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Free energy power expansion for orientationally ordered phases: energy and entropy

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Abstract

We propose a new approach for description of orientational phase transitions that utilizes the specific features of the orientational energy and entropy. The approach is applied to build a model for nematic phases in materials with non-polar parallelepiped-type molecules with symmetry D_{2h} . The model operates with complex order parameters, generalizes the Landau-deGennes theory and predicts the existence of a biaxial nematic phase for the fourth order expansion of free energy.

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Introduction. An orientational order of anisometric molecules provides a rich variety of phases and phase transitions in liquid crystals, polymers and other soft matter systems [1–3]. Recently, orientational transitions in materials with molecules of complex non-symmetric shape have attracted the strong interest because of the possibility of biaxial nematic phase, see e.g. review [4]. However there is no commonly accepted view on the existence and observation of the biaxial nematic phase in thermotropic liquid crystals yet. [5–11]. The theoretical studies of the liquid crystal phases are usually performed within three approaches: (1) the microscopic models where the specific intermolecular interaction is averaged over orientations of neighboring molecules to produce the mean potential [12–14], (2) the Landau phenomenological power expansion of the free energy in terms of the corresponding order parameters (OPs) [1, 2, 15–17], and (3) computer simulations [18]. Orientationally-ordered phases are often characterized by the multicomponent OPs, thus even the lowest fourth order Landau expansion contains many terms, e.g. 14 terms for nematic phases [19].

In this Rapid Communication, we propose a new approach for description of orientational phase transitions that utilizes the following specific features of the orientational energy E and entropy S : (a) S possesses an additional symmetry in comparison with E , being invariant under rotation of the molecular frame; and (b) E contributes only to the second order terms because the pair molecular interaction is dominant. The approach is based on minimization of the scaled orientational free energy $\bar{F} = F/T = E/T - S$ instead of F because \bar{F} obeys the standard assumption of the Landau theory that only the second order terms are temperature dependent. We apply the approach to build a model for nematic phases in materials with non-polar parallelepiped-type molecules with symmetry D_{2h} . The presented model introduces complex OPs, generalizes the Landau-de Gennes (LdeG) theory and predicts the existence of a biaxial nematic phase for the fourth order expansion of \bar{F} .

General approach. We derive \bar{F} per molecule considering \bar{F} of the isotropic state as zero reference point and using the same units for energy and temperature with the Boltzmann constant $k_B = 1$. The orientational order is described either by symmetric traceless tensor OPs [1, 15–17] or by the averaged Wigner D-functions $\langle D_{mk}^L \rangle$ [13, 20–22]. We chose the latter because $D_{mk}^L(\mathbf{\Omega})$ form a complete set of orthogonal functions of the Euler angles $\mathbf{\Omega} = \{\omega_1, \omega_2, \omega_3\}$ [23]; $\mathbf{\Omega}$ define the molecular orientation through rotation $\mathbb{L} \xrightarrow{\mathbf{\Omega}} \mathbb{M}$ from the laboratory frame \mathbb{L} to the molecular frame \mathbb{M} . A set of OPs $\langle D_{mk}^L \rangle$ obtained by averaging with the single molecule orientational distribution function $f(\mathbf{\Omega})$ is complete and is

equivalent to $f(\mathbf{\Omega})$

$$f(\mathbf{\Omega}) = \sum_{L=0}^{\infty} \frac{2L+1}{8\pi^2} \sum_{m,k=-L}^L \langle D_{mk}^L \rangle D_{mk}^{L*}(\mathbf{\Omega}) \quad (1)$$

where $D_{mk}^{L*}(\mathbf{\Omega}) = (-1)^{m-k} D_{-m-k}^L(\mathbf{\Omega})$. OPs $\langle D_{mk}^L \rangle$ provide a unified description of orientationally ordered phases: polar, nematic, and tetrahedral phases correspond to $L = 1, 2, 3$, respectively.

