Phase diagram of the face-centred cubic Blume-Emery-Griffiths model in the cluster variation method tetrahedron approximation

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The critical behaviour of the Blume–Emery–Griffiths model is analysed utilizing the cluster variation method in the tetrahedron approximation in order to include the effects of four-body correlations and to obtain an accurate determination of critical surfaces. The model has a very rich phase diagram and recently its interest has increased for it exhibits a reentrant phenomenon. In this paper the Blume–Emery–Griffiths model is proposed to describe the reentrant isotropic–nematic transition in lyotropic liquid crystals. Our results are compared with experimental data with a good success.

1. Introduction

The spin-1 Blume–Emery–Griffiths model [1] has been proposed to describe the critical behaviour of several physical systems such as ^{3}He–^{4}He mixtures, multicomponent fluids, magnetic systems [2] and also liquid crystals [3]. The model has many interesting features and has attracted a lot of attention mainly due to the richness of its phase diagram, which presents first and second order transitions and multicritical points. It also exhibits reentrant behaviour for suitable values of the coupling parameters, and of the coordination number v of the lattice [4]. The existence of a new phase, the staggered quadrupolar phase, was also predicted to occur for some special values of the coupling parameters using a Monte Carlo simulation [5]. The model has been investigated extensively and with a variety of techniques.

In this paper we utilize the Blume–Emery–Griffiths model to consider some critical properties of lyotropic liquid crystals. In lyotropics, the existence of a reentrant isotropic–nematic behaviour was discovered for a uniaxial material [6, 7]. It is just the reentrant phenomenon in lyotropics we propose to describe by means of the three-state Potts model in external fields, which in turn can be related to the Blume–Emery–Griffiths model [8].

Our investigation is carried out with the cluster variation method [9, 10] in the tetrahedron approximation. An important characteristic of the cluster variation method is that the accuracy of the method generally increases by increasing the cluster size. Thus, this four-body approximation, besides being more realistic than the mean-field one, has been also chosen in order to achieve a more accurate description of the phase diagram.

2. The model

The Blume–Emery–Griffiths model is characterized by the hamiltonian

$$H = -J \sum_{<ij>} S_i S_j - G \sum_{<ij>} S_i^2 S_j^2 + D \sum_{i=1}^{N} S_i^2 - B \sum_{i=1}^{N} S_i, \qquad (1)$$

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where S_i is the z-component of the spin-1 operator at site i ($i = 1, 2, \ldots N$) of a regular lattice and $\langle ij \rangle$ indicates summation over nearest-neighbours. J ($J > 0$) and G are respectively dipole–dipole and quadrupole–quadrupole coupling strengths, D is a single-ion anisotropy term and B an external field.

According to the cluster variation method, the entropy S of the system is evaluated, in approximate form, as a sum of suitably weighted cluster entropies [10] (associated to a selected set of clusters and of their subclusters). We assume a face-centred cubic (fcc) lattice and choose the tetrahedron as the largest cluster to carry out the calculation. In this approximation the free energy per site $f = (\langle H \rangle - TS)/N$ is given by [11]

$$f = \langle H \rangle/N + kT\{2\,\mathrm{Tr}\,(\rho_T \ln \rho_T) - 6\,\mathrm{Tr}\,(\rho_p \ln \rho_p) + 5\,\mathrm{Tr}\,(\rho_s \ln \rho_s)\}, \qquad (2)$$

where $\langle \ldots \rangle$ denotes thermal average, k is the Boltzmann constant, T the absolute temperature. ρ_s, ρ_p and ρ_T are respectively one-spin, two-spin and four-spin reduced density matrices ($\mathrm{Tr}\,\rho_s = \mathrm{Tr}\,\rho_p = \mathrm{Tr}\,\rho_T = 1$) to be determined in the minimization process of the free energy. The reduced density matrix elements can be expressed in terms of the order parameters y_1, y_2 and of the two-, three-, four-site correlations $y_3, \ldots, y_{14}$

$$\left.\begin{array}{l} y_1 = \langle S_1 \rangle, \quad y_2 = \langle S_1^2 \rangle, \quad y_3 = \langle S_1 S_2 \rangle, \quad y_4 = \langle S_1 S_2^2 \rangle, \quad y_5 = \langle S_1^2 S_2^2 \rangle, \\[2mm] y_6 = \langle S_1 S_2 S_3 \rangle, \quad y_7 = \langle S_1 S_2 S_3^2 \rangle, \quad y_8 = \langle S_1 S_2^2 S_3^2 \rangle, \quad y_9 = \langle S_1^2 S_2^2 S_3^2 \rangle, \\[2mm] y_{10} = \langle S_1 S_2 S_3 S_4 \rangle, \quad y_{11} = \langle S_1 S_2 S_3 S_4^2 \rangle, \quad y_{12} = \langle S_1 S_2 S_3^2 S_4^2 \rangle, \\[2mm] y_{13} = \langle S_1 S_2^2 S_3^2 S_4^2 \rangle, \quad y_{14} = \langle S_1^2 S_2^2 S_3^2 S_4^2 \rangle, \end{array}\right\} \qquad (3)$$

