

Maier-Saupe and Onsager approaches as limits of the nematic-isotropic phase transition

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Through a virial expansion, the long and small range properties of the interaction between ellipsoidal nematic molecules are put together in a unique approach that combines the essentials of some classical models that describe the nematic-isotropic phase transition. The Lennard-Jones potential that mediates the interaction between the centers of the mass of molecules, the long range Maier-Saupe interaction that favors their alignment and the molecular hard core that hinders their close approximation, as in the Onsager model, are combined in a unique approach that exhibits two phases transitions; the gaseous-liquid transition and the nematic-isotropic phase transition. As a conclusion, the Onsager and Maier-Saupe approaches were considered limits of the actual physical situation.

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I. INTRODUCTION

Nematic liquid crystals [1] (NLC) are composed of highly anisotropic molecules that, under convenient conditions, are aligned along a macroscopic common direction [2]. Usually, this alignment is obtained through temperature variation and changes in the molecular concentration. At high temperatures NLC molecules do not show any orientational order but, as the temperature decreases, the nematic alignment arises through a first-order phase transition, i.e., through a thermotropic nematic-isotropic phase transition (NIPT) [1]. On the other hand, in lyotropics materials, the NIPT can be obtained through a change in the molecular concentration of the mixture. As the molecular concentration increases, the packing properties of these molecules induces their alignment [1]. In general, these two kinds of transitions are considered separately. For the thermotropics, the Maier-Saupe [3] approach stresses the role of a mean field produced by other molecules, inducing a mean alignment all over the sample. For the lyotropics, the approach commonly used is that of Onsager [4], which establishes that the entropy of the system becomes reduced when the molecules come close together in a parallel arrangement.

The question whether the NIPT is a strong correlated transition, such as the liquid-crystalline transition [6,7], or if it can be understood through the use of a small density theory of fluids, in which the pair-wise interaction of the particles dominates the scenario [5] remains unanswered.

In this work the NIPT will be studied through a molecular model that contains both aspects of the theories outlined above [2]. A virial expansion [8–10] for the thermodynamic functions, the anisotropic shape of the molecules as well as their long range anisotropic interaction will be explicitly considered. These distinct components of the theory will be controlled by a parameter that, by blending them, will reveal that the Maier-Saupe and Onsager approaches act as a kind of asymptotic limits for the NIPT. That is, both (the aligning interaction at distance between the molecules and their packing properties) contribute to the NIPT and the actual NIPT

results from the balance of these contributions.

This work is divided into three main sections. In Sec. I, the model that will be used in the study of the NIPT is presented. In Sec. II, the virial expansion used to deal with this model and some numerical results are presented. In Sec. III the numeral results are interpreted.

II. ESSENTIALS OF THE MODEL

This study takes into consideration an ensemble of non-punctual and nonspherical molecules to which the individual dynamic properties can be approximated by a symmetric ellipsoidal body with three inertial moments, I_1 , I_2 , and I_3 ($I_1 = I_2$). The kinetic energy of each of these molecules is given by [2]

$$K(p_i, p_{\theta_i}, p_{\phi_i}, p_{\psi_i}) = \frac{p_i^2}{2m} + \frac{p_{\theta_i}^2}{2I_1} + \frac{p_{\psi_i}^2}{2I_3} + \frac{(p_{\phi_i} - p_{\psi_i} \cos \theta)^2}{2I_1 \sin^2 \theta_i}, \quad (1)$$

where θ , ϕ , and ψ are the Euler's angles, p_{θ} , p_{ϕ} , and p_{ψ} are the conjugated canonical moments and m and p are the mass and the linear momentum of the center of mass of the molecule, respectively. It also considers that these molecules interact through a two-body interaction

$$u = \sum_{i>j} u(r_i - r_j; \theta_i - \theta_j) = \sum_{i>j} V(r_i - r_j) \Theta(\theta_i - \theta_j) \quad (2)$$

that depends simultaneously on the distance $r_i - r_j$ between their center of mass and the relative orientation $\theta_i - \theta_j$ of their main axis, as shown in the Fig. 1.

