Generalization of the Maier-Saupe theory of the nematics within Tsallis Thermostatistics

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Abstract

In this study, one of the mean-field theories in nematics, the Maier-Saupe theory (MST), is generalized within Tsallis Thermostatistics (TT). The variation of the order parameter versus temperature has been investigated and compared with experimental data for PAA (p-azoxyanisole). So far we believe that this is the first attempt of the application of TT in liquid crystals. It is well known that MST fails to explain the experimental data for some of the nematics, one of which is PAA. However generalized MST (GMST) is able to account for the experimental data for a long range of temperatures. Also in this study, the effect of nonextensivity is shown for various values of the entropic index.

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I. INTRODUCTION

There is a growing interest in the nonextensive generalization of the conventional Boltzmann-Gibbs statistical mechanics. Tsallis Thermostatistics (TT) is one of these generalization attempts [1] and in this study, we generalize the Maier-Saupe theory (MST) [2], a mean field theory especially used in nematic liquid crystals, and the variation of the order parameter of PAA (p-azoxyanisole, a nematic liquid crystals) versus temperature is investigated within TT formalism. MST fails to explain the experimental data for some of the nematics and PAA is one of these nematics. It is well known that Boltzmann-Gibbs statistics (BG) seems to fail for the systems, (i) with long range microscopic interactions, (ii) with long range memory effects and (iii) which evolves in a multifractal space-time.

Therefore there is a tendency for nonextensive formalisms. It is seen in the literature that from 1988 up to present days, TT not only has been applied to various concepts of thermostatistics [3-20], but also achieved to solve some physical systems where BG statistics is known to be inadequate. Amongst them, stellar polytropes [21], Levy-like anomalous diffusions [22], two-dimensional Euler turbulence [23], solar neutrino problem [24], velocity distributions of galaxy clusters [25], fully developed turbulence [26], electron-positron and other high-energy collisions [27] and anomalous diffusion of Hydra viridissima [28] could be mentioned.

The axioms of TT are the following 1) the entropy of the physical system is defined by

\[ S_q = -k \left( 1 - \frac{\sum_{i=1}^{W} p_i^q}{1 - q} \right) \]

where k is a constant, p_i is the probability of the system in the i th microstate, W is the total number of configurations and q is the entropic index (q ∈ R) which is a measure of the nonextensivity of the system. It is important to note that if q→ 1, then \( S_1 = -k_B \sum_i p_i \log p_i \), which is the well known Shannon entropy.

2) q-expectation value of an observable O is given by

\[ < O >_q = \sum_{i=1}^{W} p_i^q O_i \]
which again recovers the conventional expectation value when $q=1$.

II. THE MAIER-SAUGE THEOREY

An approach that has proved to be useful in developing a theory of long range orientational order and the

where $V$ is the molar volume, $A$ is a constant independent of pressure, volume and temperature, $\theta_i$ is the angle between the long molecular axis and the preferred axis, $s$ is the order parameter and given by

$$s = \frac{1}{2} < 3 \cos^2 \theta_i - 1 > .$$

(1)

The internal energy per mole is

$$U = \frac{N}{2} \int_0^1 u_i \exp(-u_i/kT) d(\cos \theta_i)$$

$$= -\frac{1}{2} NkT Bs^2$$

(2)

where $B=A/(kTV^2)$, $(A=13 \times 10^{-9}$ erg.cm$^6$, $V=225$ cm$^3$ forPAA), $N$ is the Avogadro number, $T$ is temperature.

The partition function for a single molecule is given by

$$z_i = \int_0^1 \exp(-u_i/kT) d(\cos \theta_i)$$

(3)

so that the entropy is

$$S = -Nk \left[ \frac{1}{2}Bs(2s + 1) - \log \int_0^1 \exp(\frac{3}{2}Bs \cos^2 \theta_i) d(\cos \theta_i) \right] .$$

(4)

Then the Helmholtz free energy is

$$F = U - TS$$

$$= NKT \left[ \frac{1}{2}Bs(s + 1) - \log \int_0^1 \exp(\frac{3}{2}Bs \cos^2 \theta_i) d(\cos \theta_i) \right] .$$

(5)

The condition for equilibrium is given by

$$\left( \frac{\partial F}{\partial s} \right)_{V,T} = 0$$
or
\[
3s \frac{\partial}{\partial s} < \cos^2 \theta_i > - 3 < \cos^2 \theta_i > + 1 = 0. \tag{6}
\]

This equation is satisfied when
\[
< \cos^2 \theta_i > = \frac{2s + 1}{3}. \tag{7}
\]

The theoretical curve for \( s \) versus \( T \) could be determined from (8) namely the equilibrium condition.

