized by parameter ϕ, which is the number fraction of monomer units in one of the two segments. No regions of stability of oblate uniaxial or biaxial nematic phases have been found for $0 \leqslant \phi < 1/3$ and $2/3 < \phi \leqslant \pi$ ranges; only the I-$\mathrm{N}_{\mathrm{U}}^{+}$ transition takes place if asymmetry parameter falls in these ranges, the temperature of I-$\mathrm{N}_{\mathrm{U}}^{+}$ transition decreases for $0 < \alpha < \pi$ as parameter ϕ increases in $0 \leqslant \phi < 1/3$ or decreases in $2/3 < \phi \leqslant \pi$ ranges. For $\phi = 1/3$ or $\phi = 2/3$, there is a single Landau point in (α-$\tilde{\omega}$) plane located at $\alpha = \pi/2$, $\tilde{\omega} = 15$, at which direct continuous transition from isotropic to biaxial nematic state occurs. The stable isotropic, prolate uniaxial, and biaxial nematic phases are found for $\phi = 1/3$ and $\phi = 2/3$ values. There are two Landau points $\alpha_1^*(\phi)$ and $\alpha_2^*(\phi)$ if the asymmetry parameter varies in the range $1/3 < \phi < 2/3$. The difference $|\alpha_1^*(\phi) - \alpha_2^*(\phi)|$ grows as asymmetry parameter ϕ increases in range $1/3 < \phi \leqslant 1/2$ (or decreases in range $1/2 \leqslant \phi < 2/3$) and attains maximal value at $\phi = 1/2$. In addition to I, $\mathrm{N}_{\mathrm{U}}^{+}$, and N_{B} phases, a stable oblate uniaxial $\mathrm{N}_{\mathrm{U}}^{-}$ phase is revealed if asymmetry parameter varies in range $1/3 < \phi < 2/3$. The temperature of I-$\mathrm{N}_{\mathrm{U}}^{-}$ transition increases as ϕ varies in the range $1/3 < \phi \leqslant 1/2$ and decreases if ϕ falls within range $1/2 \leqslant \phi < 2/3$. The regions of stability of the biaxial nematic phase become considerably smaller as value of asymmetry parameter increases from $1/3$ to $1/2$ (or decreases from $2/3$ to $1/2$).

Despite the obvious drawback of using only the anisotropic interactions, the model predicts that asymmetry in lengths of arms has strong effect on the phase behavior of a melt of V-shaped molecules. Molecular asymmetry is responsible for the shift in angles that correspond to the Landau points; for special values of asymmetry parameter there is only one Landau point, while strong asymmetry in lengths of arms of V-shaped molecule results in disappearance of the Landau points and regions of stability of the biaxial nematic phase.

Coefficients of the lowest-orders gradient terms have been found that enables us to determine the dependence of the related elastic constants on the asymmetry parameter and angle between arms of a V-shaped molecule. It was found that for more symmetric molecule the coefficients of the gradient terms L_1 and L_2 Eq. (33) can become negative for some ranges of angle α. The value of the bend elastic constant K_3 (that is proportional to $(2L_1 + L_2)$ if only the lowest gradient terms are considered) also can pass through zero and become negative as angle α varies in range $[0,\pi)$. This result is consistent with the key assumption of Dozov's theory [60] of mechanism of formation of N_{TB} phase. However, it should be stressed that to describe with this model the transition into N_{TB} phase one has to find the expansion of second–fourth contributions into the Landau–de Gennes free energy at least up to q^4; note that such an expansion will correspond to taking into account of the gradient terms of higher orders like $(\nabla\mathbf{S})^4$. We hope that this will be a subject of further study.