In liquids, the dependence of the potential on the distance between the molecular center of mass will be taken as the usual Lennard-Jones interaction

$$V(r) = \mu_0 \left[\left(\frac{r_o}{r} \right)^{12} - \left(\frac{r_o}{r} \right)^6 \right], \quad (3)$$

while the direction dependent term will be taken as

$$\Theta(\theta_i - \theta_j) = \Theta[\varepsilon \cos 2(\theta_i - \theta_j)]. \quad (4)$$

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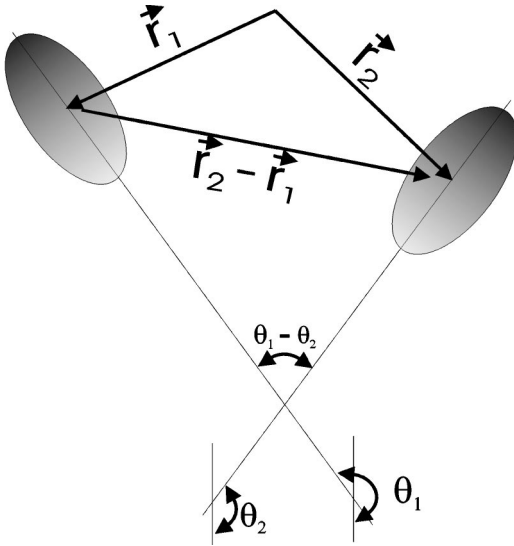


FIG. 1. Representation of two ellipsoidal nematic molecules and the respective coordinates parameters in terms of which the interacting potential between them is defined.

In Eq. (3) μ_0 and r_o give the well depth and the collision diameter, respectively. The expression $\varepsilon \cos 2(\theta_i - \theta_j)$ was introduced by Eq. (4) to make explicit the rotational periodicity of that interaction and the symmetry by a rotation of the π of each individual molecule. An ideal angular dependence would certainly take into account all Fourier components; however, only in this study, the first nontrivial term will be considered. In this approximation, the linear part of Eq. (4) coincides with the Maier-Saupe approach for this potential, [see Eq. (6) below]. Furthermore, ε gives the strength of the orientational coupling between the molecules. So, in $\varepsilon = 0$, the interaction between any two particles is spherically symmetric, while in $\varepsilon \neq 0$, the interaction induces a correlation between the direction of the long axis of the molecules.

Conversely, the existence of a repulsive hard-core characterizes the molecular local interaction of the liquids and, due to the anisotropic shape of the NLC molecules, it must be also considered direction dependent. In the Lennard-Jones potential it is described by the parameter r_0 that, as suggested by Fig. 2, which may be represented by

$$r_o = \rho(\theta_i - \theta_j) = \rho[\varepsilon \cos 2(\theta_i - \theta_j)]. \quad (5)$$

So, with Eq. (4) and Eq. (5) we have introduced in our model the main characteristics of the Maier-Saupe and Onsager approaches. From now on, only the linear parts of these equations will be considered. Consequently,

$$\Theta = \Theta_o + \frac{\partial \Theta}{\partial \varepsilon} \varepsilon \cos 2(\theta_i - \theta_j) = \Theta_o + \alpha \cos 2(\theta_i - \theta_j), \quad (6)$$

where $\Theta_o = \Theta(0)$ and $\alpha = \varepsilon \partial \Theta / \partial \varepsilon$, and, analogously

$$r_o = \rho_o - \alpha \gamma \cos 2(\theta_i - \theta_j), \quad (7)$$

where $\rho_o = \rho(0)$ and

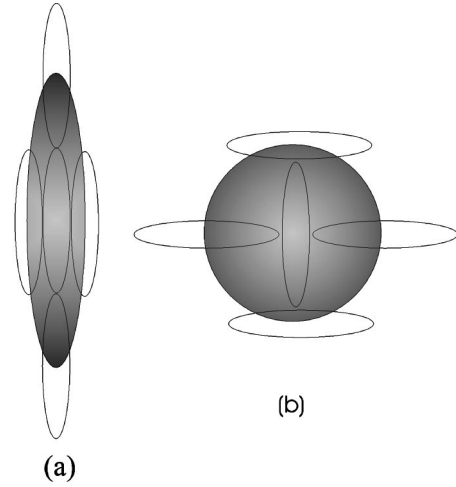


FIG. 2. The excluded volume when the calamitic molecules are touching each other is represent by the hachured area. In (a) the molecules are parallel and in (b) they are perpendicular. Equation (5) of the text expresses the assumed expression for this volume.

$$\gamma = - \frac{\frac{\partial \rho}{\partial \varepsilon}}{\frac{\partial \Theta}{\partial \varepsilon}}. \quad (8)$$

The parameter γ , defined by the above equation, measures the relative magnitude between the anisotropy of the excluded volume, given by $\partial \rho / \partial \varepsilon$, and the anisotropy of the aligning potential, given by $\partial \Theta / \partial \varepsilon$. As $|\gamma|$ increases, the contribution of the excluded volume tends to be dominant and the Onsager limit is approached. On the other hand, whenever the value of $|\gamma|$ diminishes, it is the aligning potential that becomes dominant, and the Maier-Saupe limit can be approached.

