

# Theoretical Study of Nematic to Isotropic Transition in Porous Media

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Experimental observations show that the N–I transition temperature ( $T_{NI}$ ) for liquid crystals embedded in solid porous materials is lower compared to that of the bulk liquid crystals and  $T_{NI}$  is reduced linearly with the inverse pore diameter. To explain this, various theoretical studies have been proposed. We propose to use the mean field approach. We modify the Maier–Saupe mean field theory to include the *disordering* effects of porosity as a disordering surface potential. A molecule near the surface is assumed to feel the mean field potential (the Maier–Saupe type) and also the surface induced potential. We calculate the values of the nematic order parameter and hence find the  $T_{NI}$  for different pore diameters. The weighted average of the order parameter is calculated considering the cylindrical symmetry of the pores. Our calculations on the variation of  $T_{NI}$  with pore diameter agree with experimental data. Also, the calculated values of specific heat peak decrease with decrease in pore radius, in agreement with experimental trends.

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## 1. Introduction

Liquid crystals made of rod-like organic molecules are now known to exhibit more than twenty different types of symmetries [1]. The simplest of them is the uniaxial nematic (N) which exhibits only a long-range orientational order of the rods. The relevant order parameter is a second rank tensor, as the director ( $\hat{n}$ ), which is a unit vector along the average orientation direction of the rods is *apolar* in nature. The Maier–Saupe (MS) molecular mean field theory [2] successfully captures the qualitative features of the nematic-isotropic (N–I) transition, though it is based on the attractive intermolecular interactions only.

Study of confined liquid crystals is of fundamental and technological importance as most of the liquid crystals in device components is located near hard confining interfaces. The surface effects have length scales that are comparable with the length scales of the bulk correlations [3, 4]. Hence, the equilibrium director configuration depends on the elastic constants, surface coupling, the size of the system and its density, as well as on applied external fields. There are several studies mainly with dielectric spectroscopy [5–7], differential scanning calorimetry [8], NMR [4, 9] and X-ray scattering [10], on the molecular dynamics of different alkylcyanobiphenyls in porous media. Also, self-ordered nanoporous aluminum oxide (AAO) [11, 12] has been widely used. Experiments show that the confinement imposed by the rigid AAO pore walls can suppress phase transitions [13, 14]. The nematic-to-isotropic, crystal-to-nematic, and super-cooled liquid-to-glass temperatures are studied in the

liquid crystal 4-pentyl-4'-cyanobiphenyl (5CB) confined in self-ordered nanoporous alumina and the nematic-to-isotropic and the crystal-to-nematic transition temperatures are found to reduce linearly with the inverse pore diameter [15].

Many models like Potts spin model [16], random field Ising model [17], model based on dilution [18], model based on Monte Carlo simulation [19], simple model for size-dependent transition temperature [20] have been proposed.

In this work, we consider the effect of confinement on the nematic to isotropic (N–I) transition temperature. We propose to use the molecular mean field approach. We modify the MS mean field theory [2] to include the *disordering* effects of porosity as a disordering surface potential.

## 2. Theoretical model

We have earlier proposed a simple extension of MS theory to account for the enhancement of the nematic order parameter in thin cells [21, 22] and an extension of the Mc Millan theory to account for a surface induced smectic phase [23]. In these papers [21–23], a molecule near the surface is assumed to feel the mean field potential and also surface induced potential.

The distance from the surface of the pore, into the medium is denoted by  $z$ . The medium is assumed to be made up of layers of thickness  $dz$  parallel to the pore wall.  $U_i$  is the molecular mean field potential of  $i$ -th molecule at  $z$ .  $S_z$  is the order parameter for molecules in the layer between  $z$  and  $z + dz$ . A molecule at  $z$  feels the mean field potential (MS type) and also surface induced potential. The exact nature of the variation of surface potential with respect to  $z$  is not known experimentally. The potential has to be maximum at  $z = 0$  and zero

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at large distances from the surface. Thus, as in [21] the surface induced potential for the  $i$ -th molecule is taken empirically to decay exponentially

$$U_{iS} = U_S e^{-\frac{z}{r_0}}, \quad (1)$$

where  $U_S = AU_0$  is surface potential at  $z = 0$  and  $r_0$  is the characteristic length.  $U_0$  is the MS parameter given by  $U_0 = 4.541kT_{NI}$ , where  $k$  is the Boltzmann constant. The layer thickness is taken to be quite small, comparable to molecular length [21, 22]. The constant  $A$  is to be estimated later.