APPENDIX A: COEFFICIENTS OF THE LANDAU–DE GENNES EXPANSION

The procedure of finding of the Landau–de Gennes expansion of the model at hand can be divided into several steps. At the first step, one is supposed to expand the partition function Eq. (7) in the functional power series of fields $h_{\alpha\beta}(\mathbf{x})$ and to calculate the coefficients of the expansion. These coefficients are the correlation function of nematic densities defined by

$$K^{(n)}_{(\alpha_1\beta_1)\dots(\alpha_n\beta_n)}(\mathbf{r}_1,\dots,\mathbf{r}_n) = \frac{1}{N}\overline{\hat{S}_{\alpha_1\beta_1}(\mathbf{r}_1;N)\dots\hat{S}_{\alpha_n\beta_n}(\mathbf{r}_n;N)}, \quad (\mathrm{A1})$$

where nematic density $\hat{S}_{\alpha\beta}(\mathbf{r};N)$ for the individual chain is defined by Eq. (7). The overline in Eq. (A1) denotes the averaging over conformations of molecules

$$\overline{(\dots)} = \frac{\int d\mathbf{r}_1\dots\mathbf{r}_N W(\{\mathbf{r}_j\};\alpha)(\dots)}{\int d\mathbf{r}_1\dots\mathbf{r}_N W(\{\mathbf{r}_j\};\alpha)}, \quad (\mathrm{A2})$$

where statistical weight of conformation $\{\mathbf{r}_j\}$ is given by Eq. (1). At the second step, the expansion of free energy of a single molecule Eq. (6) in the functional power series of fields $h_{\alpha\beta}(\mathbf{x})$ is to be found; the coefficients of this expansion are the irreducible correlators of nematic densities derived from the correlation functions Eq. (A1). Finally, one has to perform a Legendre transform [75] as prescribed by Eqs. (5). For the space-independent-order parameter Eq. (8) this procedure yields the following coefficients of the Landau–de Gennes expansion of free energy of a melt Eq. (9):

$$\gamma_2 = \frac{5}{3d(\alpha,\phi)}, \tag{A3}$$

$$\gamma_3 = -\frac{100}{63}\left[\frac{1-3\xi(1-P_2)}{[d(\alpha,\phi)]^3}\right], \tag{A4}$$

$$\gamma_4 = \frac{25}{441[d(\alpha,\phi)]^5}\left\{\frac{5}{2} + d(\alpha,\phi)\left[\frac{29}{2} - 73(1-P_2)\xi + \left(98{P_2}^2 - 76P_2 - 36P_4 + 14\right)\xi^2\right]\right\}, \tag{A5}$$

$$\begin{aligned}\gamma_5 = {}& \frac{1000(3\xi(1-P_2)-1)}{33\,957[d(\alpha,\phi)]^7}\Big\{\Big[-\frac{8}{3}(1-P_2)\big(539{P_2}^2 - 298P_2 - 234P_4 - 7\big)\Big]\xi^3 + \Big[\frac{12\,449}{9}{P_2}^2 - \frac{16\,378}{9}P_2 - 284P_4 + \frac{6485}{9}\Big]\xi^2\\ & - \frac{1}{27}\Big[\frac{13\,201{P_2}^2 - 26\,822P_2 + 126P_4 + 13\,495}{1-P_2}\Big]\xi + \frac{2}{81}\Big[\frac{3484{P_2}^2 - 6758P_2 + 3337 - 63P_4}{(1-P_2)^2}\Big]\Big\},\end{aligned} \tag{A6}$$

$$\begin{aligned}\gamma_6^{(1)} = {}& \frac{500}{305\,918\,613[d(\alpha,\phi)]^9}\Big\{-360\,150\xi^3[d(\alpha,\phi)]^3P_6 + 6\,115\,824\xi^4[d(\alpha,\phi)]^2{P_4}^2 - 9\xi^2 d(\alpha,\phi)117\,975\\ & + d(\alpha,\phi)(330\,748 + 36\big(77\,077{P_2}^2 - 40\,319P_2 + 994\big)\xi^2 + 2(981\,541P_2 - 1\,089\,586)\xi)]P_4\\ & + \frac{196\,625}{8} + d(\alpha,\phi)\Big[\frac{5\,485\,447}{8} + 176(P_2-1)\big(343\,343{P_2}^4 - 427\,427{P_2}^3 + 188\,169{P_2}^2 - 40\,124P_2 + 5537\big)\xi^5\\ & + 22\big(5\,290\,285{P_2}^4 - 12\,023\,500{P_2}^3 + 9\,438\,582{P_2}^2 - 2\,402\,644P_2 - 24\,731\big)\xi^4 + 11\big(7\,685\,435{P_2}^3 - 15\,898\,365{P_2}^2\\ & + 10\,527\,657P_2 - 2\,458\,787\big)\xi^3 + \frac{11}{2}\big(6\,031\,355{P_2}^2 - 9\,615\,130P_2 + 4\,318\,049\big)\xi^2 + \frac{28\,606\,985}{4}(P_2-1)\xi\Big]\Big\},\end{aligned} \tag{A7}$$

