The Influence of Nonextensivity on Orientational Ordering in Liquid Crystal Systems with Variable Molecular Shape

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Abstract

A generalized model taking into account the photoisomerization influence on the nematic ordering is presented. This generalized theory is used to investigate the effect of the nonextensivity on the concentration dependence of the long-range order parameter. The $q$-dependent variation of the concentration of cis – trans isomers and of the order parameter with the time of exposure to the illumination is investigated within nonextensivity. It is also shown that for sufficiently long exposition of the mesophase to the illumination the nematic phase cannot disappear for some value of the entropic index, coming from Tsallis statistics. Moreover it is shown that long range interactions or the fractal structure in the liquid crystalline system might affect the characteristics of the phase transition in the physical system. We think therefore that this conclusion might shed light on the interaction potential energy terms in the similar system in future possible experiments, even to be performed on new objects with different symmetries.

Keywords: Tsallis thermostatistics, Liquid Crystals, Order Parameter.

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I. INTRODUCTION

A nonextensive entropy definition was proposed in 1988 [1] by Tsallis,

\[ S_q = -k \frac{1 - \sum_{i=1}^{W} W_i p_i^q}{1 - q} \]

(1)

where \( k \) is a positive constant, \( p_i \) is the probability of the system in the \( i \)th microstate, \( W \) is the total number of the configurations of the system and \( q \) is any real number. Since then, Tsallis thermostatistics (TT) has commonly been used for the investigation of the physical systems. As well-known, Boltzmann-Gibbs (BG) statistics is a powerful one to study a variety of the physical systems. However it falls for the systems which 1) have long-ranged interactions, 2) have long-ranged memory effects, and 3) evolve in multifractal space-time. In this manner, it has been understood that extensive BG statistics fails to study nonextensive physical systems not having these conditions. Consequently the standard BG thermostatistics is not universal and is appropriate for extensive systems. The parameter, \( q \), in Eq.(1) is called the entropy index and measures the degree of the nonextensivity of the system under consideration. After a few years from 1988, the formalism was revised [2] introducing the unnormalized constraint to the internal energy. This generalization included the celebrated BG thermostatistics, which could be recovered when \( q = 1 \). After this work, this formalism has been commonly employed to study various physical systems. Some of them can be given such as; self gravitating systems [3,4], turbulence [5-8], anomalous diffusion [9-12], solar neutrinos [13], liquid crystals [14-18] etc.

In spite of the successes of TT, some drawbacks were noted in the original formalism. These can be summarized as follows: \( i \) the density operator was not invariant under a uniform translation of energy spectrum, \( ii \) the \( q \)-expected value of the identity operator was not the unity, \( iii \) the energy of the physical system was not conserved. To overcome these difficulties, Tsallis et al. introduced the normalized constraint to the internal energy of the system [19]:

\[ \frac{\sum_{i=1}^{W} p_i^q \varepsilon_i}{\sum_{i=1}^{W} p_i^q} = U_q. \]

(2)
The optimization of Tsallis entropy given by Eq. (1) according to this internal energy constraint results in

\[ p_i = \left[ 1 - (1 - q)\beta^*(\varepsilon_i - U_q) / \sum_{j=1}^{W} (p_j)^q \right]^{1/q} \]

(3)

with

\[ Z_q = \sum_{i=1}^{W} \left[ 1 - (1 - q)\beta^*(\varepsilon_i - U_q) / \sum_{j=1}^{W} (p_j)^q \right]^{1/q}, \]

(4)

where

\[ \beta^* = \frac{\beta}{(1/Tr \{ \hat{\rho}^q \}) + (1 - q)U_q \beta}, \quad \beta = 1/kT. \]

Therefore the \( q \)-expectation value of any observable is defined as

\[ \langle A_i \rangle_q = \frac{\sum_{i=1}^{W} p_i^q A_i}{\sum_{i=1}^{W} p_i^q}, \]

(5)

where \( A \) represents any observable quantity which commutes with Hamiltonian. As can be expected, the \( q \)-expectation value of the observable reduces to the conventional one when \( q = 1 \).

