

## CLUSTER VARIATION THEORY FOR THE ISOTROPIC–NEMATIC PHASE TRANSITION

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In this paper, we extend the cluster variation theory for the isotropic-nematic phase transition to the three particle cluster approximation. Like in the magnetic case, for structures where there are triangles of nearest neighbours the extension from two to three particle clusters leads to improved values for the quantities that characterize the phase transition.

### 1. Introduction

On the whole, the simple Maier–Saupe<sup>1)</sup> mean field theory gives a reasonably good description of the isotropic-nematic phase transition. It fails to explain however two important experimentally observed features.

(i) For symmetry reasons the isotropic-nematic phase transition is first order and the temperature  $T_c^*$  at which the isotropic phase becomes absolutely unstable, with respect to nematic ordering, lies somewhat below the isotropic-nematic phase transition temperature  $T_c$ . From the temperature dependence of the magnetically induced birefringence in the isotropic phase in MBBA Stinson and Litster<sup>2)</sup> deduced that  $T_c - T_c^* \cong 1$  K. The Maier–Saupe theory yields

$$\frac{T_c - T_c^*}{T_c} = 0.092,$$

which results for MBBA ( $T_c = 318$  K) in a theoretical value  $T_c - T_c^* \cong 30$  K.

(ii) The orientational order of a nematic liquid crystal can be described by an orientational distribution function  $f(\theta)$ , where  $\theta$  is the angle between the long axis of the molecules and the director  $n$ . Although there is no direct experimental means of determining  $f(\theta)$ , it is possible to measure the averages

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of the second and fourth Legendre polynomials  $P_2(\cos \theta)$  and  $P_4(\cos \theta)$  over the distribution function. Whereas the experimental values for  $\langle P_2(\cos \theta) \rangle$  are in reasonable agreement with the Maier–Saupe theory the experimental values<sup>3,4</sup>) for  $\langle P_4(\cos \theta) \rangle$  are found to be considerably lower than those predicted by this theory.

The question naturally arises whether these discrepancies between theory and experiment are due to the shortcomings of the mean field approximation. A simple and systematic way to improve upon the mean field theory by introducing correlations is provided by the variational cluster expansion method<sup>5</sup>), developed in the theory of magnetism. Recently, the simplest form of this theory, the two particle cluster treatment (which is identical to the earlier developed constant-coupling approximation<sup>6</sup>) was applied to the isotropic-nematic phase transition<sup>7,8</sup>). It leads indeed to a considerable improvement over the mean field approximation. In this paper we go one step further and apply the three-particle cluster approximation. Like in the magnetic case<sup>5</sup>), for structures where there are triangles of nearest neighbours the extension yields again an encouraging improvement.

In section 2 we present the essential features of the cluster variation method as applied to the isotropic-nematic phase transition. In the next section we discuss the results obtained in the three-particle cluster approximation.

## 2. Cluster variation method

In the cluster variation method, the free energy is expanded in a series

$$F = F_0 + F'_{(2)} + F'_{(3)} + \dots, \quad (1)$$

where the zeroth order term corresponds to the mean field approximation and the next terms represent the additional contributions of 2-particle, 3-particle, . . . clusters. Here, we will use the rotationally invariant Maier–Saupe hamiltonian

$$H = -J \sum_{(i,j)} P_2(\mathbf{a}_i \cdot \mathbf{a}_j), \quad (2)$$

where the summation is over all distinct pairs of nearest neighbour molecules and  $\mathbf{a}_i$  is a unit vector pointing in the direction of the long axis of molecule  $i$ .

Using hamiltonian (2) one obtains for the zeroth order term in the cluster variation method<sup>7</sup>)

$$-\beta F_0 = \frac{1}{2} N \gamma \beta \bar{S}^2 + N \ln Z_1, \quad (3)$$

with

$$Z_1 = \int d\mathbf{a}_1 \exp[\beta\gamma J \bar{S} P_2(a_{1z})].$$

Further,  $N$  is the total number of particles,  $\gamma$  is the number of nearest neighbours and  $\bar{S}$  is a variation parameter which best value is determined by minimizing the free energy. This yields the following equation for  $\bar{S}$

$$\bar{S} = \langle P_2(a_{1z}) \rangle. \quad (4)$$

Here  $\langle \dots \rangle$  denotes an average over the orientational distribution function

$$f(a_{1z}) = \frac{\exp[\beta\gamma J \bar{S} P_2(a_{1z})]}{Z_1}.$$

Equations (3) and (4) are just the usual mean field equations. In addition to  $\bar{S} = 0$  (which is a solution for all temperatures), eq. (4) has also non-trivial solutions of which the behaviour as a function of temperature is sketched in fig. 1. In fig. 2 we present the behavior of the free energy as a function of  $\bar{S}$  for various temperatures. The temperature  $T_c$  is the temperature for which the two minima in the free energy for  $\bar{S} = 0$  (isotropic phase) and  $\bar{S} \neq 0$  (nematic phase) are equally deep. Further,  $T_c^*$  is the temperature for which