Finally, when using the above approximations, the resulting Hamiltonian

$$H = \sum_i K(p_i, p_{\theta_i}, p_{\phi_i}, p_{\psi_i}) + \sum_{i>j} V(r_i - r_j) \Theta(\theta_i - \theta_j) \quad (9)$$

does not lead to a computable partition function. In Sec. III we will explore the virial expansion to study some thermodynamical properties of this system.

III. THE VIRIAL EXPANSION

An outstanding result of the many-body physics is that very simple hypotheses are enough to explain the gross behavior of the gaseous-liquid transition. At this limit, the pairwise additivity of the molecular interaction is an acceptable approximation and, therefore, any low density approach to fluids can be employed. At higher densities, however, such approach does not give sound results and, therefore, the liquid-crystalline transition cannot be explained by means of virial expansion [6]. As the NIPT takes place inside the liquid state, surrounded by the gaseous-liquid transition on one

side and by the liquid-crystalline transition on the other, it is appropriate to ask if a mean-field expansion is a sound approach to it. Interestingly enough, low density formulations, as the approaches of Maier Saupe and Onsager, have been used to explain the NIPT, and the results seem to agree with the experimental results. In this aspect, this work will be no different from those mentioned before. So, the system described by the preceding Hamiltonian will be expanded to the lowest-order virial coefficients and, in Sec. IV, the resulting equations will be used to explain the NIPT.

Due to the Hamiltonian form in Eq. (9), which separates the momentum from the coordinates, the canonical form of the Partition function

$$Z = \int D[\vec{p}] D[\vec{r}] \exp[-\beta H(\vec{p}, \vec{r})], \quad (10)$$

where \vec{p} and \vec{r} indicates all the generalized momentum and coordinates appearing in Eq. (9), and $\beta = 1/k_B T$, can be factored as

$$Z = Z_p Z_r \quad (11)$$

in the momentum partition function

$$Z_p = \int D[\vec{p}] \exp\left[-\beta \sum_i K(p_i, p_{\theta_i}, p_{\phi_i}, p_{\psi_i})\right] \quad (12)$$

and in the configurational partition function

$$Z_r = \int D[\vec{r}, \theta] \exp\left[-\beta \sum_{i>j} V(r_i - r_j) \Theta(\theta_i - \theta_j)\right]. \quad (13)$$

The calculation of the momentum partition function

$$Z_p = (64\pi^6 k_B^6 T^6 I_1^2 I_3 m^3)^{\frac{N}{2}} \prod_{i=1}^N \sin \theta_i, \quad (14)$$

(is an immediate exercise [2]), where N is the number of particles. However, the computation of the configurational partition function is a tremendous difficult problem, representing one in the fundamental problems in the theory of the fluids. Anyway, the combination of Eq. (13) and Eq. (14) leads to

$$Z = \tau \int \prod_{i=1}^N d^3 r_i d\delta \theta_{ij} \sin \theta_i \times \exp\left[-\beta \sum_{i>j} V(r_i - r_j) \Theta(\delta \theta_{ij})\right], \quad (15)$$

where $\tau = (128\pi^7 k_B^6 T^6 I_1^2 I_3 m^3)^{N/2}$ and $\delta \theta_{ij} = \theta_i - \theta_j$.

In the lowest order of the virial expansion Z can be written as

$$Z = \tau \left[V^N + \frac{N}{2!} (N-1) V^{N-1} B_2(T) + \dots \right], \quad (16)$$

where

$$B_2(T) = \frac{1}{2} \int d^3 r_{12} d\delta \theta_{12} \cos(\delta \theta_{12}) \times \{1 - \exp[-\beta V(\vec{r}_{12}) \Theta(\delta \theta_{12})]\}, \quad (17)$$

is the two-body cluster integral.