As for our motivation in this study, it was found in literature [20] that the structure of the micellar and liquid crystalline phases can be considered as self-similar. Based on this fact, recently a model of self-similar aggregation of alkylbenzenesulphonates (ABS) molecules was proposed [21]. Then the fractal structure of the sample was investigated experimentally [20] where the influence of the geometry of ABS molecules on the formation of their liquid crystalline phases was reported and the authors emphasized that ABS molecules are the fractal objects. As mentioned above, the nonextensivity may appear in systems where fractality exists. Therefore the main motivation of the present study comes from having fractal structure of some liquid crystals.

As well-known from the literature and our last studies on nematic liquid crystals, Maier-Saupe theory (MST), which is a mean-field one, has some insufficiencies coming from; 1) as being a mean-field theory, 2) neglecting higher interaction terms in the interaction potential.
function. Due to these insufficiencies, MST gives, for instance, the critical value of the long range order parameter $P_2 = 0.429$ for all nematics. Considering these terms (i.e. the possibility of the fractality in liquid crystals and the insufficiencies of the mean-field approach), we apply TT to the nematic liquid crystals. To this end, in [14], MST was generalized within TT and it was showed the influences of the nonextensivity on the nematic-isotropic transition. Next the dimerization process was handled using TT in [15] which can be regarded as the first application of TT to a liquid crystalline system. In [15], the influence of the dimerization process on the nematic ordering is investigated by using a nonextensive thermostatistics (TT). A theoretical model taking into account the dimerization influence on the nematic scalar order parameter has been summarized and theoretical predictions for the nematic order parameter are improved by using TT. Then the $P_4$ model with $P_4$-interaction ($P_4$ indicates the Legendre polynomial for $L = 4$) was investigated and generalized within TT in [16]. The dependence of the second order parameter ($P_2$) on the fourth one ($P_4$) was studied in [17] and the generalized theory was applied to PAA (para-azoxyanisole), a nematic liquid crystal. In [18], a generalized mean-field theory was presented relating helix tilt in a bilayer to lipid disorder. It has been observed from all these studies that if one uses a generalized form of the MST within TT, the deviations between the theory (MST) and the experimental data are minimized and the obtained results agree with the experimental data very well.

In this study, the influence of the photoisomerization on the orientational ordering is handled by using a generalized theory. The standard theory has been recently proposed in literature [22]. It is an extension of the MST and could be an appropriate one to investigate the variation of the concentration of cis – trans isomers and of the scalar order parameter with the time of exposure to the illumination. As expected, as it is an extension of a mean-field theory (MST), it might have some deviations form the experimental data; for instance it also gives a universal value of the long range order parameter at transition point, 0.429. To overcome similar insufficiencies (considering the possible fractality of the liquid crystalline system), we use a generalized form of the standard theory and investigate the
physical quantities concerning physical system. To this end, we first summarize the standard and generalized theories. Then we investigate the effects of nonextensivity on the nematic-isotropic transition and also on the evolution of the concentration of cis—trans isomers and of the scalar order parameter with the time of exposure to the illumination.

II. THE GENERALIZED THEORY

The standard theory [22] assumes that the liquid crystalline system is formed by a mixture of two elements, namely two miscible nematogens $N_1$ and $N_2$. According to the system under consideration can be dimers and monomers, if an energy to break the hydrogen bonding is considered [23], or trans and cis isomers in the case of azobenzene materials [24]. Both kinds of molecules, namely $N_1$ and $N_2$, are supposed to be rodlike. In the mean-field approximation, the total nematic potential function can be given by [25-27]

$$V(\theta_1, \theta_2) = \sum_{i,j} V_{ij} = V_{11} + V_{12} + V_{21} + V_{22}, \quad (6)$$

where $\theta_1$ and $\theta_2$ are the angles formed by the molecular long axes of the molecules of $N_1$ and $N_2$ with the nematic director of the mixture respectively, $V_{11}$ and $V_{12}$ are the mean-field potentials acting on a molecule of $N_1$ due to the other molecules of $N_1$ and due to the molecules of $N_2$ respectively. A similar meaning has $V_{21}$ and $V_{22}$. These potential functions can be written as

$$V_{ij} = -\alpha_{ij} P_2(\theta_i) \langle P_2(\theta_j) \rangle, \quad (7)$$

in the MST, where $\alpha_{ij}$’s are coupling constants and they depend on the distance between the center of mass of the molecules, on a molecular property and also on the concentration of one of the constituents in the system [23]. Using these terms above, we can write the nematic potential function as