The mean field is not provided by the entire bulk medium since the interaction beyond few layers is negligible. Also the effect of gradient  $dS/dz$  and its elastic energy effects are shown to be very small [24]. Hence, for MS type mean field also, we use  $S$  instead of  $S_z$  as in the earlier paper [21, 22]. As the pores are cylindrical, it is convenient to measure the distance  $r$  from the axis of the cylinder and we use  $r = R - z$  where  $R$  is the radius of the pore. Weighted average of  $S$  is found due to cylindrical symmetry as

$$S_{av} = \frac{\int_0^R S(r) 2\pi r dr}{\int_0^R 2\pi r dr}. \quad (2)$$

### 3. Expression for free energy and order parameter

As explained above, the potential of the  $i$ -th molecule at  $z$  is written as

$$U_i = -U_0 S P_2(\cos \theta_i) + U_{iS} P_2(\cos \theta_i), \quad (3)$$

where  $P_2$  is the 2nd Legendre polynomial and  $\theta_i$  is the angle between nematic director and the long axis of the  $i$ -th molecule.

The average internal energy per molecule is

$$\frac{U}{N} = -\frac{U_0 S^2}{2} + AU_0 e^{-\frac{z}{r_0}} S, \quad (4)$$

where  $N$  is the Avogadro number, the factor  $1/2$  appears since each pair is counted twice while averaging over the mutual interactions. The order parameter  $S$  is found using Eq. (2).

The molar entropy is  $\xi = -Nk \langle \ln f \rangle$ , where  $\langle \ln f \rangle = \int_0^1 f \ln f dx$  with  $x = \cos \theta$ ,  $f$  is the probability distribution function and  $\langle \rangle$  represents the statistical average.

The average Helmholtz free energy per molecule is  $F = U - T\xi$  given by

$$\frac{F}{NkT} = -\frac{U_0 S^2}{2kT} + \frac{AU_0}{kT} e^{-\frac{z}{r_0}} S + \langle \ln f \rangle. \quad (5)$$

Hence the order parameter is

$$S = \int_0^1 f P_2(x) dx, \quad (6)$$

minimizing  $F$  with respect to  $f$  we get,

$$f = \frac{\exp\left(\frac{U_0}{kT} \left(S - A e^{-\frac{z}{r_0}}\right) P_2(x)\right)}{Z}, \quad (7)$$

where  $Z = \int_0^1 f dx$  is the partition function.

Substituting for  $\langle f \ln f \rangle$  we get

$$\frac{F}{NkT} = \frac{U_0 S^2}{2kT} - \ln Z. \quad (8)$$

The terms of surface potential depending on  $P_2(\cos \theta)$  in Eq. (3) cancel out in  $F$  on substituting for entropy part in Eq. (5). However, it affects  $S$  and hence  $F$  through  $f$  (see Eqs. (7)).

Minimizing  $F$  with respect to  $S$ , we get

$$S = \int_0^1 f P_2(x) dx, \quad (9)$$

which satisfies the self-consistency condition.

The molar specific heat at constant volume is given by

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V. \quad (10)$$

### 4. Calculations and results

The constant  $A$  is taken to be positive since the random pore walls have disturbing effect. The weak anchoring energies are of the order of  $10^{-5}$  J m $^{-2}$  [1]. Typical molecular weights and density of liquid crystal compounds are 250 and 1 g/cm $^3$ , respectively [1], the anchoring energy per molecule is found to be of the order of  $10^{-3}kT$  for  $T = 300$  K. Thus, we use  $A = 0.003$ . The necessary integrals are evaluated numerically using 32-point Gaussian quadrature method in double precision. Numerical iteration is used to adjust  $S$  for self consistency. Weighted average of  $S$  is found using Eq. (2) for a given value of  $R$ . Free energy is the calculated and  $T_{NI}$  is found. The calculations are repeated for different pore diameters  $D = 2R$ . Variation of  $T_{NI}$  as a function of  $1/D$  is shown in Fig. 1.