So, in this approximation, all that is needed is the computation of the integral in Eq. (17). But, for the Lennard-Jones potential given in Eq. (3), this integral is not known and the usual hard-sphere approximation [6] will be used

$$V(r) = u_0 \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right] \approx \begin{cases} +\infty & \text{for } r < r_0 \\ u(r) = -u_0 \left(\frac{r_0}{r} \right)^6 & \text{for } r > r_0, \end{cases} \quad (18)$$

where r_0 is given by Eq. (7). Using this approximation, a straightforward calculation shows that

$$B_2(T) = \frac{V_m}{8} \left(C_0 - \beta \mu_0 C_1 - \frac{\beta^2 \mu_0^2}{6} C_2 \right), \quad (19)$$

where $V_m = 4\pi\rho_0^3/3$, and

$$C_0 = 4 - \frac{1228}{3675} \gamma^3 \alpha^3 - \frac{4}{3} \gamma \alpha + \frac{452}{75} \gamma^2 \alpha^2,$$

$$C_1 = 4 + \frac{4}{9} \alpha - \frac{4}{3} \alpha \gamma - \frac{452}{75} \alpha^2 \gamma + \frac{452}{75} \alpha^2 \gamma^2 + \frac{1228}{1225} \alpha^3 \gamma^2$$

$$- \frac{1228}{3675} \alpha^3 \gamma^3 - \frac{149732}{99225} \alpha^4 \gamma^3,$$

$$C_2 = 4 + \frac{8}{9} \alpha - \frac{4}{3} \alpha \gamma + \frac{452}{225} \alpha^2 - \frac{904}{75} \alpha^2 \gamma + \frac{452}{75} \alpha^2 \gamma^2 + \frac{2456}{1225} \alpha^3 \gamma^2 - \frac{1228}{3675} \alpha^3 \gamma^3 - \frac{1228}{1225} \alpha^3 \gamma + \frac{149732}{33075} \alpha^4 \gamma^2 - \frac{299464}{99225} \alpha^4 \gamma^3 - \frac{669524}{2401245} \alpha^5 \gamma^3. \quad (20)$$

The partition function of a theory is a straightforward exercise in computing its thermodynamic functions [6,11,12]. For example, using the results computed above, the corresponding van der Waals' equation has the following form:

$$\frac{pv}{k_B T} \approx 1 + \frac{V_m}{8v} \left(C_0 - \beta \mu_0 C_1 - \frac{\beta^2 \mu_0^2}{6} C_2 \right). \quad (21)$$

Likewise, the mean value of the potential that describes the interaction between the nematic molecules, given in Eq. (2), takes the following form:

$$\langle u \rangle = -\frac{V_m}{4V} \left(\mu_0 C_1 + \frac{\mu_0^2}{3k_B T} C_2 \right). \quad (22)$$

In Sec. IV these results will be used to study the NIPT.

IV. RESULTS

In this section the preceding results will be interpreted. First, it should be observed that the interaction between two anisotropic molecules, [Eq. (2)], is composed of two terms: the Lennard-Jones force, given by Eq. (3) and Eq. (18), and the orientational potential, given by Eq. (4) and Eq. (6). The Lennard-Jones potential has a twofold purpose; it not only commands the long range attractive character of the molecular interaction but also takes care of the short range repulsive interaction that forbids any close encounter of the molecules. Consequently, it describes the molecular aggregation that characterizes the gaseous-liquid transition and the corresponding density change, which can be recognized through the transformation that it provokes in the isotherms of the PV diagram of the van der Waals equation [5]. So, normally [13], through the establishment of the inflexion points

$$\left(\frac{\partial p}{\partial v} \right)_{T=T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial v^2} \right)_{T=T_c} = 0, \quad (23)$$

the critical points

$$v_c = \frac{3V_m C_0}{8},$$

$$T_c = \frac{4\mu_0 C_1}{27C_0 k_B} \left[1 \pm \left(1 + \frac{9C_0 C_2}{4C_1^2} \right)^{1/2} \right],$$

$$p_c = \frac{16\mu_0 C_1}{27V_m C_0^2} + \frac{4k_B w}{V_m C_0} - \frac{8\mu_0 C_1}{9V_m C_0^2} - \frac{8\mu_0^2 C_2}{8\mu_0 V_m C_0 C_1 + 54V_m k_B C_0^2 w}, \quad (24)$$

are found, where $w \equiv 4\mu_0 [4(C_1/C_0)^2/9 + C_2/C_0]^{1/2}/18k_B$.