III. GENERALIZATION OF THE MAIER-SAUGE THEORY

In the frame of TT, the generalized partition function is written as
\[
z_q = \int_0^1 [1 - (1 - q)\beta u_i]^{1-q} \tag{8}
\]
where \( \beta = 1/kT \). The average value of \( \cos^2 \theta_i \) is
\[
\overline{\cos^2 \theta_i} = \frac{\int_0^1 \cos^2 \theta_i \exp(-u_i/kT) d(\cos \theta_i)}{\int_0^1 \exp(-u_i/kT) d(\cos \theta_i)}. \tag{9}
\]

For the sake of simplicity, we replace \( \cos \theta_i \) with \( x_i \). In Eq.(10), let us write
\[
\exp_q(-u_i/kT) = [1 - (1 - q)\beta u_i]^{1-q}
= \left[ 1 + (1 - q)\frac{Bs}{2}(3x_i^2 - 1) \right]^{1-q}. \tag{10}
\]

Substituting Eq.(11) into Eq.(10), we obtain
\[
\overline{x^2} = \overline{x_i^2} = \frac{\int_0^1 x_i^2 \left[ 1 + (1 - q)\frac{Bs}{2}(3x_i^2 - 1) \right]^{1-q} dx_i}{\int_0^1 \left[ 1 + (1 - q)\frac{Bs}{2}(3x_i^2 - 1) \right]^{1-q} dx_i}. \tag{11}
\]

To integrate the terms in Eq.(12), the series expansions of \( \exp_q(-u_i/kT) \) is written in terms of \( q \) and then the leading two terms are taken:
\[
\exp_q(-u_i/kT) \cong \exp \left[ \frac{1}{2}Bs(3x_i^2 - 1) \right] - \frac{1}{8} \exp \left[ \frac{1}{2}Bs(3x_i^2 - 1) \right] B^2 s^2(3x_i^2 - 1)^2(1 - q). \tag{12}
\]
Then, we have solved equation (12) and plotted $s=f(T)$ curve for various values of $q$. In Figure 1, the order parameter versus temperature for various values of $q$ are presented. As seen from Fig.1, GMST is in good agreement with the experimental data for $q=0.988$. It seems that with a small departure from the standard theory one could be able to explain some of the experimental data available in the study of nematics. GMST recovers MST when $q=1$. Near the nematic-isotropic phase transition temperature, the agreement between GMST and the experimental data is broken. In Table 1, the variations of the density of PAA with respect to temperature are given. In addition, in the recent studies, the entropic index is related to the number of particles of the system [29,30]. Then a better agreement with the experimental data could be obtained, which will be the subject of a forthcoming study.

From GMST, the value of the order parameter $s$ at $T_{NI}$ is determined as 0.4 which is in good agreement with the experimental values [31-35], whereas 0.443 is given for $s$ in MST.

**IV. CONCLUSION**

MST is the most widely used molecular field theory in the nematic liquid crystals. Although this theory is successful in the study of some of the nematics, it fails for some others, one of which is PAA, p-azoxyanisole. In this study, it is observed that, after the generalization of MST, the variation of the order parameter versus the temperature shows a better agreement with the experimental data. Fig.1 exhibits the effect of nonextensivity. It is remarkable to note that the value of $s$ at $T_{NI}$ is 0.4 which is given in refs.[31,32,33].

Another important point is the variation of the density of PAA with respect to the temperature[2], presented in Table 1. As temperature increases, the density of PAA decreases. Moreover, as mentioned earlier, in recent studies, the entropic index is related to the number of particles of the system [29,30]. Therefore it is expected that $q$, the entropic index, could be related to the density, which will be the subject of another study in near future and the variation of $s$ near $T_{NI}$, nematic-isotropic phase transition temperature, could be explained hopefully by GMST.
Following this study, a tendency to investigate liquid crystals within nonextensive formalisms could be expected.

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REFERENCES

[1] C. Tsallis, J. Stat Phys. 52, 479 (1988); E.M.F. Curado, C. Tsallis, J. Phys. A24, L69 (1991); corrigenda : 24, 3187 (1991); 25, 1019 (1992).

[2] Maier, W. and Saupe, A., A15, 287 (1960).

[3] N. Ito, C. Tsallis, Nuovo Cimento D11, 907 (1989).

[4] R.F.S. Andrade, Physica A175, 285 (1991); A203, 486 (1994); U. Tiranaki, D. Demirhan, F. Buyukkilic, Acta. Phys. Pol. A91, 1035 (1997).

[5] A.M. Mariz, Phys. Lett. A165, 409 (1992); J.D. Ramshaw, Phys. Lett. A175, 169 and 171 (1993).

[6] F. Buyukkilic, D. Demirhan, Phys. Lett. A181, 24 (1993); F.Buyukkilic, D.Demirhan, A. Gulec, Phys. Lett. A197, 209 (1995).

[7] A. Plastino, A.R. Plastino, Phys. Lett. A177, 177 (1993).

[8] A.R. Plastino, A. Plastino, Physica A202, 438 (1994).

[9] E.P. da Silva, C. Tsallis, E.M.F. Curado, Physica A199, 137 (1993).

[10] A. Plastino, C. Tsallis, J. Phys. A26, L893 (1993).

[11] D.A. Stariolo, Phys. Lett. A185, 262 (1994).

[12] A.R. Plastino, A. Plastino, C. Tsallis, J. Phys. A27, 5707 (1994).

[13] F. Buyukkilic, D. Demirhan, Z. Phys. B99, 137 (1995).