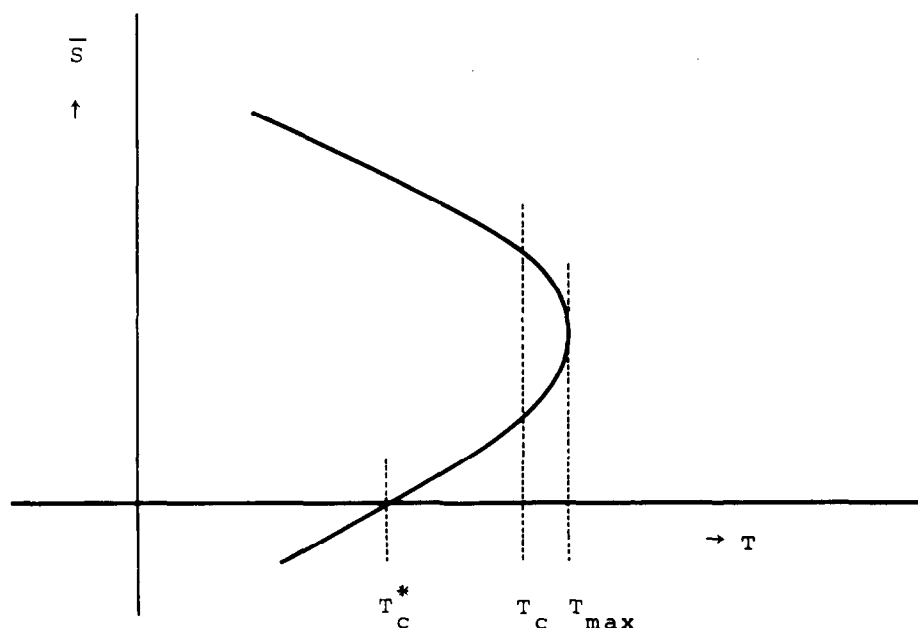


Fig. 1. Qualitative representation of the behavior of the variation parameter  $\bar{S}$  as a function of temperature.

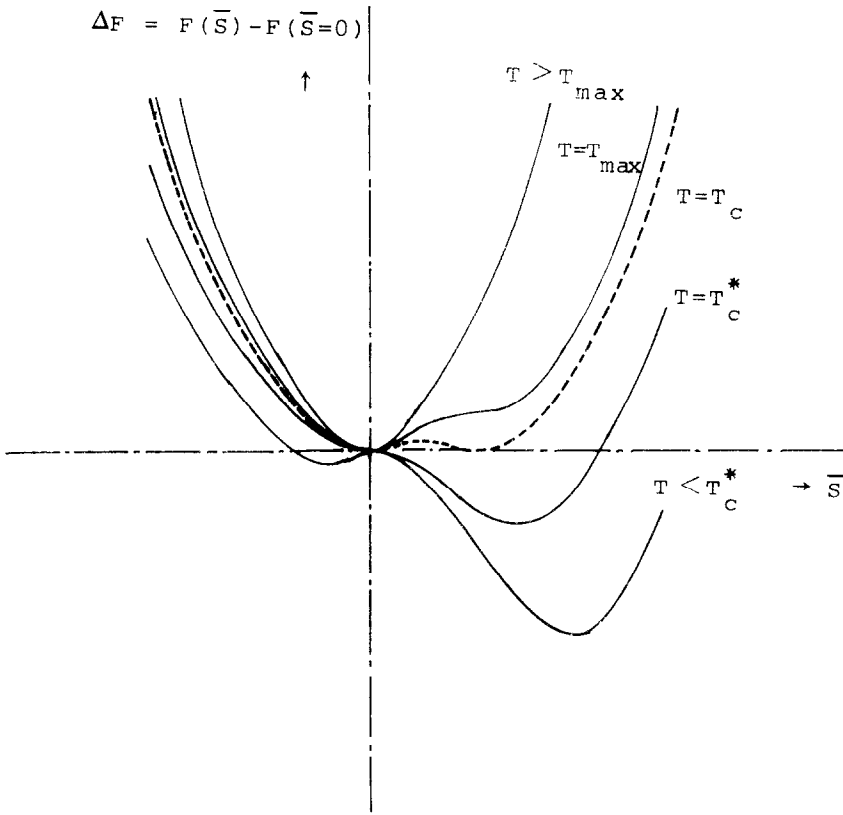


Fig. 2. Qualitative representation of the behavior of the free energy as a function of the variation parameter  $\bar{S}$  for various temperatures.