$$V(\theta_1, \theta_2) = V_1(\theta_1) + V_2(\theta_2)$$

$$= -\left( \alpha_{ii} P_2(\theta_i) + \alpha_{ij} P_2(\theta_j) \right) P_2(\theta_i), \quad (8)$$
where $P_2(\theta_i) = \langle P_2(\theta_i) \rangle$ is the scalar order parameters of the molecules of $N_i$. The scalar order parameters are determined by solving the set of coupled equations according to Eq. (5) for $i = 1, 2$ self consistently. These coupled equations depend on the temperature $T$ and on the quantities $\alpha_{ij}$ appearing in the nematic potential function. The $\alpha_{ij}$ quantities contain the strengths of mean-field interaction among the molecules forming the nematic 1, among the molecules forming the nematic 2, and among the molecules of 1 and those of 2. $\alpha'_{ij}$s are assumed as

$$
\alpha_{ij} = u_{ij}n_j,
$$

where $u_{ij} = u_{ji}$ and $n_i = N_i/(N_1 + N_2)$, with $N_i$ being the number of molecules of the nematic $i$ [23].

The generalized free energy of the system is given by

$$
F_q = - \sum_i \left( \frac{1}{2} N_i \langle V_i \rangle + N_i kT \ln_q(Z_{i,q}) \right),
$$

where $\ln_q(Z_{i,q}) = (Z_{i,q}^{1-q} - 1)/(1 - q)$ and $\langle V_i \rangle = - \sum_j \alpha_{ij} P_2(\theta_j) P_2(\theta_i)$. Since we assume $u_{12} = u_{21} = u$, the free energy density of the system can be given by

$$
F_q = N \left\{ - \sum_i \left[ \frac{1}{2} n_i^2 u_{ii} \langle P_2(\theta_i) \rangle^2 + n_i kT \ln_q(Z_i) \right] + u n_1 n_2 P_2(\theta_1) P_2(\theta_2) \right\},
$$

where $N = N_1 + N_2$.

Let us now consider the case in which one of the constituents do not contribute to the nematic order. The experimental evidence shows that the molecules of the cis isomers are of banana shape. According to recent investigations, this banana shape can be approximated by two linear parts forming an angle between them not very far from $\pi/2$ [22]. As a result of this configuration, the molecules of the cis isomer behave as spherical objects due to the spinning and tumbling motions of thermal origin. Consequently in the liquid phase they can originate just an isotropic phase. In this manner, the molecules of cis isomer lead to a kind of neutral background, where the molecules of trans isomer are responsible for nematic order. So we will consider that the trans isomers have cylindrical symmetry and can exhibit
a nematic order, whereas the cis isomers will tend to reduce this orientational order. In addition, we also assume that at zero temperature the system under consideration is made by \( N_{\text{trans}} = N \) isomers. At a given temperature \( T \) we have

\[
n_{\text{trans}} + n_{\text{cis}} = 1, \tag{12}
\]

where \( n_{\text{trans}} \) and \( n_{\text{cis}} \) are the equilibrium concentration of trans and cis isomers and are given by

\[
n_{\text{trans}} = N_{\text{trans}}(T)/N,
\]
\[
n_{\text{cis}} = N_{\text{cis}}(T)/N
\]

at a given temperature respectively. Thus the quantities \( \alpha_{ij} \) are reduced to the case of trans isomer-trans isomer interaction, i.e., \( \alpha_{ij} = \alpha_{\text{trans}} \) and \( \alpha_{\text{trans}} = u_{\text{trans}} \) [23].

In the case of one component, \( P_2(\theta) = \langle P_2(\theta) \rangle \) will be the scalar order parameter of trans isomers. The standard theory is based on MST with an ingredient represented by temperature-dependent concentration. This dependence in the standard theory plays an important role and it departs from the one represented by the concentration dependence characteristic of the excluded volume theories of Onsager type [28,29]. As well-known, in Onsager model the number of particle is fixed. In this manner, the critical density, below which the isotropic phase is stable, follows from a balance between the energy connected with the excluded volume and the thermal energy. In contrast, according to the standard model which will be generalized below, the number of particles responsible for the nematic phase depends on the temperature. In Onsager’s theory, this is equivalent to having an excluded volume that is temperature dependent.