Being scalars, E and S are invariant under the rotation $\mathbb{L} \xrightarrow{\mathbf{\Phi}} \mathbb{L}'$ from one laboratory frame \mathbb{L} to another \mathbb{L}' with the Euler angles $\mathbf{\Phi}$. If we neglect the intermolecular correlations, E contains only the second order terms with the same L [22]

$$E = -\frac{1}{2} \sum_{L=1}^{\infty} \sum_{m,k=-L}^L U_L(k_1 k_2) \langle D_{mk_1}^L \rangle \langle D_{-mk_2}^L \rangle \quad (2)$$

where $U_L(k_1 k_2)$ are the parameters of intermolecular interactions.

We assume that S possesses an additional symmetry: the expression for S does not depend on the choice of the molecular frame and thus is invariant under the rotation $\mathbb{M} \xrightarrow{\mathbf{\Psi}} \mathbb{M}'$ from one molecular frame \mathbb{M} to another \mathbb{M}' . The reason for this 'molecular isotropy' is that S is expressed through the invariant integral of the orientational distribution function $f_\nu(\mathbf{\Omega}^\nu)$ over the orientational space $\mathbf{\Omega}^\nu$ of the ν molecules' system

$$S = -\nu^{-1} \int f_\nu(\mathbf{\Omega}^\nu) \log [(8\pi^2)^\nu f_\nu(\mathbf{\Omega}^\nu)] \mathbf{d}\mathbf{\Omega}^\nu. \quad (3)$$

We can directly prove this assumption if we neglect the orientational correlations and $f_\nu(\mathbf{\Omega}^\nu) = \prod_{n=1}^{\nu} f(\mathbf{\Omega}_n)$, where $\mathbf{\Omega}_n$ is a set of the Euler angles of the n^{th} molecule. Then

$$S = - \int f(\mathbf{\Omega}) \log [8\pi^2 f(\mathbf{\Omega})] \mathbf{d}\mathbf{\Omega}, \quad (4)$$

and we construct S as an invariant power series in $\langle D_{mk}^L \rangle$ using the power expansion for $\log(1+x)$ in (4), where 1 stems from the term $L=0$ in (1); expressions (4) and (1) remain the same in different \mathbb{M} and therefore the power series does not depend on \mathbb{M} either.

In the standard models, the energy (2) usually contains OPs with one or few values of L , $L \in \{\bar{L}_i\}$. In this case, we can *a priori* maximize S with respect to all $\langle D_{mk}^L \rangle$ with $L \notin \{\bar{L}_i\}$. Then the maximized entropy \bar{S} remains invariant and contains only terms with $L \in \{\bar{L}_i\}$ that can be derived using their transformational properties.

Thus the proposed approach contains the following steps: (a) selection of the orientational OPs $\langle D_{mk}^L \rangle$ that describe the phases of interest and determine the expression for orientational energy E , (b) derivation of the invariant terms of \bar{S} that contain $\langle D_{mk}^L \rangle$, (c) determination of the phase diagram by minimization of scaled free energy $\bar{F} = E/T - S$.

Free energy for nematics with molecular symmetry D_{2h} . To illustrate our approach and demonstrate how the invariant form of \bar{S} is derived, we present a model for nematic phases in materials with molecular symmetry D_{2h} . The nematic phases are described by the OPs $R_{mk} = \langle D_{mk}^2 \rangle$ and by energy (2) with $L = 2$. D_{2h} molecules in nematic phases have four independent OPs, that have the simplest representation R_{00} , $R_{20} = R_{\pm 20}$, $R_{02} = R_{0\pm 2}$, $R_{22} = R_{\pm 2\pm 2}$ in the molecular frame defined by the symmetry axes and planes and in the laboratory frame along the directors [20, 21]. R_{00} and R_{20} describe, respectively, the uniaxial and biaxial orientational orderings of the long molecular axis $\hat{\mathbf{e}}_3$ and related to the traceless tensor order parameter $\mathbf{Q} = \langle \hat{\mathbf{e}}_3 \otimes \hat{\mathbf{e}}_3 \rangle - \mathbf{I}/3$ [1, 3]. R_{02} and R_{22} describe, respectively, the uniaxial and biaxial orderings of the short axes $\hat{\mathbf{e}}_{1,2}$ and are equivalent to the tensor $\mathbf{B} = \langle \hat{\mathbf{e}}_1 \otimes \hat{\mathbf{e}}_1 - \hat{\mathbf{e}}_2 \otimes \hat{\mathbf{e}}_2 \rangle$ [14]. The scaled orientational energy $\bar{E} = E/T$ is defined as [22]