As the position of these critical points depends on the values of C_0 , C_1 , and C_2 , the state of the alignment of the molecules introduces changes in the positional gaseous-liquid transition. However, it is known that in $\alpha=0$, the model describes an isotropic system. At this point, the above critical points become

$$v_c = \frac{3V_m}{2},$$

$$T_c = \frac{4\mu_0}{27k_B} [1 + (13)^{1/2}],$$

$$p_c = 0.1038 \frac{\mu_0}{V_m}, \quad (25)$$

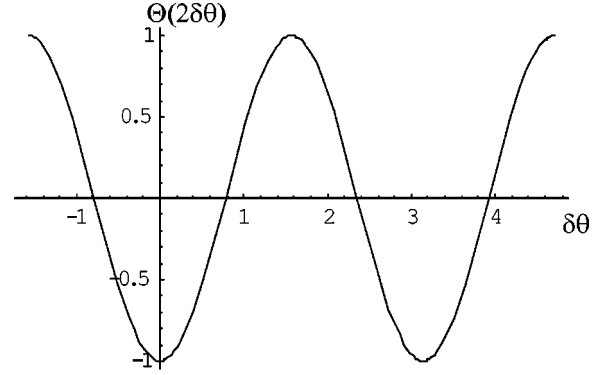


FIG. 3. Graphic representation of the angular part of the interacting potential for $\alpha > 0$, as defined in Eq. (6). For this value of α there are two minima for the aligning potential, one at $\delta\theta=0$ and another at $\delta\theta=\pi$. They correspond to the two possible aligned configurations of the molecules of the NLC.

which correspond to the known values of these coefficients.

Up to this point, this analysis has given us the gaseous-liquid transition. In order to obtain the NIPT, the configurations that give the minimum to $\langle u \rangle$, [Eq. (22)], will be determined. As, through parameter α , this potential depends on the angular interaction between the molecules, this study begins by establishing the characteristics of this dependence. As mentioned above, when $\alpha=0$, the potential is spherically symmetric and the system must be in the isotropic phase. However, for $\alpha \neq 0$, there are two possibilities, either $\alpha < 0$ or $\alpha > 0$. In Fig. 3 and Fig. 4, a graph of the angular potential for each of these values is shown. It can be observed that for $\alpha < 0$, the potential has two minima, at $\delta\theta=0$ and $\delta\theta=\pi$, separated by a maximum around $\delta\theta=\pi/2$. Furthermore, for $\alpha > 0$, the role of these extremes are inverted and there are two maxima at $\delta\theta=0$ and $\delta\theta=\pi$, separated by a minimum, at $\delta\theta=\pi/2$. So, for $\alpha > 0$, the angular interaction drives the molecules to become aligned, while for $\alpha < 0$, the molecules are impelled to become perpendicular (antialigned). So, α is the parameter that governs the molecular alignment. From now on it will be assumed that the system looks for the thermodynamical equilibrium through the adjustment of this parameter. Using this prescription in Eq. (22) the value of α can be obtained from the rule

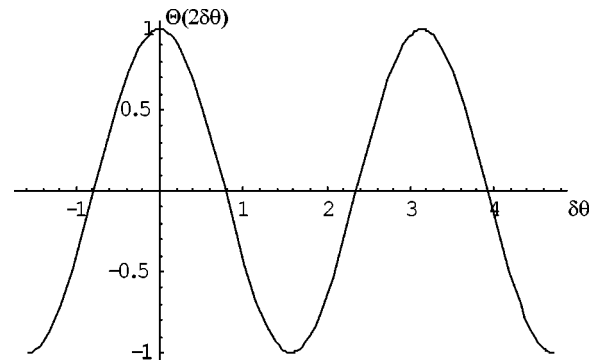


FIG. 4. Graphic representation of the angular part of the interacting potential for $\alpha < 0$, as defined in Eq. (6). For this value of α there are only one minima, at $\delta\theta=\pi/2$. They correspond to an antiparallel alignment for the nematic molecules.