In Fig.(1), we show the dependence of the long range order parameter on the concentration of cis isomers for a fixed reduced temperature \( T_R = 0.1 \) \( u/k \) and for some \( q \) values. The nematic scalar order parameter vs. the concentration of the cis isomers in the system for \( T_R = 0.1 \) \( u/k \) (reduced temperature) is illustrated in Fig.(1). Since the standard theory \( (q = 1) \) depends on Maier-Saupe mean-field interaction energy, the system, as expected, ex-
hibits a first-order phase transition to the isotropic phase for \( n_{\text{cis}}^c = 0.55 \) and \( (T_2)_c \) decreases suddenly to zero from 0.429 which MST gives for all nematic liquid crystals. However it is experimentally known [30] that the critical value of the nematic order parameter varies from one nematic to the other and it lies in a range of 0.25 – 0.5 for nematic liquid crystals. We think therefore that the standard model based on mean-field approach appears to be insufficient and alternative approach is needed. On the other hand, as \( q \) is varied, we observe that the critical value of the order parameter changes. The obtained results are summarized in Table in which the entropy change at transition point is also reported as a function of \( q \). We denote the entropy of the system as \( S_q \).

In Fig.(2), the phase diagram of temperature vs. concentration of cis component for the system is plotted. One observes that the usual critical temperature \( (T_R \approx 0.2202u/k) \) for MST [31] is reached when \( n_{\text{cis}} = 0 \) as expected, since the concentration of the molecules leading to the nematic phase is fixed in MST. An interesting point is that the experimental data reported in [25] show that the critical temperature for the nematic-isotropic phase transition of the mixture is a linear function of the concentration of the solute. In this framework, we observe from Fig.(2) that the entropic index \( q \) just affects the slope of the line associated with this linear dependency.

### III. ORDER PARAMETER VS. EXPOSURE TIME FOR ILLUMINATION

At a given temperature, the isomerization reaction follows the reaction scheme \( \text{trans} \rightarrow \text{cis} \), depending on some rate constants that, in turn, depend on the intensity of the light in the illumination process [32,33]. Then time variation of the concentrations of two constituents can be approximated by

\[
n_{\text{trans}}(T, t) = c n_{\text{trans}}(T) + (1 - c) n_{\text{trans}}(T) \exp_q(-t/\tau) \tag{13}
\]

within \( TT \), where \( \tau \) is a characteristic time and \( c \) is a parameter to control the fraction of trans-cis isomers at a given temperature after the illumination. When \( t = 0 \), we have
\( n_{\text{trans}}(T, 0) = n_{\text{trans}}(T) \). From \( n_{\text{trans}} + n_{\text{cis}} = 1 \) and assuming for \( n_{\text{trans}} \) the approximate expression given by Eq.(13), we obtain

\[
 n_{\text{cis}}(T, t) = 1 - n_{\text{trans}}(T, t). \tag{14}
\]

It is the experimental fact that with the exposure time to the illumination, the concentration of cis isomers increases, whereas the trans isomer concentration does not tend to zero, but to some fraction, controlled by the parameter \( c \), of the equilibrium concentration \( n_{\text{trans}}(T) \).

Now we would like to discuss about the equilibrium distribution of the concentrations of the different constituents forming the mixture. At a given temperature, the equilibrium distributions of cis and trans isomers in TT could be given by

\[
 n_{\text{cis}} = \exp_q(-\beta(\mu + E))
\]

\[
 n_{\text{trans}} = \exp_q(-\beta\mu) \tag{15}
\]

respectively, where \( \mu \) is the chemical potential of the mixture. Now if the above results are used in Eq.(12), it is possible to observe the behaviour of the order parameter with the exposure time to the illumination. In Fig.(3), we illustrate the variation of the order parameter with the exposure time for the reduced temperature of \( T_R = 0.1u/k \); \( c = 0.3 \) and for some \( q \) values. We observe that for a given value of \( c \), the entropic index \( q \) plays an important role and has a considerable effect on the variation of scalar order parameter with the exposure time. The similar behaviour can be easily seen in Fig.(4) in which the order parameter vs. exposure time is plotted for \( c = 0.4 \) and some values of \( q \). Probably the most interesting result is seen in Fig.(5); for \( q = 1 \) (standard theory) and \( c \geq 0.55 \), there is no phase transition at temperature \( T_R = 0.1u/k \). However for \( q \leq 0.5 \) and \( c = 0.55 \), a first order phase transition occurs at this temperature \( (T_R = 0.1u/k) \). This conclusion implies that the permanence of the liquid crystalline phase depends not only on the concentration of cis isomers in the system, but also on the entropic index \( q \) (i.e. probably long range interactions or fractality).
IV. SUMMING UP

