Isotropic solid– nematic solid transitions in fluids of hard spheres

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Abstract
We study in this paper the phase behaviour of a system of particles interacting via the isotropic Yukawa and nematic Mayer-Saupe interactions. We perform a similar study as in [A. Oukouiss, A. Chourak, and L. Zealouk, AIP Conference Proceedings 2345, 020033 (2021)] but for the nematic solid phase. We have developed the calculation of free energy for this phase. We have found that the topology of the phase diagram depends sensitively on the relative strengths of the isotropic and nematic interactions.

Keywords: liquid crystals, phase diagrams, nematic interactions, free energy

Introduction

Liquid crystals are an interesting class of soft-matter materials with a broad spectrum of applications. These range from the more traditional ones in displays technology [1] over biosensors [2, 3] and tribological applications [4] to photonic [5] and organic electronic devices [6].

In view of the diversity of applications for liquid - crystalline materials a deeper theoretical understanding of their properties is a necessary prerequisite. As a first step in such a venture the nature of various phase transitions in liquid crystals needs to be elucidated. In the context of this work the isotropic-nematic (IN) phase transition is of particular relevance. There are three distinct types of liquid crystals: thermotropic, lyotropic and polymeric. The most widely used liquid crystals, and extensively studied are thermotropic liquid crystals [7],

Systems which exhibit transition to a nematic phase have already been examined by many authors [8-24], *but all these authors do not calculate exactly the free energy of the solid phase in their theories.*

In our early extensive study of the phase behaviour of the Heisenberg model [25, 26] we have generalized the van der Waals (vdW) theory for anisotropic interactions to study the phase behaviour of a system of particles with magnetic exchange interactions. By using this vdW theory we have developed the calculation of free energy in a nematic fluid phase. We have used the nematic Maier-Saupe interaction as anisotropic interaction and the inverse power interaction as isotropic interaction [27, 28]. The stability of the nematic fluid has been recently studied by us [29].

In the present investigation we perform a similar study as in [29] but for the nematic solid phase. The isotropic interaction is represented here by the Yukawa interaction.

This paper is organized as follows. In sec.2 we introduce our model for the anisotropic potential and calculate the free energy for nematic solid. The phase diagrams for nematic solid are discussed in sec.3. Our conclusions are gathered in the final sec.4.

Extended van der Waals theory for anisotropic solids

We consider a system of N identical spherical molecules whose translational degrees of freedom can be described in terms of the position r of the centre of mass of the molecule, while its orientational degrees of freedom will be described in terms of classical spin variable s, with $s^2 = 1$. This spin variable can be viewed as defining the orientation of some internal property of the molecules, $V(r_1, r_2, s_1.s_2)$, will be taken to be of the form [29]:

$$V(r_{12}, s_1.s_2) = -\varepsilon_1 \phi_1(x_{12}) - \varepsilon_2 \phi_2(x_{12}) P_2(s_1.s_2) \quad (1)$$

Where $\phi_l(x) = \dfrac{e^{-k_l(x-1)}}{x}$; ($l$=1, 2) and P_2 is the Legendre polynomial of order 2.

Our final reduced vdW free energy, $\overline{f} = f / \varepsilon_1$, can thus be written as [29]:

$$\overline{f} = t\left\{ \ln(\rho \Lambda^3) - \ln \alpha(\rho) - 1 \right\} - F_1 + \lambda F_2 S^2 - t \ln M(q) \quad (2)$$

Where $F_l = \dfrac{1}{2N} \int dr_1 \int dr_2 \rho(r_1) \phi_l(x_{12}) \rho(r_2)$ and $\alpha(\rho) = \left[1 - \left(\dfrac{\rho}{\rho_{cp}} \right)^{1/3} \right]^3$

with ρ_{cp} is the close packing density. For a solid phase,

$\rho(r) \equiv \sum_j \delta(r - r_j)$, F_l become:

$$F_l = \frac{1}{2} \sum_j \phi_l(x_j) \quad (3)$$

Where the sum runs overs the lattice sites, $r_j / \sigma = x_j > 1$, of a periodic lattice without defects, r_j being the distance of site j to the site at the origin.