$$\bar{E} = -\frac{u}{2} [R_{00}^2 + 2R_{20}^2 + 4\gamma (R_{00}R_{02} + 2R_{20}R_{22}) + 4\lambda (R_{02}^2 + 2R_{22}^2)], \quad (5)$$

where $u = U_2(00)/T$ is proportional to the inverse temperature and $\gamma = U_2(\pm 20)/U_2(00)$ and $\lambda = U_2(\pm 2, \pm 2)/U_2(00)$ are dimensionless parameters that describe the anisotropy of intermolecular interaction [24].

The general expression of the power expansion of \bar{S} in R_{mk}

$$\bar{S} = - \sum_{N, m_n, k_n} H_N(m_1, k_1, \dots, m_N, k_N) \prod_{n=1}^N R_{m_n k_n} \quad (6)$$

is invariant with respect to the rotations of the laboratory $\mathbb{L} \xrightarrow{\Phi} \mathbb{L}'$ and molecular $\mathbb{M} \xrightarrow{\Psi} \mathbb{M}'$ frames. Because of the independence of the rotations with Φ and Ψ , we present H_N as

$$H_N(m_1, k_1, \dots, m_N, k_N) = \sum_{\alpha\beta} H_N^{\alpha\beta} h_N^\alpha(m_1, \dots, m_N) h_N^{\beta*}(k_1, \dots, k_N). \quad (7)$$

Here $H_N^{\alpha\beta}$ is an arbitrary numeric coefficient for an invariant term and $h_N^\alpha(m_1, \dots, m_n, \dots, m_N)$ is the α^{th} solution of the equation

$$\sum_{m_n} h_N^\alpha(m_1, \dots, m_N) \prod_{n=1}^N D_{m_n l_n}^2(\Phi) = h_N^\alpha(l_1, \dots, l_N). \quad (8)$$

for an arbitrary Φ . Using the standard expressions for the products of D-functions [23], we obtain the solutions of (8)

$$h_N^\alpha(m_1, \dots, m_N) = \prod_{n=1}^N \langle M_{n-1} \bar{m}_{n-1} \ 2m_n | M_n \bar{m}_n \rangle, \quad (9)$$

where $\bar{m}_n = \bar{m}_{n-1} + m_n$, $M_0 = \bar{m}_0 = M_N = \bar{m}_N = 0$, and α runs over α_N possible sets $\{M_1 \dots M_{N-1}\}$ that provide non-zero products of Clebsch-Gordan coefficients $\langle M_{n-1} \bar{m}_{n-1} \ 2m_n | M_n \bar{m}_n \rangle$ in (9), see Fig. 1. There is no solution for $N = 1$, and there are single solutions for $N = 2$ and for $N = 3$. For higher orders $N \geq 4$, the number of solutions of (9) α_N drastically increases: $\alpha_4 = 5$, $\alpha_5 = 16$, $\alpha_6 = 65$, etc. Thus expressions (6),(7), and (9) contain α_N^2 invariant N^{th} order terms, however these α_N^2 terms may contain the same combinations of R_{mk} and the actual number of independent invariants is substantially smaller.

We use MathematicaTM to analyze terms in \bar{S} , (6), and have found that the fourth order entropy \bar{S}_4 has 4 independent invariants:

$$\bar{S}_4 = - \left(\frac{a}{2} I_2 - \frac{b}{3} I_3 + \frac{c_1}{4} I_2^2 + \frac{c_2}{4} I_4 \right) \quad (10)$$

where $I_2 = R_{00}^2 + 2(R_{20}^2 + R_{02}^2) + 4R_{22}^2$, $I_3 = R_{00}^3 + 24R_{20}R_{02}R_{22} + 6R_{00}(2R_{22}^2 - R_{20}^2 - R_{02}^2)$, and $I_4 = J_2^2$. $J_2 = 4(R_{00}R_{22} - R_{20}R_{02})$ is the second order so-called pseudoinvariant because it changes its sign under $\pi/2$ rotation around the long molecular axis or the long director.

