An Investigation of MBBA nematic within Generalized Maier-Saupe Theory

O. Kayacan*

Department of Physics, Faculty of Art and Science, Celal Bayar University,
Muradiye/Manisa-TURKEY

Abstract

Generalized Maier-Saupe theory (GMST) within Tsallis thermostatistics (TT) has been used to investigate the second rank order parameter in a nematic liquid crystal, N-p-methoxybenzylidene p-n-butylaniline (MBBA). Also, the free energy has been investigated at the nematic-isotropic phase transition temperature and the effect of the nonextensivity has been demonstrated.

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*e-mail: ozhan.kayacan@bayar.edu.tr
I. INTRODUCTION

So far, many statistical theories of nematic liquid crystals have been proposed. One of the most popular theories of the nematics is Maier-Saupe (MST) [1,2] which is a mean field study. Although MST is successful to describe the nematic-isotropic transition for some nematics, it is not sufficient for some others. In this study, we used generalized Maier-Saupe theory (GMST) to study a nematic liquid crystal, N-p-methoxybenzylidene p-n-butylaniline (MBBA), where MST is known to fail. Most molecular theories of nematic liquid crystals assume that the constituent molecules are cylindrically symmetric and MST is one of these molecular theories. This may be a useful approximation. However, the molecules of real nematogens are lower symmetry. Therefore the dependence of the orientational properties of the uniaxial mesophase on the deviation from molecular cylindrical symmetry was calculated from the series expansion of the pseudopotential [3]. This points out that the entropy of the system according to MST is of course not appropriate for the nematics. Because the molecules have lower symmetry, we should use another entropy definition, i.e. another thermostatistics. In this context, I use GMST within TT to investigate the nematics. The aim of this study is to show that the TT may be an appropriate one of these thermostatistics.

We start describing the Tsallis thermostatistics (TT). Since the paper by Tsallis [4], there has been a growing tendency to nonextensive statistical formalism. It has been shown that this formalism is useful, because it provides a suitable theoretical tool to explain some of the experimental situations, where standard thermostatistics seems to fail, due to the presence of long-range interactions, or long-range memory effects, or multi-fractal space-time constraints. The axioms of TT are the following:

TT has been applied to various concepts of thermostatistics and achieved in solving some physical systems, where Boltzmann-Gibbs statistics is known to fail [5]. Recently, MST has been generalized within TT and GMST has been applied to p-azoxyanisole (PAA) in [6] in which Kayacan et al. used the second choice for the internal energy constraint which will
be given below.

TT considers three possible choices for the form of a nonextensive expectation value. These choices have been studied in [7] and applied to two systems; the classical harmonic oscillator and the quantum harmonic oscillator. In that study, Tsallis et al. studied three different alternatives for the internal energy constraint. The first choice is the conventional one and used in [3] by Tsallis

$$\sum_{i=1}^{W} p_i \varepsilon_i = U_q^{(1)}. \quad (1)$$

The second choice is given by

$$\sum_{i=1}^{W} p_i^q \varepsilon_i = U_q^{(2)} \quad (2)$$

and regarded as the canonical one. Both of these choices have been applied to many different systems in the last years [8]. However both of them have undesirable difficulties. The third choice for the internal energy constraint is

$$\frac{\sum_{i=1}^{W} p_i^q \varepsilon_i}{\sum_{i=1}^{W} p_i^q} = U_q^{(3)}. \quad (3)$$

This choice is commonly considered to study physical systems because it is the most appropriate one, and is denoted as the Tsallis-Mendes-Plastino (TMP) choice. $q$ index is called the entropic index and comes from the entropy definition [3],

$$S_q = k \frac{1 - \sum_{i=1}^{W} p_i^q}{q - 1}. \quad (4)$$

where $k$ is a constant, $\sum_i p_i = 1$ is the probability of the system in the $i$ microstate, $W$ is the total number of configurations. In the limit $q \to 1$, the entropy reduces to the well-known Boltzmann-Gibbs (Shannon) entropy.

The optimization of $S_q$ leads to

$$p_i^{(3)} = \left[ 1 - (1 - q) \beta (\varepsilon_i - U_q^{(3)}) / \sum_{j=1}^{W} (p_j^{(3)})^q \right]^{1/q} Z_q^{(3)} \quad (5)$$

with
\[ Z_q^{(3)} = \sum_{i=1}^{W} \left[ 1 - (1 - q)\beta (\varepsilon_i - U_q^{(3)}) / \sum_{j=1}^{W} (p_j^{(3)})^q \right]^{\frac{1}{1-q}}. \] (6)

This equation is an implicit one for the probabilities \( p_i \). Therefore the normalized \( q - \) expectation value of an observable is defined as

\[
A_q = \frac{\sum_{i=1}^{W} p_i^q A_i}{\sum_{i=1}^{W} p_i^q} = \langle A_i \rangle_q
\] (7)

where \( A \) denotes any observable quantity which commutes with the Hamiltonian. This expectation value recovers the conventional quantity which commutes with the Hamiltonian. This expectation value recovers the conventional expectation one when \( q = 1 \). As mentioned above, Eq.(7) is an implicit one and in order to solve this equation, Tsallis et al. suggest two different approaches; "iterative procedure" and "\( \beta \rightarrow \beta' \)" transformation.