For our potentials, we have

$$F_l = \frac{1}{2}\sum_{j=1}^{N}\phi_l(x_j) = \frac{1}{2}\sum_{k}^{shells}n_k\phi_l(x_k) = \frac{1}{2}\alpha_{n_l}\left(\rho/\rho_{cp}\right)^{n_l/3}, \qquad (4)$$

For a crystal of close-packing density ρ_{cp} and Madelung constant α_{n_l}:

$$\alpha_{n_l} = \sum_{j}\left(\frac{x_1}{x_j}\right)^{n_l} \qquad (5)$$

With $x_j \geq x_1$ and x_1 the reduced nearest neighbour distance ($\rho = \rho_{cp}/x_1^3$).

The first term of (2) represent the ideal gaz contribution from the translational degrees of freedom. The second term represents the free-volume entropy due to the hard-spheres repulsions. The third term represents the mean field energy of the isotropic attraction. The last two terms represent the contribution of the angular degrees of freedom.

Phase Diagrams for Solid Phase

Below we will use the packing fraction $\eta = (\frac{\pi}{6})\rho\sigma^3$ as the reduced density variable. The two-phase equilibrium conditions can then be written

$$P_1(\rho_1,t) = P_2(\rho_2,t), \qquad (6)$$

$$\mu_1(\rho_1,t) = \mu_2(\rho_2,t), \qquad (7)$$

Where the indexes 1 et 2 refer, respectively, to phases 1 (isotropic solid) and 2 (nematic solid). The stable lattice structure (solid phase) is seen to be a compact lattice such as face-centred-cubic or hexagonal close packed.

In this paper we take this lattice structure to be of the hexagonal close packed (*HCP*) type, because, exact computer simulations and theoretical work on mono-disperse colloidal hard spheres indicate that the stable crystal structure is *fcc* or *hcp* [33, 34].

We will consider here the competition between two types of phases: the isotropic solid (IS) phase (phase 1) without orientational order (*S = 0*), and the nematic solid (NS) phase (phase 2) for which the spin variables are, on average, aligned along some director ($S \neq 0$). The reduced free energy of our system is given now by Eq. (2) where

$$\phi_1(x) = \frac{e^{-k_1(x-1)}}{x} \text{ and } \phi_2(x) = \frac{e^{-k_2(x-1)}}{x}$$

The resulting solid-solid transitions are then isostructural *hcp-hcp* transitions. The phase diagram of the solid phase depends explicitly on the three parameters $\{\gamma, k_1, k_2\}$. In the following we will consider the long-ranged isotropic interactions ($k_1 = 6$) and long-ranged nematic interactions ($k_2 = 6$). Depending on the value of these parameters, two topologically distinct phase diagrams are considered (see Fig.1). For $0 < \gamma < 0.614$ all phase diagrams have an isotropic expanded solid (IES)-isotropic condensed solid (ICS) and an IS-NS transitions (see Fig.1.a). For $\gamma > 0.614$ only the IS-NS transitions survive (see Fig.1.b).
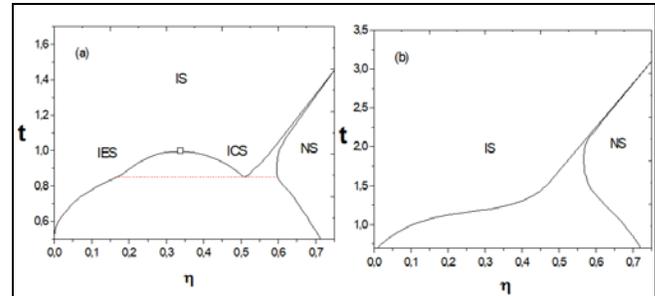
Fig 1: Phase diagram for solid phase. (a) The open square marks the solid-solid critical point. (The case shown corresponds to $k_1 = k_2 = 6$ and $\gamma = 0.4$). (b) The critical point has disappeared so that there are only two phases. (The case shown corresponds to $k_1 = k_2 = 6$ and $\gamma = 0.7$. The triple point at which the three phases NS, ICS and IES coexist disappears for $\gamma = 0.614$