with the advantage of utilizing only independent variables [11]. Also the internal energy part of the free energy can be written in terms of the order parameters and of the multi-site correlations

$$\frac{\langle H \rangle}{N} = -by_1 + dy_2 - \tfrac{1}{2}y_3 - \tfrac{1}{2}\xi y_5. \qquad (4)$$

In (4) we have introduced the dimensionless quantities $b = B/12J$, $d = D/12J$, $\xi = G/J$ (12 is the coordination number for the fcc lattice). The minimization of the free energy, now expressed in terms of $y_1, \ldots, y_{14}$, requires the solution of the system of fourteen coupled non linear equations

$$\frac{\partial f}{\partial y_i} = 0, \quad i = 1, 2, \ldots, 14. \qquad (5)$$

However, after a careful analysis, this set may be manipulated in order to express the three- and four-site correlations as explicit functions of the order parameters y_1, y_2 and of the two-site correlations y_3, y_4, y_5. That can be performed by rewriting equations (5) in terms of the elements of the reduced density matrices and by solving them for the four-site density matrix elements (an analogous procedure has been adopted in [11] where the cluster variation method tetrahedron approximation has been applied to

analyse the Blume–Capel model). The remaining five equations (in the variables $y_1, \ldots, y_5$)

$$
\begin{aligned}
y_1 &= [3(V_{1+} - V_{1-}) + V_{2+} - V_{2-} + V_{3+} - V_{3-} + 3(V_{4+} - V_{4-}) + 2(V_{5+} - V_{5-}) \\
&\quad + 3(V_{6+} - V_{6-})]/W, \\
y_2 &= [3(V_{1+} + V_{1-}) + V_{2+} + V_{2-} + V_{3+} + V_{3-} + 3(V_{4+} + V_{4-}) + 4(V_{5+} + V_{5-}) \\
&\quad + 9(V_{6+} + V_{6-}) + 6V_0 + 6V_7]/W, \\
y_3 &= [V_{1+} + V_{1-} + V_{3+} + V_{3-} + 2(V_{4+} + V_{4-}) - 2(V_{6+} + V_{6-}) - 2V_0 - 2V_7]/W, \\
y_4 &= [V_{1+} - V_{1-} + V_{3+} - V_{3-} + 2(V_{4+} - V_{4-}) + 2(V_{5+} - V_{5-}) + 2(V_{6+} - V_{6-})]/W, \\
y_5 &= [V_{1+} + V_{1-} + V_{3+} + V_{3-} + 2(V_{4+} + V_{4-}) + 4(V_{5+} + V_{5-}) + 6(V_{6+} + V_{6-}) \\
&\quad + 2V_0 + 6V_7]/W
\end{aligned}
\tag{6}
$$

can be solved by iteration.

These equations indeed possess characteristics similar to the equations of Kikuchi's Natural Iteration Method [12]; moreover they have the advantage of being considerably reduced in number. In (6) we have introduced the following quantities

$$
\begin{aligned}
W &= 1 + 6(V_{1+} + V_{1-}) + 4(V_{2+} + V_{2-}) + V_{3+} + V_{3-} + 4(V_{4+} + V_{4-}) + 4(V_{5+} + V_{5-}) \\
&\quad + 12(V_{6+} + V_{6-}) + 12V_0 + 6V_7, \\
V_0 &= \gamma_0 A_+ A_- E_-^2 C_0 E_-^2, \quad V_{1\pm} = \gamma_1 A_\pm^2 C_\pm E_\pm^4, \quad V_{2\pm} = \gamma_2 A_\pm E_\pm^3, \\
V_{3\pm} &= \gamma_1^6 \gamma_2^{-8} A_\pm^4 C_\pm^6, \\
V_{4\pm} &= \gamma_1^3 \gamma_2^{-3} A_\pm^3 C_\pm^3 E_\pm^3, \quad V_{5\pm} = \gamma_1^3 \gamma_0^3 \gamma_2^{-8} A_\pm^3 A_\mp C_\pm^3 C_0^3, \\
V_{6\pm} &= \gamma_1 \gamma_0 \gamma_2^{-3} A_\pm^2 A_\mp C_\pm E_\pm^2 C_0^2 E_\mp, \quad V_7 = \gamma_1^2 \gamma_0^4 \gamma_2^{-8} A_+^2 A_-^2 C_+ C_- C_0^4,
\end{aligned}
\tag{7}
$$