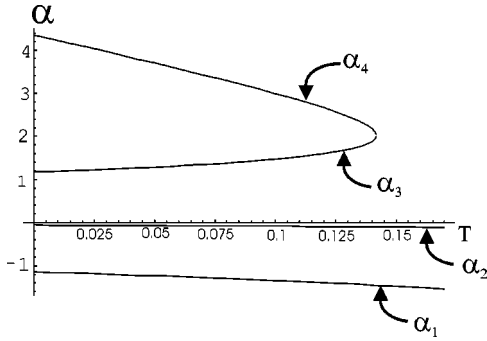


FIG. 5. The four solutions of Eq. (27) that are extremes of the energy as function of the temperature. For high temperatures only two solutions exist and they correspond to antialigned configuration ($\alpha < 0$). Nevertheless, observe that α_2 assumes a very small value and, as it is shown in Fig. 6, it is effectively indistinguishable from the solution with $\alpha = 0$.

$$\frac{\partial \langle u \rangle}{\partial \alpha} = 0, \quad (26)$$

which leads to

$$\frac{\partial C_1}{\partial \alpha} + \frac{\mu_0}{3k_B T} \frac{\partial C_2}{\partial \alpha} = 0. \quad (27)$$

This equation generates a fourth-order polynomial in α , and its solutions were found numerically. An example of one of these solutions is presented in Fig. 5, where it was assumed that $\gamma = 1$. Changes in γ will be considered ahead. According to these numerical studies, there are only two real solutions with negative values of α for high temperatures. Consequently, as stated in preceding analysis, both of them correspond to a perpendicular alignment. Furthermore, one of them, indicated as α_2 in the figure, assumes such a small value ($\alpha_2 \approx -0.1$) that it would be indistinguishable from the $\alpha = 0$ solution. In Fig. 6 a superimposed graph of the energy corresponding to the solution $\alpha_2 \approx -0.1$ on the energy graph corresponding to the solution for $\alpha = 0$ is presented. From these figures, it becomes clear that these two solutions are effectively indistinguishable and, certainly, the small difference between them would be attributed to the

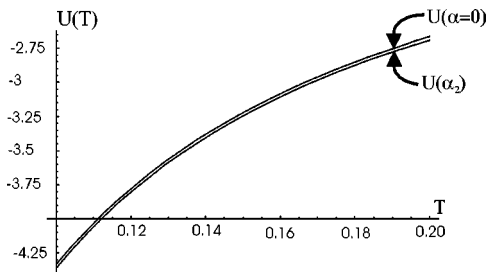


FIG. 6. The energy of the solution α_2 and the energy of the isotropic solution, $\alpha = 0$, are shown in the same picture. The energies of these two states are very close and, therefore, they are thermodynamically indistinguishable. To see this clearly compare the energy scale shown in this figure with the scale for the energies shown in Fig. 7.

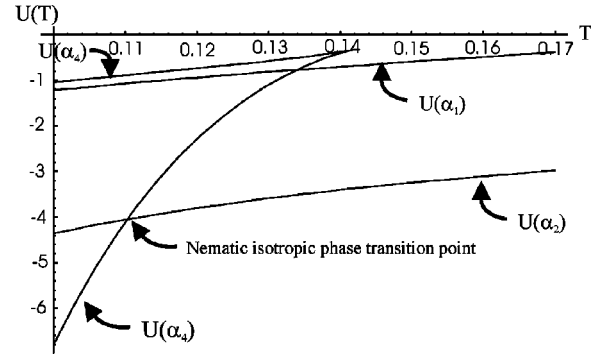


FIG. 7. The dependence on temperature of the extremes of the energy. Observe that at high temperatures only two solutions exist and the configuration corresponding to α_2 gives the energy minimum. As the temperature is reduced two new solutions corresponding to aligned state arise. Nevertheless, only at the nematic-isotropic phase transition point the molecules become thermodynamically aligned.

approximation errors used. Assuming that this energy difference is real, it is so small that the thermal agitation will easily destroy any antialignment and the solution will be effectively indistinguishable from the isotropic solution. Furthermore, when the temperature is reduced, with values lower than $T \approx 0.14$ (in the units presented in the figure), two new solutions arise. These solutions have $\alpha > 0$ and, therefore, correspond to the aligned states. These results show clearly that there is a well-defined upper bound (temperature) for the acceptability of the aligned states, since at higher temperatures, even as metastable states, they cannot survive.

The preceding analysis revealed that, in the scope of the approximation used, there are solutions that at high temperatures are compatible with a disordered configuration and that at low temperatures describe aligned configurations. According to Fig. 5, there are some possibilities for the configuration that the system can assume at each temperature. For a consistent analysis, it must be assumed that, at each temperature, the configuration assumed by the system is the one that has the least energy. In Fig. 7 the energy for each of the four solutions in Fig. 5 are shown. As expected in high temperatures, the most stable solution is the one corresponding to the nonaligned configuration. But as the temperature is reduced, there is a point, indicated in the figure as the NIPT point, where the energy of one of the aligned states becomes lower than the energy of the isotropic configuration. This must certainly be the point of the NIPT.