$(\partial^2 F / \partial \bar{S}^2)_{\bar{S}=0} = 0$ . In the mean field approximation one easily obtains

$$\frac{kT_c^*}{\gamma J} = \frac{1}{5}.$$

From fig. 2 it is clear that below  $T_c^*$  the isotropic phase is completely unstable with respect to nematic ordering. For the free energy in the two-particle cluster approximation one obtains<sup>7)</sup>

$$-\beta F_{(2)} = -\beta(F_0 + F'_{(2)}) = \frac{1}{2} N \gamma \ln Z_{12} - N(\gamma - 1) \ln Z_1. \tag{5}$$

Minimizing  $F_{(2)}$  with respect to the variation parameter  $\bar{S}$  yields the consistency relation

$$\frac{1}{2} \langle P_2(a_{1z}) + P_2(a_{2z}) \rangle_{12} = \langle P_2(a_{1z}) \rangle, \tag{6}$$

where  $\langle \dots \rangle_{12}$  denotes an average over the two-particle distribution function

$$f(a_1, a_2) = \frac{\exp[\beta J\{(\gamma - 1)\bar{S}[P_2(a_{1z}) + P_2(a_{2z})] + P_2(a_1 \cdot a_2)\}]}{Z_{12}}$$

As in the case of eq. (4)  $\bar{S} = 0$  is also a solution of eq. (6) and both the behavior of the non-trivial solutions and the free energy  $F_{(2)}$  are as sketched in fig. 1 and 2, respectively. From the condition

$$\left(\frac{\partial^2 F_{(2)}}{\partial \bar{S}^2}\right)_{\bar{S}=0} = 0,$$

one now obtains that the temperature  $T_c^*$  is determined by satisfying the equation

$$(\gamma - 1)\langle [P_2(a_{1z}) + P_2(a_{2z})]^2 \rangle_{12(\bar{S}=0)} = \frac{2}{3} \gamma. \tag{7}$$

Straightforward application of the cluster variation method yields for the free energy in the three particle cluster approximation

$$\begin{aligned} -\beta F_{(3)} = & -\beta(F_0 + F'_{(2)} + F'_{(3)}) = \frac{N\gamma\gamma_1}{3!} \ln Z_{123} + \frac{1}{2} N\gamma(\gamma - \gamma_1 - 1) \ln Z'_{123} \\ & + \frac{1}{2} N\gamma(\gamma_1 - 2\gamma + 3) \ln Z_{12} + \frac{1}{2} N(\gamma - 1)(\gamma - 2) \ln Z_1. \end{aligned} \tag{8}$$

Here,  $\gamma_1$  is the number of common nearest neighbours of a pair of nearest neighbours. Further

$$\begin{aligned} Z_{123} = & \int da_1 \int da_2 \int da_3 \exp \beta J\{(\gamma - 2)\bar{S}[P_2(a_{1z}) + P_2(a_{2z}) + P_2(a_{3z})] \\ & + P_2(a_1 \cdot a_2) + P_2(a_2 \cdot a_3) + P_2(a_3 \cdot a_1)\} \end{aligned}$$

and

$$\begin{aligned} Z'_{123} = & \int da_1 \int da_2 \int da_3 \exp \beta J\{(\gamma - 1)\bar{S}[P_2(a_{1z}) + P_2(a_{3z})] + (\gamma - 2)\bar{S}P_2(a_{2z}) \\ & + P_2(a_1 \cdot a_2) + P_2(a_2 \cdot a_3)\}. \end{aligned}$$

Minimizing  $F_{(3)}$  with respect to the variation parameter  $\bar{S}$  yields

$$\begin{aligned} (\gamma - 1)(\gamma - 2)\langle P_2(a_{1z}) \rangle + (\gamma - 1)(\gamma_1 - 2\gamma + 3)\langle P_2(a_{1z}) + P_2(a_{2z}) \rangle_{12} \\ + \frac{1}{3}(\gamma - 2)\gamma_1\langle P_2(a_{1z}) + P_2(a_{2z}) + P_2(a_{3z}) \rangle_{123} + (\gamma - \gamma_1 - 1)\{(\gamma - 1)\langle P_2(a_{1z}) \\ + P_2(a_{3z}) \rangle_{123} + (\gamma - 2)\langle P_2(a_{2z}) \rangle_{123}\} = 0. \end{aligned} \tag{9}$$