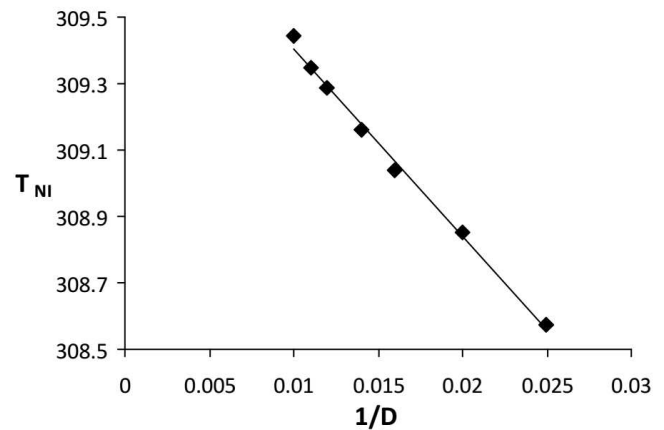


Fig. 1. Variation of  $T_{NI}$  [°C] as a function of  $1/D$  [nm $^{-1}$ ] is shown for  $A = 0.003$ .

On fitting a straight line, we get  $T_{NI} = 309.97 - \frac{56.3}{D}$ . We see that the  $T_{NI}$  is found to reduce linearly with

the inverse pore diameter as seen in the experiment [15]. Also, experimentally [15],  $T_{NI} = 310 - \frac{55}{D}$  by differential scanning calorimetry and  $T_{NI} = 307.3 - \frac{47}{D}$  by dielectric spectroscopy. It is seen that the calculated values agree well with experimental data.

We have also calculated molar specific heat at constant volume using Eq. (10). The variation of  $\frac{C_V^{\text{peak}}}{NkT_{NI}}$  as a function of pore radius  $R$  is shown in Fig. 2.

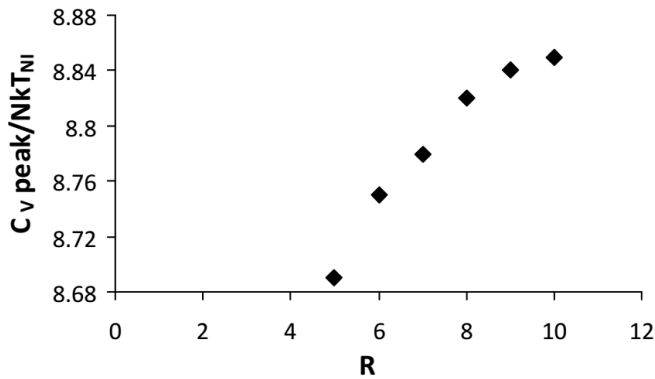


Fig. 2. Variation of  $(C_V/NkT_{NI})$  as a function of  $R$  [nm] is shown for  $A = 0.003$ .

It is seen that the specific heat peak decreases with decrease in pore radius. This trend agrees with experiment [7, 25]. The values cannot be compared since we have found  $C_V$  whereas experimentally  $C_P$  is measured.

## 5. Conclusion

We have extended MS theory to include a disturbing surface potential to explain the reduction in nematic to isotropic transition temperature compared to the bulk when the liquid crystal is embedded in a porous material. Experimental data show that  $T_{NI}$  reduces linearly with the inverse pore diameter and the specific heat peak decreases with decrease in pore radius. Calculated values agree well with the experimental data. Also,  $T_{NI}$  is higher compared to bulk in larger pores, which may be attributed to density driven effects [15]. We are extending the model to include polar nature of molecules where short range parallel or antiparallel configurations and effect of density on their relative mole fraction are considered as in [22]. Further work is under progress.

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