The sixth order expansion has additional 7 terms:

$$\bar{S}_6 = \bar{S}_4 - \left(\frac{d_1}{5} I_2 I_3 + \frac{d_2}{5} I_5 + \frac{e_1}{6} I_2^3 + \frac{e_2}{6} I_3^2 + \frac{e_3}{6} I_2 I_4 + \frac{e_4}{6} I_{6s} + \frac{e_5}{6} I_{6a} \right), \quad (11)$$

where $I_5 = J_2 J_3$, $I_{s6} = J_3^2$, $J_3 = 6R_{00}R_{20}R_{02} + 3R_{22}(R_{00}^2 - 2R_{20}^2 - 2R_{02}^2) + 4R_{22}^3$ is the third order pseudoinvariant, and $I_{a6} = 4(R_{02}^2 - R_{22}^2)^3 + 3[(R_{00}^2 + 2R_{20}^2)^2 (R_{02}^2 + 2R_{22}^2) + 2(R_{00}R_{02} + 2R_{20}R_{22})^2 (R_{00}^2 + 2R_{20}^2 - 2R_{02}^2 - 4R_{22}^2)]$. The obtained invariants are similar to the terms in Refs.[25, 26].

Expressions (6),(7), and (9) provide a general explicit form for the power expansion of the maximized entropy \bar{S} for nematic OPs ($L = 2$). This form is further simplified by extracting independent combinations of OPs taking into account the molecular symmetry D_{2h} (10,11). The method is straightforward and can be easily applied for phases with other orientational OPs.

Complex order parameters. To simplify analysis of nematic phases we introduce uniaxial $\tilde{s} = R_{00} + i\sqrt{2}R_{02} = s e^{i\alpha}$ and biaxial $\tilde{p} = \sqrt{2}R_{20} + 2iR_{22} = p e^{i\beta}$ complex OPs, where their phases α and β determine the ratios between the short and long molecular axis orderings. \tilde{s} and \tilde{p} are equivalent to any set of four order parameters, systematized in [27], e.g. $\tilde{s} = S + iU$, $\tilde{p} = P + iF$. They also allow us to build the complex tensor OP $\mathbf{C} = \mathbf{Q} + \frac{i}{\sqrt{3}}\mathbf{B}$ with the diagonal form $\{-(\tilde{s} - \sqrt{3}\tilde{p})/3, -(\tilde{s} + \sqrt{3}\tilde{p})/3, 2\tilde{s}/3\}$ in the laboratory frame along the directors.

Complex OPs provide several advantages. First, \mathbf{C} determines any second-rank susceptibility tensor $\bar{\chi}$ that is an orientational average of molecular tensor χ

$$\bar{\chi} = \chi_{iso}\mathbf{I} + \text{Re}[\tilde{\chi}\mathbf{C}], \quad (12)$$

where \mathbf{I} is a unit tensor and $\tilde{\chi} = \chi_u - i\sqrt{3}\chi_b/2$. Here $\chi_{iso} = (\chi_1 + \chi_2 + \chi_3)/3$, $\chi_u = \chi_3 - (\chi_1 + \chi_2)/2$ and $\chi_b = \chi_1 - \chi_2$ are, respectively, isotropic, uniaxial and biaxial combinations of the diagonal components χ_i of the molecular tensor that is diagonal in the molecular frame $\chi_{ij} = \chi_i\delta_{ij}$.