Here  $\langle \dots \rangle_{123}$  and  $\langle \dots \rangle_{123'}$  denote averages over three-particle distribution for which  $Z'_{123}$  and  $Z_{123}$  are the normalisation factors. Again  $\bar{S} = 0$  is a solution of the consistency relation (9) and the qualitative behavior of the non-trivial solutions as well as the qualitative behavior of the free energy  $F_{(3)}$  is as sketched in fig. 1 and 2. In the three-particle cluster approximation, the

temperature  $T_c^*$  is determined by satisfying the equation

$$\begin{aligned}
 & (\gamma_1 - 2\gamma + 3)(\gamma - 1)^2 \langle [P_2(a_{1z}) + P_2(a_{2z})]^2 \rangle_{12(\bar{s}=0)} + \frac{1}{3} \gamma_1 (\gamma - 2)^2 \langle [P_2(a_{1z}) \\
 & + P_2(a_{2z}) + P_2(a_{3z})]^2 \rangle_{123(\bar{s}=0)} + (\gamma - \gamma_1 - 1) \langle \{(\gamma - 1)[P_2(a_{1z}) + P_2(a_{3z})] \\
 & + (\gamma - 2)P_2(a_{2z})\}^2 \rangle_{123(\bar{s}=0)} = \frac{-\gamma(\gamma - 1)(\gamma - 2)}{5}. \quad (10)
 \end{aligned}$$

### 3. Results and discussion

The three-particle cluster approximation has been applied successfully to magnetic systems<sup>5</sup>) and eqs. (8)–(10) are just the transcription to the isotropic-nematic phase transition. We have applied these equations to various lattices for which the number of nearest neighbours and common nearest neighbours are listed in table I. The integrals, appearing in the consistency equations were calculated using the quadrature formula of Gauss. The use of 32 Gauss-points per integration variable gave an accuracy of 1 part in  $10^8$  or better. The consistency points were located with a predictor-corrector method.

In table II, we present the values for the transition temperatures for the various lattices, listed in table I. For the sake of comparison, we have added the results for the mean field approximation, two-particle cluster approximation<sup>7</sup>) (constant coupling approximation) and Monte-Carlo calculations<sup>9</sup>).

TABLE I  
Number of nearest neighbours and common nearest neighbours for various lattices. h.l.: hexagonal layer lattice; s.c. simple cubic; b.c.c.: body centered cubic; f.c.c.: face centered cubic.

	h.l.	s.c.	b.c.c.	f.c.c.
$\gamma$	6	6	8	12
$\gamma_1$	2	0	0	4

TABLE II  
Values of  $(kT_c/\gamma J)$  for various lattices

	h.l.	s.c.	b.c.c.	f.c.c.
Mean field	0.2202	0.2202	0.2202	0.2202
Two-particle cluster	0.1933	0.1933	0.2012	0.2082
Three-particle cluster	0.1822	0.1933	0.2012	0.2049
Monte Carlo	—	0.186	—	—

For the h.l. and the f.c.c. lattice, the transition temperature predicted by successive approximations (mean field approximation, two-particle cluster, three-particle cluster) decreases monotonically, but for the s.c. and b.c.c. lattice, the calculated transition temperature increases slightly (in the fifth decimal) in going from the two-particle cluster to the three-particle cluster approximation. The same qualitative behavior has been observed for the Heisenberg ferromagnet<sup>5</sup>).

In table III, we present the values for  $(T_c - T_c^*)/T_c$ . Again we see that only for the h.l. and the f.c.c. lattice (i.e. those lattices with common nearest neighbours) the three-particle cluster approximation leads to an improvement over the two particle cluster approximation.