This study is the second one which use the GMST to study the nematics. Therefore another aim of this study is to take a step towards the enlargement of the use of TT in liquid crystals and application domain of GMST by using the third choice for the internal energy constraint. It is worthwhile to note that in the previous paper [6], Kayacan et al. used the second choice whereas the third choice is considered in the present study. It is well-known from the literature that the first two choices have some disadvantages, so we use the third choice which is the most appropriate one, as mentioned above.

Also, there are some extensions of the MST, including molecular field terms into the potential energy, using BG statistics [9,10]. In this study, long-range interactions have been taken into account for \( q \neq 1 \), without including the terms into the interaction potential energy, and the experimental data have been successfully explained for second rank order parameter of MBBA, within TT, with a small departure from the standard theory.

II. RESULTS AND DISCUSSION

MST assumes the intermolecular potential energy as

\[ u_i = -\frac{A}{V^2} P_2 \left( \frac{3\cos^2 \theta_i - 1}{2} \right) \] (8)
which bases on dispersion forces. In this equation, $A$ is a constant independent of pressure, volume and temperature, $V$ is molar volume, and $\theta_i$ is the angle between the long molecular axis and the preferred axis, $P_2$ is the second rank order parameter and given by

$$P_2 = \left\langle \frac{3 \cos^2 \theta_i - 1}{2} \right\rangle = s$$  

in which $P_2$ denotes the Legendre polynomial with $l = 2$. The generalized second rank order parameter is calculated from

$$\langle P_2 \rangle_q = \frac{\int_0^1 P_2(x_i) p_i^q d(x_i)}{\int_0^1 p_i^q d(x_i)}$$

within TT, where $x_i$ denotes the direction cosine of the long axis of an individual molecule with respect to the nematic axis.

Now let us treat the Helmholtz free energy of the system and the equilibrium condition within TT. The Helmholtz free energy is written as

$$F_q = U_q - T S_q$$

where

$$U_q = \frac{N}{2} \frac{\int_0^1 u_i(x) p_i^q dx_i}{\int_0^1 p_i^q dx_i}.$$  

Thus the entropy of the system can be expressed as

$$S_q = k \beta U_q + k \log_q (Z_q^{(3)})$$

in which $Z_q^{(3)}$ is given by Eq.(6). If substituting Eqs.(12) and (13) into Eq.(11), the Helmholtz free energy associated with the system is obtained. The condition for the equilibrium in the nematic-isotropic liquid phase transition reads

$$\left( \frac{\partial F_q}{\partial s_q} \right)_{V,T} = 0$$

and this condition may be called "the consistency relation".

G. Sigaud et al. reported the measurements of the magnetic anisotropy and $\langle P_2 \rangle$ data of MBBA [11]. Fig.(1) shows the second rank order parameter as a function of temperature.
The curves are plotted in nematic range of MBBA. It is seen that the fit to $\langle P_2 \rangle$ data is very good for $q = 0.978$, whereas the result of MST is very poor. The variation of the free energy as a function of the order parameter at nematic-isotropic phase transition temperature is shown in Fig.(2). It is seen that the free energy has two minima, one at $s = 0$ representing the isotropic phase, and the other one at $s = s_c$ corresponding to the nematic phase. The two states have equal free energies and at this temperature, a discontinuous transition takes place. The minima corresponding to the nematic phase are at $s_c = 0.43$ for $q = 1$ (MST) and at $s_c = 0.35$ for $q = 0.978$. This result is in far better agreement with the experimental one, $s_c = 0.32$ [12] than MST.

It is worthwhile to imply that the experimental values of $\langle P_2 \rangle$ are higher than those predicted by MST for most nematics[13]. The most-known exceptions are PAA and MBBA for which MST predicts higher values of $\langle P_2 \rangle$ than the experimental ones. Therefore, it seems that the $\langle P_2 \rangle$ curves of most nematics might be expected to be fitted appropriately with $q$ values greater than unity. Since the nematics are a class of the liquid crystals, this case is the expected one.

III. CONCLUSION

It is seen from this study that MST can be improved by using TT. In this manner, GMST explains the variation of the second rank order parameter and the value of the order parameter at the transition temperature for MBBA. It is seen from the present and previous studies on some kinds of nematics that GMST is a useful tool to study the nematics. Some disadvantages of MST can be improved by using TT.

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**Figure Caption**

Figure 1. Orientational order parameter as a function of temperature in MBBA for $q = 0.978$ and $q = 1$. The curves are plotted in nematic range of MBBA. Filled circles represent the experimental data[11].

Figure 2. The Helmholtz free energy as a function of generalized order parameter in MBBA for $q = 0.978$ and $q = 1$. 
Figure 1
Figure 2