Second, energy (5) and invariants I_n in (10,11) are even functions of the amplitude p ; e.g. \bar{E} contains the defined above $I_2 = \frac{3}{2}\text{Tr}(\mathbf{C}\mathbf{C}^*) = s^2 + p^2$ and the complex invariant $\tilde{I}_2 = \frac{3}{2}\text{Tr}(\mathbf{C}^2) = \tilde{s}^2 + \tilde{p}^2$:

$$\begin{aligned} \bar{E} &= -\frac{u}{2} \left[(1 - \tilde{v} - \tilde{v}^*) I_2 + \tilde{v} \tilde{I}_2 + \tilde{v}^* \tilde{I}_2^* \right] \\ &= -\frac{u}{2} \left\{ s^2 + p^2 - 2v \left[s^2 \sin \alpha \sin(\alpha - \theta) + p^2 \sin \beta \sin(\beta - \theta) \right] \right\}, \end{aligned} \quad (13)$$

where $\tilde{v} = \frac{1}{2} - \lambda - i\sqrt{2}\gamma = v e^{-i\theta}$ is the complex parameter that describes the anisotropy of intermolecular interaction, $0 \leq \theta \leq \pi/2$.

Third, the complex OP representation demonstrates that the presented model is a generalization of the LdeG theory [1, 15, 16], because the sixth order expansion $\bar{F}_6 = \bar{E} - \bar{S}_6$ reduces to the LdeG theory under the assumption $\alpha = \beta = 0$, that corresponds to the free molecular rotation around the long axis. However, this assumption is not valid (does not correspond to the absolute minimum) if $\gamma \neq 0$ or $\lambda \neq 0$, see below.

Phase diagram for uniaxial and biaxial nematics. The LdeG theory forbids N_b phase in the fourth order expansion, allowing its existence only with the sixth order terms [1, 15, 16]. However, in our model N_b phase already appears in the fourth order expansion $\bar{F}_4 = \bar{E} - \bar{S}_4$, which we analyze using $\tilde{s} = s e^{i\alpha}$ and $\tilde{p} = p e^{i\beta}$ representation

$$\bar{F}_4 = \bar{F}_{uni} + \frac{1}{2} [g_0 - g_2 \cos(2\beta - \psi)] p^2 + \frac{c_1}{4} p^4 \quad (14)$$

where

$$\bar{F}_{uni} = \frac{s^2}{12} [6(a - u + uv \cos \theta - uv \cos(2\alpha - \theta)) - 4bs \cos 3\alpha + 3s^2 c_1] \quad (15)$$

and $g_0 = a - u + uv \cos \theta + (c_1 + c_2) s^2$; g_2 and ψ are, respectively, the amplitude and phase of the complex term $g_2 e^{i\psi} = uv \cos \theta + c_2 s^2 - 2bs \cos \alpha + i[uv \sin \theta + 2s(b + c_1 s \cos \alpha) \sin \alpha]$.

The uniaxial phase is described by s_u and α_u , obtained by minimization of F_{uni} , (15). The last two terms in \bar{F}_{uni} create 2-fold and 3-fold radial valleys in polar coordinates (s, α) with minima at $\alpha = \pi n + \theta/2$ and $\alpha = 2\pi n/3$, respectively. Thus the absolute minimum corresponds either to calamitic phase, $0 < \alpha < \theta/2$, if $0 \leq \theta \leq \pi/3$, or to discotic phase, $\pi + \theta/2 < \alpha < 2\pi/3$ if $\pi/3 \leq \theta \leq \pi/2$. The phase transition between calamitic and discotic phases is impossible because the balance between them is not affected by temperature factor u . Below we consider the case, when $0 \leq \theta \leq \pi/3$ and the uniaxial phase is calamitic with $0 < \alpha < \theta/2 \leq \pi/6$.

To simplify analysis of (14,15), we set $a = c_1 = 1$ without losing generality, because (14,15) transform into the normalized free energies $(\hat{F}_4, \hat{F}_{uni}) = (\bar{F}, \bar{F}_{uni}) a^2/c_1$, with normalized OP amplitudes $(\hat{s}, \hat{p}) = (s, p) \sqrt{c_1/a}$ and parameters $\hat{b} = b/\sqrt{c_1 a}$, $\hat{c}_2 = c_2/c_1$, $\hat{u} = u/a = T^*/T$, where T^* is the low temperature limit of the metastable isotropic phase; parameter $\tilde{v} = v e^{-i\theta}$ and phases α, β, ψ remain unchanged. The normalization also allows us to analyze the nematic phases only when $\hat{u} < 1.6$, because the temperature range of nematic phases rarely exceeds 150° .