In tables IV and V, we present the values for  $\langle P_2(\cos \theta) \rangle_c$  and  $\langle P_4(\cos \theta) \rangle_c$ , where the subscript c indicates that the average is taken at the transition temperature, and in fig. 3, we give the variation of  $\langle P_2(\cos \theta) \rangle$  and  $\langle P_4(\cos \theta) \rangle$  as a function of the reduced temperature  $\epsilon = (T - T_c)/T_c$  for the h.l. lattice. Notice that the value of  $\langle P_4(\cos \theta) \rangle$  for the h.l. and f.c.c. lattice predicted by successive approximations decreases monotonically and that the decrease in

TABLE III  
Values of  $(T_c - T_c^*)/T_c$  for various lattices

	h.l.	s.c.	b.c.c.	f.c.c.
Mean field	0.0917	0.0917	0.0917	0.0917
Two-particle cluster	0.0538	0.0538	0.0620	0.0708
Three-particle cluster	0.0322	0.0534	0.0620	0.0559

TABLE IV  
Values of  $\langle P_2(\cos \theta) \rangle_c$  for various lattices

	h.l.	s.c.	b.c.c.	f.c.c.
Mean field	0.4290	0.4290	0.4290	0.4290
Two-particle cluster	0.3866	0.3866	0.3986	0.4096
Three-particle cluster	0.3192	0.3893	0.4000	0.3659
Monte Carlo	—	0.333 ± 0.009	—	—

TABLE V  
Values of  $\langle P_4(\cos \theta) \rangle_c$  for various lattices

	h.l.	s.c.	b.c.c.	f.c.c.
Mean field	0.1199	0.1199	0.1199	0.1199
Two-particle cluster	0.0972	0.0972	0.1033	0.1091
Three-particle cluster	0.0664	0.0985	0.1041	0.0871

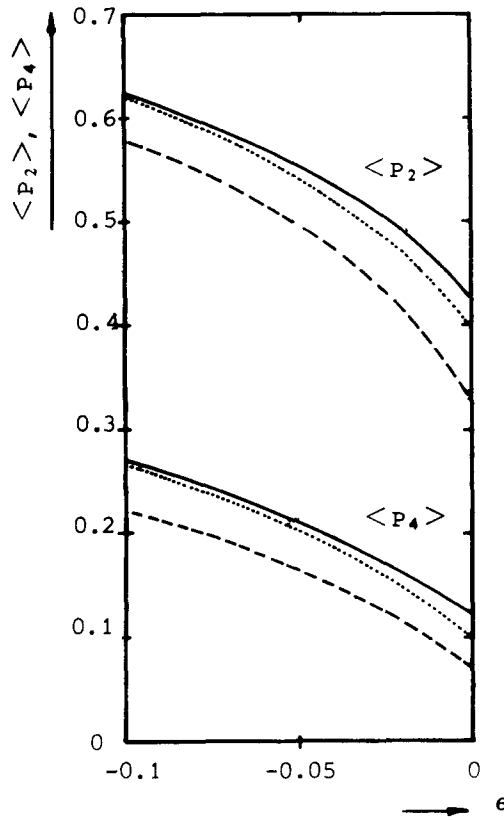


Fig. 3.  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  as a function of the reduced temperature  $\epsilon = (T - T_c)/T_c$  for the h.l. lattice mean field approximation [—], two-particle cluster approximation [...], three-particle cluster approximation [---].

going from the two-particle to the three-particle cluster approximation is even slightly larger than the decrease in going from the mean field approximation to the two-particle cluster approximation.

The conclusion of this work is that for lattices where a pair of nearest neighbours has common nearest neighbours the three-particle cluster approximation leads to an appreciable improvement over the two-particle cluster approximation, whereas if this is not the case no improvement results.

## References

- 1) W. Maier and Saupé, *Z. Naturforsch.* **A13** (1958) 564; **A14** (1959) 882; **A15** (1960) 287.
- 2) T.W. Stinson and J.D. Litster, *Phys. Rev. Lett.* **25** (1970) 503.
- 3) S. Jen, N.A. Clark, P.S. Pershan and E.B. Priestly, *Phys. Rev. Lett.* **31** (1973) 1552.



- 4) E.B. Priestly and P.S. Pershan, *Mol. Cryst. Liq. Cryst.* **23** (1973) 369.
- 5) B. Strieb, H.B. Callen and G. Hornitz, *Phys. Rev.* **130** (1963) 1798.
- 6) P.W. Kasteleyn and J. Van Kranendonk, *Physica* **22** (1956) 317.
- 7) J.G.J. Ypma, G. Vertogen and H.T. Koster, *Mol. Cryst. Liq. Cryst.* **37** (1976) 57.
- 8) P. Sheng and P.J. Wojtonicz, *Phys. Rev.* **A14**, (1976) 1883.
- 9) H.J.F. Jansen, G. Vertogen and J.G.J. Ypma, *Mol. Cryst. Liq. Cryst.* **38** (1977) 87.