$$\begin{aligned}\gamma_6^{(2)} = {}& \frac{1000}{101\,972\,871\big[d(\alpha,\phi)\big]^9}\Big\{29\,400\xi^3[d(\alpha,\phi)]^3P_6 - 45\xi^2 d(\alpha,\phi)[(6985 - 7056(1-P_2)\xi^2\\ & + 2(51\,601P_2 - 49\,837)\xi)d(\alpha,\phi) + 9438]P_4 + \Big[\frac{617\,595}{4} + (258\,720(5P_2-3)(1-P_2)^2)\,\xi^5\\ & + 660(P_2-1)\big(28\,028{P_2}^3 - 37\,174{P_2}^2 + 6297P_2 + 3633\big)\xi^4 + 330\big(P_2\big(52\,205{P_2}^2 - 103\,355P_2 + 67\,053\big) - 15\,511\big)\xi^3\\ & + 330\Bigg(P_2(21\,362P_2 - 35\,259) + \frac{32\,273}{2}\Bigg)\xi^2 - \frac{3\,323\,925}{2}(1-P_2)\xi\Big]d(\alpha,\phi) + \frac{39\,325}{4}\Big\},\end{aligned} \tag{A8}$$

where $d(\alpha,\phi)$ and ξ are given by Eqs. (32). The Legendre polynomials $P_n = P_n[\cos(\alpha)]$ $(n = 2,4,6)$ are given by the following expressions [76]:

$$\begin{aligned}P_2[\cos(\alpha)] &= [3\cos^2(\alpha) - 1]/2,\\ P_4[\cos(\alpha)] &= [35\cos^4(\alpha) - 30\cos^2(\alpha) + 3]/8,\\ P_6[\cos(\alpha)] &= [231\cos^6(\alpha) - 315\cos^4(\alpha) + 105\cos^2(\alpha) - 5]/16.\end{aligned} \tag{A9}$$

For the case of symmetric V-shaped chains ($\phi = 1/2$) the coefficients Eqs. (A3)–(A8) coincide with those given earlier in Ref. [27].

APPENDIX B: CALCULATION OF EXPANSION OF PAIR CORRELATION FUNCTION

The expression for the second-order correlation function Eq. (29) can be written as follows:

$$\begin{aligned}&\tilde{K}_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(\mathbf{q},-\mathbf{q})\\ &= \frac{1}{N}\frac{1}{4\pi}\sum_{l=0}^{\infty}P_l[\cos(\alpha)]\sum_{m=-l}^{l}\Bigg\{\sum_{j_1=1}^{N_1}\sum_{j_2=1}^{N_1}\int d\Omega_1 Y_{lm}^*(\theta_1,\phi_1)T_{\alpha_1\beta_1}(\theta_1,\phi_1)T_{\alpha_2\beta_2}(\theta_1,\phi_1)\exp{[iqb|j_2-j_1|\cos(\theta_1)]}\\ &\quad\times\int d\Omega_2 Y_{lm}(\theta_2,\phi_2) + 2\sum_{j_1=1}^{N_1}\sum_{j_2=N_1}^{N_1+N_2}\int d\Omega_1 Y_{lm}^*(\theta_1,\phi_1)T_{\alpha_1\beta_1}(\theta_1,\phi_1)\exp{[iqb(N_1-j_1)\cos(\theta_1)]}\end{aligned}$$

$$\times \int d\Omega_2 Y_{lm}(\theta_2,\phi_2) T_{\alpha_2\beta_2}(\theta_2,\phi_2) \exp\left[iqb(j_2-N_1)\cos(\theta_2)\right] + \sum_{j_1=N_1}^{N_1+N_2} \sum_{j_2=N_1}^{N_1+N_2} \int d\Omega_1 Y^*_{lm}(\theta_1,\phi_1)$$

$$\times \int d\Omega_2 Y_{lm}(\theta_2,\phi_2) T_{\alpha_1\beta_1}(\theta_2,\phi_2) T_{\alpha_2\beta_2}(\theta_2,\phi_2) \exp\left[iqb|j_2-j_1|\cos(\theta_2)\right] \Bigg\}. \tag{B1}$$