For small v , both N_u and N_b phases occur; typical temperature dependencies of OPs are shown in Fig.2. The N_b phase is enclosed by two N_u phases with second order phase transitions between them, $N_u \xleftrightarrow{2} N_b$, Fig.2.

When $\theta < \pi/4$, the effect of θ on the phase diagram is rather small, because $\alpha \lesssim \theta/8$ and $\beta = \psi/2 \approx \pi/2$, Fig.2. Figure 3 presents phase diagrams in $\{v, \hat{u}\}$ coordinates for several sets of $\{\hat{b}, \hat{c}_2\}$ parameters, when $\theta = 0$ and \hat{F}_4 reaches the minimum at $\alpha = 0$ and $\beta = \pi/2$. N_b phase occurs if $v < v_b = (\hat{b}^2 - 4\hat{c}_2 + 2\sqrt{\hat{b}^2 - 2\hat{b}^2\hat{c}_2 + 4\hat{c}_2})/(8 - 2\hat{b}^2)$. N_b phase appears under the cooling (\hat{u} increasing) through $N_u \xleftrightarrow{2} N_b$ transition when $v_b > v > v_t = \hat{b}^2(3 - 2\hat{c}_2)/(9 - 2\hat{b}^2)$, or through $I \xleftrightarrow{1} N_b$ transition when $v < v_t$; $\{v_t, \hat{u}_t = 1 - 2\hat{b}^2/9\}$ is the triple point. If $\hat{c}_2 > 0$,

the further cooling can result in the second low-temperature N_u phase either through the second order transition, $N_b \xleftrightarrow{2} N_u$ or through the first order transition, $N_b \xleftrightarrow{1} N_u$, Fig.3. The temperature range of N_b phase is enhanced by \hat{b} and is suppressed by \hat{c}_2 and v . The shape of the phase diagrams in Fig.3 is similar to that observed in lyotropic materials [28]. However, this similarity should not be overstated as both calamitic and discotic uniaxial phases are present and may be caused by micelle shape transformation that effectively changes the interaction between micelles [28].

The obtained results clearly demonstrate why the LdeG theory shows no N_b phase for the fourth order expansion. The LdeG theory corresponds to the assumption $\beta = 0$ where as the minimum of \bar{F}_4 for N_b phase occurs when $\beta = \psi/2 \approx \pi/2$.

Conclusions. We demonstrated a new approach for description of orientational phase transitions. The approach provides a straightforward method for minimization of scaled free energy $\bar{F} = E/T - S$ in the space of selected orientational OPs that describe the phases of interest. We applied this approach for nematic phases with molecular symmetry D_{2h} building a model that generalizes the LdeG theory and predicts the biaxial N_b phase for the fourth order expansion of \bar{F} . \bar{F} has only the second order temperature dependent term in other theoretical models, e.g. Bragg-Williams theory, and may be useful for description of various types of phase transitions.

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Figure Captions

FIG. 1 Chains of arrows represent the solutions (9); each arrow $\{M_{n-1}, M_n\}$ corresponds

to $\langle M_{n-1} \tilde{m}_{n-1} \ 2m_n | M_n \tilde{m}_n \rangle$.

FIG. 2. (Color online) Temperature dependencies of normalized OP amplitudes \hat{s}, \hat{p} (solid) and OP phases α, β (dashed) in N_u (thin) and N_b (thick) phases for $\hat{b} = 0.5$, $\hat{c}_2 = 0.2$, $v = 0.09$, and $\theta = \pi/18$. The vertical line at $\hat{u}_{iu} = T^*/T_{iu}$, corresponds to the phase transition between isotropic and N_u phases at the temperature T_{iu} . Note that $\hat{s} = 0.37$ at \hat{u}_{iu} , thus the normalization factor for \hat{s} and \hat{p} is close to 1.