Conclusion

In summary, we have presented a detailed analysis of the phase behaviour of hard sphere Maier-Saupe spin systemes, with the aid of the Van der Waals theory. According to this theory this system undergoes a first-order isotropic solid-nematic solid transition. We have found that the phase diagrams for solid phase do depend not only on the relative strength of the nematic and isotropic interactions but also on the range of these interactions. We have considered here the long-ranged isotropic interactions ($k_1 = 6$)-long-ranged nematic interactions $(k_2 = 6)$ case. We have investigated whether the presence of Yukawa interaction instead the inverse power interaction can impose the thermodynamic stability of the nematic solid phase.

References
1. Hikmet RAM, Kempermann H. Nature,1998:392:476.
2. Hussain A, Pina AS, Roque ACA, Biosensors, Bioelectronics, 2009:25:1.
3. Shiyanovskii SV, Schneider T, Smalyukh II, Ishikawa T, GD, Niehaus KJ *et al*. Lavrentovich, Phys. Rev. E,2005:71:020702.
4. Carri´on FJ, Mart´ınez-Nicol´as G, Iglesias P, Sanes J, Berm´udez MD, Int. J. Mol. Sci,2010:10:4102.

5. Juodzakis S, Mizeikis V, Misawa H, J. Appl. Phys,2009:106:051101.
6. Pisula W, Zorn M, Chang JY, M¨ullen K, Zentel R, Macromol. Rapid Commun,2009:30:1179.
7. Khoo IC. *Liquid crystals,*2nd edition. Hoboken: Jhon Wiley and Sons, Inc,2007, 114.
8. Chaikin PM, Lubensky TC. Prinxipes of condensed matter physics (Cambridge University Press, Cambridge)
9. Onsager L, *Proc.N.Y. Acad. Sci,*1994:51:627.
10. Colot JL, Wu XG, *Xu* H. Baus M, Phys. Rev. A,1998:38:2022.
11. Frenkel D. Mol. Phys,1987:60:1.
12. Frenkel D, Lekkerkerker HNW, Stroobants A. Nature,1998:332:822.
13. Frenkel D. J. Phys. Chem,1998:92:3280.
14. Veerman JAC Frenkel D. Phys. Rev. A,1990:41:3237.
15. McGrother SC, Williamson DC, Jackson GJ. Chem. Phys,1996:104:6755.
16. Blair MJ, Patey GN. Phys. Rev. E,1997:57:5682.
17. Mishra P,Singh Y. *Phys. Rev. let*,2006:97:177801.
18. Mishra P, Lata Singh S, Ram J, Singh Y. J.Chem.Phys,2007:127:044905.
19. Singh RC. J. Phys, Condens. Matter,2007:19:376101.
20. Phoung NH, Schmid F, J. Chem. Phys,2003:119:1214.
21. Lomba E, Martin C, Almarza N, Phys. Rev. E,2006:74:021503.
22. Holovko MF. Condensed Matter Physics, 13(3):33002(1.29).
23. Giura S, Schoen M. Phys. Rev. E,2014:90:022507.
24. Eduardo dos S. Nascimento Eur. Phys. J. E,2018:41:136.
25. Oukouiss A, Baus M. Phys. Rev. E,1997:55:7242.
26. Oukouiss A, Baus M. J. Chem. Phys,1998:109:6157.
27. Oukouiss A, Daanoun A, Phys. Chem. News,2009:50:37-45.
28. Oukouiss A. J. Sci. Res,2010:2(3):419-43.
29. Oukouiss A, Chourak A, Zealouk L. AIP Conference Proceedings,2021:2345:020033. https://doi.org/10.1063/5.0049718
30. Achrayah R, Baus M. Phys. Rev. E,1998:57:4361.
31. Baus M, Achrayah R. J. Phys. Condens. Matter,1996:8:9633
32. Goodstein DL. States of matter (Dover, New York), 1985.
33. Edison JR, Dasgupta T, Dijkstra M. J. Chem. Phys,2016:145:054902.
34. Yang JX, Zhao HL, Gong HR, Song M, Ren QQ. Scientific Reports, 1992(2018), 8.