We have presented a generalized model to study on the behaviour of the scalar order parameter in liquid crystalline systems, consisting of more than one nematogen component. It is the experimental fact that some liquid crystals have fractal structure. This fact implies that TT can be applied to the liquid crystalline systems. In addition, the standard model, which has been generalized, is an extension of MST and thus some drawbacks coming from insufficiencies of mean-field approach could be expected. In this framework, a generalized model which is an extension of MST has been used. The generalized theory can be successfully applied to distinct systems, such as one formed by cyclic dimers and monomers, and also to the systems where azobenzene compounds play an important role. For example, a similar system, consisting of closed and open dimers, has been studied in [15], where the experimental data related to the dimeric system has been successfully explained by using a generalized theory. It must be noted that the success of the generalized mean-field theories in our earlier studies may come from being fractal structure of liquid crystals, apart from considering long range interactions. Similar successful explanations can be expected in other dimeric and liquid crystalline systems.

It has been also studied on the systems where the illumination process gives rise to the appearance of new objects with different symmetries in the systems. We have shown that fractality or long range interactions (i.e. \( q \neq 1 \)) might affect the characteristics of the phase transition in the physical system. This conclusion might shed light on the interaction potential energy terms or fractal structure in the similar system in future possible experiments, even to be performed on new objects with different symmetries.
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FIGURE AND TABLE CAPTIONS

Figure 1. The variation of the scalar order parameter with the concentration of cis isomer for a fixed reduced temperature $T_R = 0.1u/k$ and for some $q$ values. As $q$ increases, the critical value of the scalar order parameter at transition point also increases.

Figure 2. $q$-dependent phase diagram in the reduced temperature vs. cis concentration plane. The critical lines represent the first order phase transition, namely nematic-isotropic transition, induced by the variation in the concentration of cis isomers in the nematic medium.

Figure 3. The variation of the scalar order parameter with the exposure time for uv illumination for $c = 0.3$ and some $q$ values. $\tau$ is a characteristic time. As seen from figure, the entropic index $q$ affects the variation of scalar order parameter with the exposure time considerably.

Figure 4. The variation of the scalar order parameter with the exposure time for uv illumination for $c = 0.4$ and some $q$ values. As seen from figure, the entropic index $q$ affects the variation of scalar order parameter with the exposure time considerably.

Figure 5. The variation of the scalar order parameter with the exposure time for uv illumination for $c = 0.55$ and some $q$ values. As seen from figure, whereas there is no phase transition in the standard theory ($q = 1$) for $c \geq 0.55$, the generalized theory assumes a first order phase transition for $q \leq 0.5$.

Table. Entropy change of the system at transition point for some values of the entropic index $q$.\"
Figure 1

\( (P_2)_q \)

\( n_{cis} \)

\( T_R = 0.1 \, u/k \)

- \( q = 0.98 \)
- \( q = 0.99 \)
- \( q = 1 \)
- \( q = 1.01 \)
- \( q = 1.02 \)
Figure 2

- $q=0.98$
- $q=0.99$
- $q=1$
- $q=1.01$
- $q=1.02$

$n_{cis}$ vs. $T_R$
Figure 3

\[
(P_2)_q = 0.3, q = 0.6, q = 0.8, q = 1, q = 1.2, q = 1.4
\]

Exposure time \((\tau^{-1})\)
Figure 4

\[
(P_2)_q = \begin{cases} 
0.4 & \text{if } q = 0.4 \\
0.6 & \text{if } q = 0.6 \\
0.8 & \text{if } q = 0.8 \\
1 & \text{if } q = 1 \\
1.2 & \text{if } q = 1.2 \\
1.4 & \text{if } q = 1.4 
\end{cases}
\]
Figure 5

\[ (P_2)_q = \begin{cases} 
0.55 & q=0.5 \\
0.8 & q=0.8 \\
1 & q=1 
\end{cases} \]

\[ c = \begin{cases} 
0.55 & c=0.55 
\end{cases} \]

Exposure time \((\tau^{-1})\)