FIG. 3 (Color online) Phase diagrams in $\{\hat{u}, v\}$ plane for $\theta = 0$ and different sets of \hat{b} and \hat{c}_2 : (1) $\hat{b} = 0.5$, $\hat{c}_2 = 0.0$; (2) $\hat{b} = 0.5$, $\hat{c}_2 = 0.2$; (3) $\hat{b} = 0.6$, $\hat{c}_2 = 0.2$. Curves correspond to phase transitions: $I \xleftrightarrow{1} N_u$ (thin solid), $I \xleftrightarrow{1} N_b$ (thick solid), $N_u \xleftrightarrow{2} N_b$ (dotted), $N_u \xleftrightarrow{1} N_b$ (dashed).

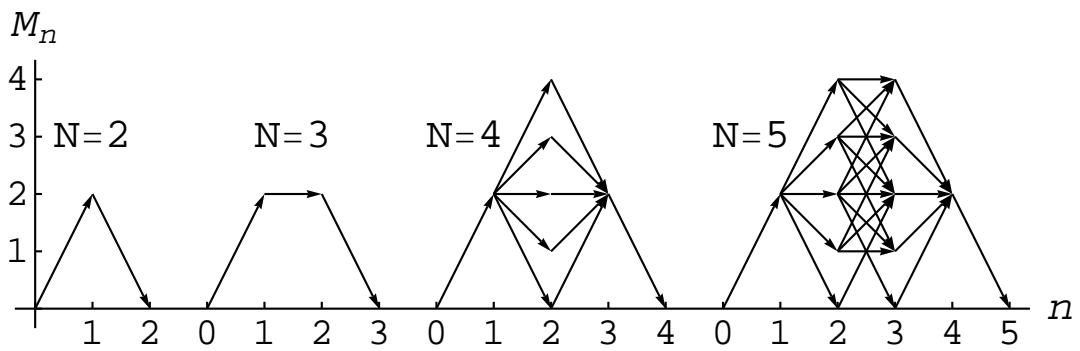


Figure 1

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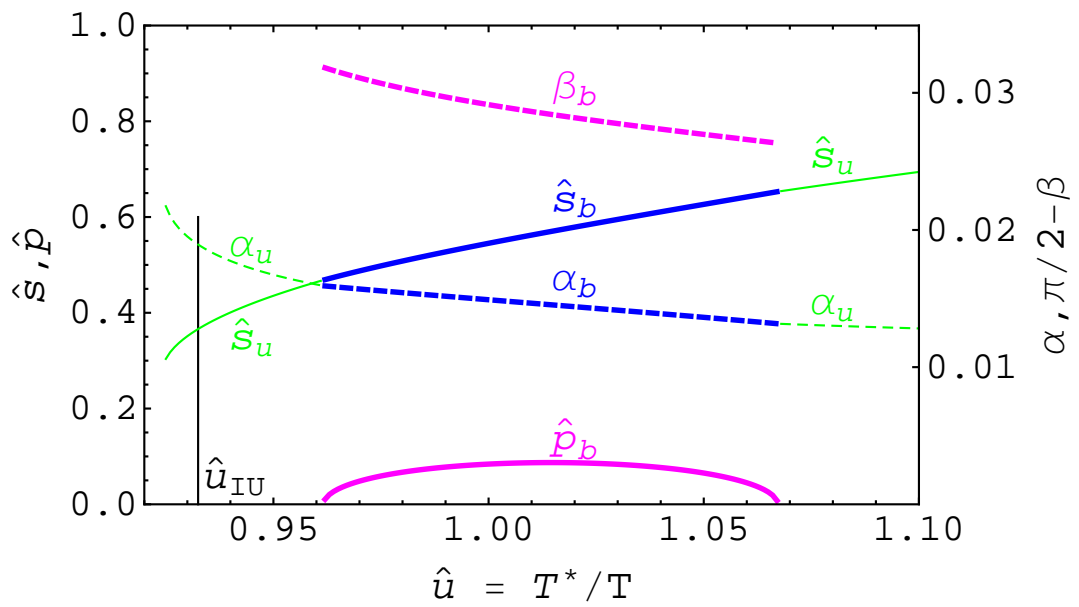