[14] S. Curilef, C. Tsallis, Physica A215, 542 (1995).

[15] F. Buyukkilic, D. Demirhan, U. Tiranaki, Physica A238, 285 (1997).

[16] C. Tsallis, F.C. Sa Barreto, E.D. Loh, Phys. Rev. E52, 1447 (1995).

[17] U. Tiranaki, F. Buyukkilic, D. Demirhan, Physica A240, 657 (1997).

[18] A.K. Rajagopal, Phys. Rev. Lett. 74, 1048 (1995); Physica B212, 309 (1995).

[19] A.K. Rajagopal, Phys. Rev. Lett. 76, 3469 (1996).

[20] U. Tiranaki, S.F. Ozeren, F. Buyukkilic, D. Demirhan, Z. Phys. B104, 341 (1997).

[21] A.R. Plastino, A. Plastino, Phys. Lett. A174, 384 (1993).
[22] P.A. Alemany, D.H. Zanette, Phys. Rev. E49, R956 (1994); C. Tsallis, S.V.F. Levy, A.M.C. Souza, R. Maynard, Phys. Rev. Lett. 75, 3589 (1995); D.H. Zanette, P.A. Alemany, Phys. Rev. Lett. 75, 366 (1995); M.O. Careres, C.E. Budde, Phys. Rev. Lett. 77, 2589 (1996); D.H. Zanette, P.A. Alemany, Phys. Rev. Lett. 77, 2590 (1996).

[23] B.M. Boghosian, Phys. Rev. E53, 4754 (1996).

[24] G. Kaniadakis, A. Lavagno, P. Quarati, Phys. Lett. B369, 308 (1996).

[25] A. Lavagno, G. Kaniadakis, M.R. Monteiro, P. Quarati, C. Tsallis, Astrophys. Lett. and Comm. 35, 449 (1998).

[26] T. Arimitsu and N. Arimitsu, Phys. Rev. E 61, 3237 (2000); T. Arimitsu and N. Arimitsu, J. Phys. A 33, L235 (2000); C. Beck, Physica A 277, 115 (2000); C. Beck, G.S. Lewis and H.L. Swinney, Phys. Rev. E 63, 035303 (2001).

[27] D.B. Walton and J. Rafelski, Phys. Rev. Lett. 84, 31 (2000); G. Wilk and Z. Wlodarczyk, Nucl. Phys. B (Proc. Suppl.) 75A, 191 (1999); G. Wilk and Z. Wlodarczyk, Phys. Rev. Lett. 84, 2770 (2000); M.L.D. Ion and D.B. Ion, Phys. Lett. B 482, 57 (2000); I. Bediaga, E.M.F. Curado and J. Miranda, Physica A 286, 156 (2000); C. Beck, Physica A 286, 164 (2000).

[28] A. Upadhyaya, J.-P. Rieu, J.A. Glazier and Y. Sawada, Physica A 293, 549 (2001).

[29] S. Abe, S. Martinez, F. Pennini, A. Plastino, Phys. Lett. A278, 249 (2001).

[30] C. Tsallis, R.S. Mendes, A.R. Plastino, Physica A261, 534 (1998).

[31] V. Zwetkoff, Acta Physicochim. URSS 16, 132 (1942).

[32] W. Maier, A. Saupe, Z. Naturforschg. 13a, 564 (1958).

[33] W. Maier, G. Englert, Z. Electrochem. (1960).

[34] P. Chatelain, Bull. Soc. Franç. Min. Crist. 78, 262 (1955).

[35] H. Lippmann, Ann. Phys., Lpz. (6) 20, 265 (1957).

[36] Chandrasekhar S., Madhusudana N.V., Journal Phys. Radium 30, c4-24 (1969).

[37] P. Chatelain and M. Germain, C.R.hebd. Seances Acad. Sci. 259, 127 (1964).
FIGURE AND TABLE CAPTIONS

Table 1: The variation of the density of PAA versus temperature [2].

Figure 1: Plot of the order parameter versus reduced temperature $T/T_c$. Continuous line: Maier-Saupe approximations ($q \to 1$). Dashed lines: GMST approximation for various values of $q$. Filled circles: optical data [36]. Filled triangles: from refractive index measurements [37].
| T(°C) | ρ(g.cm$^{-3}$) | T(°C) | ρ(g.cm$^{-3}$) |
|-------|----------------|-------|----------------|
| 100   | 1.1824         | 134   | 1.1504         |
| 105   | 1.1781         | 135   | 1.1490         |
| 110   | 1.1737         | 135.5 | 1.1482         |
| 115   | 1.1694         | 135.9 | 1.14392        |
| 120   | 1.1649         | 136   | 1.14380        |
| 122   | 1.1630         | 136.5 | 1.14328        |
| 124   | 1.1611         | 137   | 1.14279        |
| 126   | 1.1592         | 138   | 1.14186        |
| 128   | 1.1572         | 140   | 1.14004        |
| 130   | 1.1551         | 142   | 1.13830        |
| 132   | 1.1528         | 144   | 1.13659        |
| 133   | 1.1516         |       |                |
Figure 1