In Eq. (B1), $d\Omega = \sin(\theta)d\theta d\phi$, $Y_{lm}(\theta,\phi)$ is the spherical harmonics [77], $Y^*_{lm}(\theta,\phi)$ is the conjugated one, and the following notation has been used:

$$T_{\alpha\beta}(\theta,\phi) = \tfrac{1}{2}(3\zeta_\alpha\zeta_\beta - \delta_{\alpha\beta}), \quad \alpha,\beta = x,y,z,$$
$$\zeta_x = \sin(\theta)\cos(\phi), \quad \zeta_y = \sin(\theta)\sin(\phi), \quad \zeta_z = \cos(\theta). \tag{B2}$$

After replacement of the summations in Eq. (B1) with an integrals the expansion of function $\tilde{K}_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(\mathbf{q},-\mathbf{q})$ yields in the lowest order

$$\tilde{K}_{(\alpha_1\beta_1)(\alpha_2\beta_2)}(\mathbf{q},-\mathbf{q}) = A_{(\alpha_1\beta_1)(\alpha_2\beta_2)} + (qb)^2 B_{(\alpha_1\beta_1)(\alpha_2\beta_2)} + \ldots, \tag{B3}$$

where $q = |\mathbf{q}|$ and the following notations have been used:

$$\begin{aligned}
A_{(xx)(xx)} &= -2A_{(xx)(yy)} = A_{(yy)(yy)} = \frac{4}{3}A_{(xy)(xy)} \\
&= \frac{4}{3}A_{(xz)(xz)} = \frac{4}{3}A_{(yz)(yz)} = a, \\
B_{(xx)(xx)} &= B_{(yy)(yy)} = b_1 + b_2, \quad B_{(xx)(yy)} = b_1 - \frac{1}{4}b_2, \\
B_{(xy)(xy)} &= \frac{5}{8}b_2, \quad B_{(xz)(xz)} = B_{(yz)(yz)} = \frac{9}{4}b_1 + b_2, \\
a &= \frac{N}{5}[1 - 2\xi(1 - P_2)], \\
b_1 &= \frac{N^3}{900}\left[-(2\xi^2 + 1 - 4\xi) - 6\xi^2 P_1 + 4\xi(2\xi - 1)P_2\right], \\
b_2 &= \frac{N^3}{350}\left[-(2\xi^2 + 1 - 4\xi) + 4\xi(2\xi - 1)P_2 - 6\xi^2 P_3\right],
\end{aligned} \tag{B4}$$

where only nonzero elements of matrix Eq. (B3) are presented in Eqs. (B4). In turn, to the lowest order in q^2 the elements of matrix $\tilde{K}^{(-1)}(\mathbf{q},-\mathbf{q})$ Eq. (29) are given by

$$\begin{aligned}
\left(\tilde{K}^{(-1)}(\mathbf{q},-\mathbf{q})\right)_{(\alpha_1\beta_1)(\alpha_2\beta_2)} &= \hat{A}_{(\alpha_1\beta_1)(\alpha_2\beta_2)} + (qb)^2 \hat{B}_{(\alpha_1\beta_1)(\alpha_2\beta_2)} + \ldots, \\
\hat{A}_{(xx)(xx)} &= 2\hat{A}_{(xx)(yy)} = 2\hat{A}_{(yy)(xx)} = \hat{A}_{(yy)(yy)} \\
&= \hat{A}_{(xy)(xy)} = \hat{A}_{(xz)(xz)} = \hat{A}_{(yz)(yz)} = \frac{4}{3a}, \\
\hat{B}_{(xx)(xx)} &= \hat{B}_{(yy)(yy)} = \hat{B}_{(xz)(xz)} = \hat{B}_{(yz)(yz)} = -\frac{4(9b_1 + 4b_2)}{9a^2}, \\
\hat{B}_{(xx)(yy)} &= \hat{B}_{(yy)(xx)} = -\frac{(36b_1 + 11b_2)}{9a^2}, \quad \hat{B}_{(xy)(xy)} = -\frac{10b_2}{9a^2}.
\end{aligned} \tag{B5}$$

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