Figure 2 LS12872ER 03Jun2013

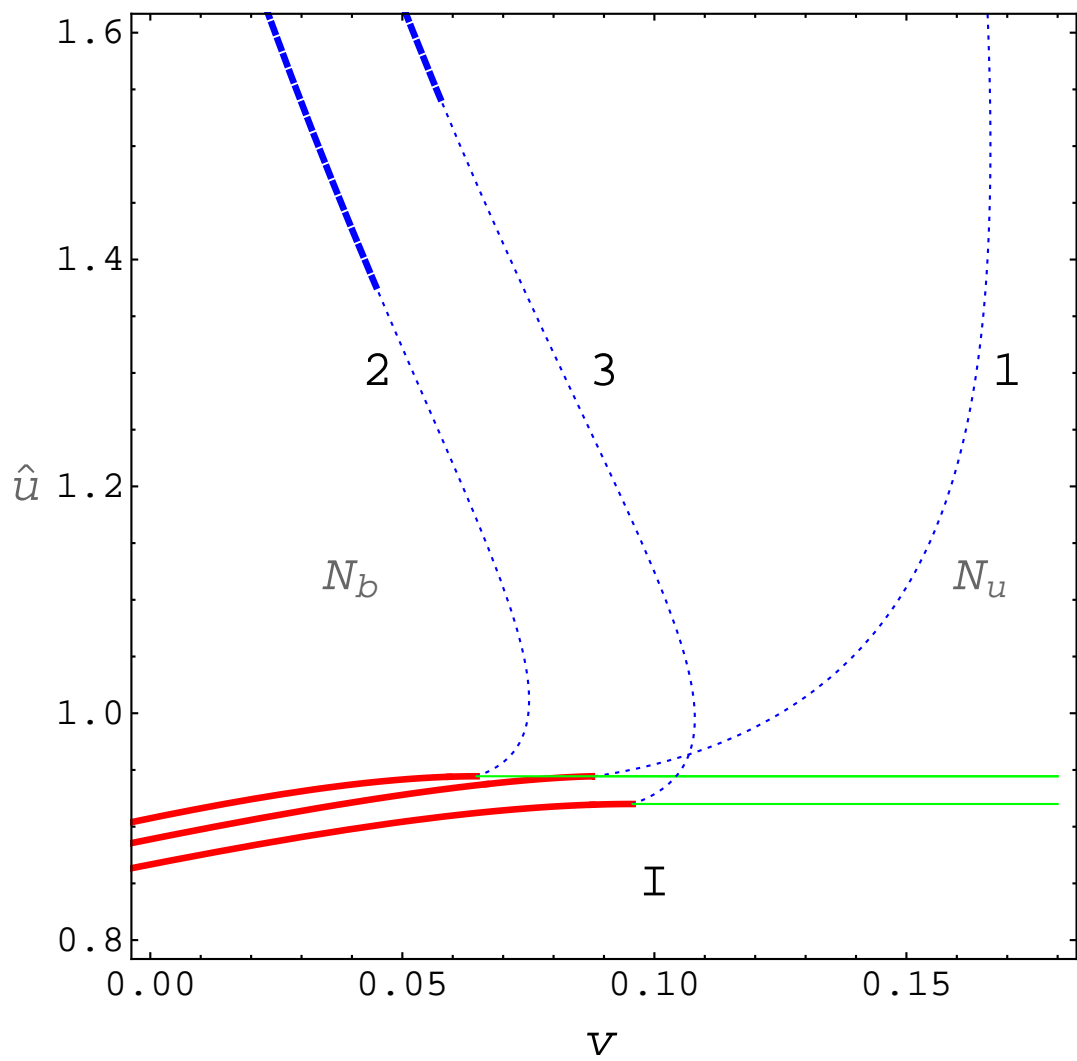


Figure 3 LS12872ER 03Jun2013