where

$$
\gamma_0 = \exp[\beta(-1 + \xi - 6d)/24], \quad \gamma_1 = \exp[\beta(1 + \xi - 6d)/24],
$$

$$
\gamma_2 = \exp(-\beta d/8), \quad \beta = 12J/kT,
$$

$$
A_+ = (a_+)^{5/8}, \quad C_0 = (c_0)^{1/2}, \quad C_+ = (c_+)^{1/2}, \quad E_+ = (e_+)^{1/2}
$$

and

$$
a_\pm = \frac{2(1 - y_2)}{y_2 \pm y_1}, \quad c_0 = \frac{y_5 - y_3}{4(1 - 2y_2 + y_5)}, \quad c_\pm = \frac{y_3 \pm 2y_4 + y_5}{4(1 - 2y_2 + y_5)}, \quad e_\pm = \frac{y_2 \pm y_1 - (y_5 \pm y_4)}{2(1 - 2y_2 + y_5)}.
$$

The expressions of the three-and four-site correlations in terms of $y_1, \ldots, y_5$ are

$$
\begin{aligned}
y_6 &= [V_{3+} - V_{3-} + V_{4+} - V_{4-} - 2(V_{5+} - V_{5-}) - 3(V_{6+} - V_{6-})]/W, \\
y_7 &= [V_{3+} + V_{3-} + V_{4+} + V_{4-} - V_{6+} - V_{6-} - 2V_7]/W, \\
y_8 &= [V_{3+} - V_{3-} + V_{4+} - V_{4-} + 2(V_{5+} - V_{5-}) + V_{6+} - V_{6-}]/W, \\
y_9 &= [V_{3+} + V_{3-} + V_{4+} + V_{4-} + 4(V_{5+} + V_{5-}) + 3(V_{6+} + V_{6-}) + 6V_7]/W, \\
y_{10} &= [V_{3+} + V_{3-} - 4(V_{5+} + V_{5-}) + 6V_7]/W, \quad y_{11} = [V_{3+} - V_{3-} - 2(V_{5+} - V_{5-})]/W, \\
y_{12} &= [V_{3+} + V_{3-} - 2V_7]/W, \quad y_{13} = [V_{3+} - V_{3-} + 2(V_{5+} - V_{5-})]/W, \\
y_{14} &= [V_{3+} + V_{3-} + 4(V_{5+} + V_{5-}) + 6V_7]/W.
\end{aligned}
\tag{8}
$$

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The second order critical surface can be deduced from equations (6) in limit case $y_1 \to 0$. It is given by the following equation.

$$1 - \lambda_2 + \lambda_3 - \lambda_4 + \lambda_5 + \lambda_2(\lambda_4 - \lambda_6) + \lambda_5(\lambda_3 - \lambda_1) - \lambda_3\lambda_4 + \lambda_1\lambda_6 = 0, \qquad (9)$$

where, again for compactness, we have defined

$$
\left.
\begin{aligned}
\lambda_1 &= (12v_3 + 18v_4 + 6v_{\bar{1}} + 12v_5 + 6v_6)/w(y_3 + y_5), \\
\lambda_2 &= (9v_4 + 12v_1 + 3v_2 + 3v_6)/w(y_2 - y_5), \\
\lambda_3 &= [5v_3 + (45/4)v_4 + (15/2)v_1 + (5/4)v_2 + 5v_5 + (15/4)v_6]/wy_2, \\
\lambda_4 &= (12v_3 + 12v_4 + 2v_1 + 12v_5 + 4v_6)/w(y_3 + y_5), \\
\lambda_5 &= (6v_4 + 4v_1 + 2v_6)/w(y_2 - y_5), \\
\lambda_6 &= [5v_3 + (15/2)v_4 + (5/2)v_1 + 5v_5 + (5/2)v_6]/wy_2,
\end{aligned}
\right\} \qquad (10)
$$

with the quantities

$$w = W(y_1 = 0, y_4 = 0), \quad v_i = V_{i+}(y_1 = 0, y_4 = 0), \quad i = 1, \dots, 6.$$

The determination of the first order critical surface is numerically performed by comparing the free energy when more than one minimum arises. The above equations are the basic tool for a detailed analysis of the critical properties of the model.