When the results shown in Fig. 7 are compared with the results in Eq. (24) our model can predict at least two transition points; that of the gaseous-liquid transition and that of the NIPT. These values were computed by assuming $\gamma = 1$. To gain further insights into the meaning of the NIPT, the position of the NIPT point has been computed for many γ values. The corresponding results are shown in Fig. 8, where the NIPT position is strongly dependent on γ . As γ diminishes, the NIPT point approaches the gaseous-liquid transition and, inversely, whenever γ increases, the NIPT approaches the liquid crystalline. This change in the NIPT point can be easily interpreted by considering the meaning of

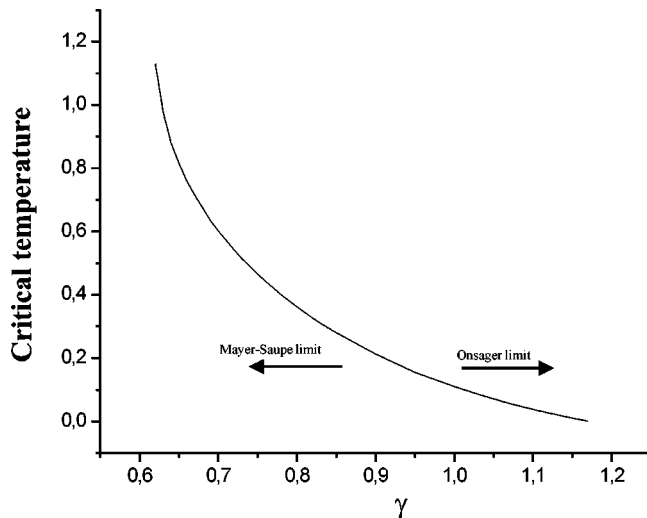


FIG. 8. The dependence of the position of the nematic-isotropic phase transition point on the parameter γ . As γ is diminished the aligning potential becomes stronger, the Maier-Saupe limit is approached and the critical temperature increases. When γ is increased the contribution due to the anisotropic shape of the molecules (and the consequent excluded volume) become dominant, the Onsager limit is approached and the critical temperature is reduced.

γ given in Eq. (25). When $\gamma > 1$, the molecular anisotropy prevails over the aligning potential, whilst for $\gamma < 1$, it is the aligning potential that overcomes the molecular anisotropy. Consequently, γ measures the relative contribution of the Maier-Saupe and the Onsager approaches to the NIPT, therefore, the change of the position of the NIPT point expresses the change of their relative weight for the phase transition. When γ is reduced, the aligning potential becomes stronger, the critical temperature increases, and the Maier-Saupe limit is approached. On the other hand, when γ is increased, the contribution of the anisotropic shape of the molecules to the excluded volume becomes dominant, the critical temperature is reduced, and the Onsager limit is approached.

V. CONCLUSION

It is usually assumed that the nematic-isotropic phase transition can be induced by two diverse kinds of interactions; the long range interaction that, through a mean field, stimulates the overall alignment on the molecules, and the short ranged interaction, that presupposes that the entropy of the system becomes reduced when the molecules come close together in a parallel arrangement. Assuming implicitly that these two approaches underline two distinct aspects of the same actual phase transition, they are managed separately as the Maier-Saupe and the Onsager approaches, respectively. In this work, we have put them together in a unique mean-field formalism. We have constructed a theory using a parameter that combines these two approaches and, as this parameter is changed, one or the other of the previously mentioned interactions is emphasized. We have shown that, when the scenario is dominated by the long ranged aligning mean field, the position of the phase-transition point is displaced towards the gaseous-liquid transition. However, when the short ranged interactions, responsible for the excluded volume, dominate the scene, the position of the phase-transition point is displaced towards the nematic-crystalline transition point. Consequently, the findings in this study have shown that the Maier-Saupe and the Onsager approaches are limits of a complex phase transition that mix some physical aspects of the phase transitions neighboring it. The NIPT is neighbored by the gaseous-liquid transition that stresses the mean field and the long range properties of a phase transition. At the low temperature, however, it is neighbored by the nematic-crystalline transition that stresses the local packing properties of a phase transition.

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