We can now consider the model in the context of lyotropic liquid crystals. Experiments carried out on a three-component lyotropic mixture of potassium laurate, 1-decanol, and water have revealed the existence of a reentrant isotropic-nematic transition [7]. Theoretical efforts have been made to explain this phenomenon, in particular, de Oliveira and Figueiredo Neto [13] have proposed the three-state Potts model [8] to account for the interaction between the micelles. They give a simplified description of the physical system, by restricting the allowed orientations of the micelles to the three cartesian axes of the laboratory frame of reference. The three-state Potts model (which corresponds to the Blume–Emery–Griffiths model for $\xi = 3$, $d = 2$) does not exhibit reentrance [4]. In [13] the reentrant behaviour is then introduced by assuming a linear dependence of the micellar shape anisotropy with temperature. In this paper we still propose the three-state Potts model (as in [13]) but now adding two external field terms. The hamiltonian is

$$H_P = \sum_{<i,j>} [K\delta_{Kr}(\sigma_i, \sigma_j) + M\delta_{Kr}(\sigma_i, 0)\delta_{Kr}(\sigma_j, 0)] + L\sum_i \delta_{Kr}(\sigma_i, 0), \qquad (11)$$

where $\sigma_i = 0, 1, 2$ are the labels for the three orientations and $\delta_{Kr}(\sigma_i, \sigma_j) = 1$ if $\sigma_i = \sigma_j$, 0 otherwise. In equation (11) the first term represents the three-state Potts model, the last term accounts for the interaction with an external field. The remaining term contains an additional field M which applies to neighbouring micelles when they are both oriented in the direction labelled by 0. The hamiltonian (see equation (11)) can be regarded as that of a spin-1 system whose spin variables are $S_i = -1, 0, 1$. In terms of the new variables we write

$$\delta_{Kr}(S_i, S_j) = 1 + \tfrac{1}{2}S_iS_j + \tfrac{3}{2}S_i^2S_j^2 - S_i^2 - S_j^2, \quad \delta_{Kr}(S_i, 0) = 1 - S_i^2. \qquad (12)$$

If the state $S_i = 0$ is identified as the Potts state $\sigma_i = 0$, we obtain the Blume–Emery–Griffiths model described by the hamiltonian (1), apart from an additive constant. The parameters J, G and D of the Blume–Emery–Griffiths model are related to the

parameters K, M, L of the three-state Potts model with external fields by: $J = K/2$, $G = M + 3K/2$ and $D = 12(K + M) + L$. A convenient choice of the values for the external fields L and M allow us to obtain a set of values for the parameters of the Blume–Emery–Griffiths model for which the reentrant behaviour is found.

In [4] the Blume–Emery–Griffiths model has been studied with the cluster variation method in the pair approximation, determining the regions of the parameter space where the reentrance occurs. In the present paper the phase diagram is analysed in a more accurate approximation. The regions of the parameter space where the model exhibits reentrant behaviour are slightly modified. We have chosen a set of values for the parameters of the Blume–Emery–Griffiths model which allows us to compare the
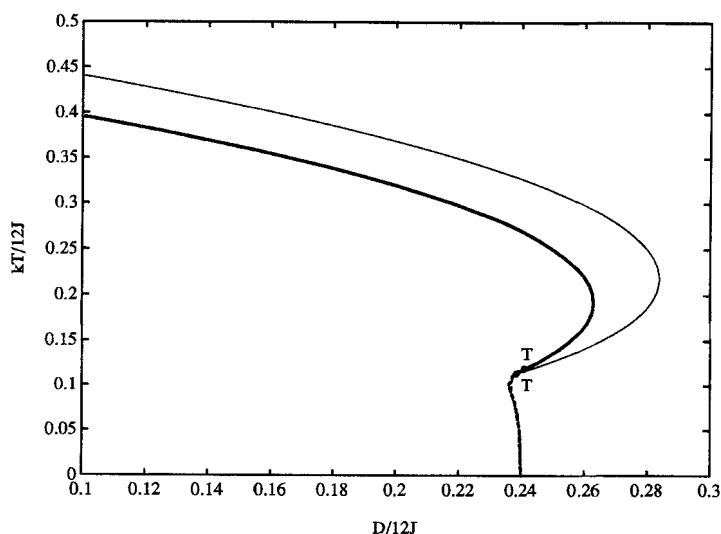

Figure 1. Critical temperatures versus $d = D/12J$ for $\xi = -0.52$ in the tetrahedron (thick line) and in the pair approximation (thin line). Solid lines denote second order phase transitions and broken lines first order phase transitions. T is a tricritical point.
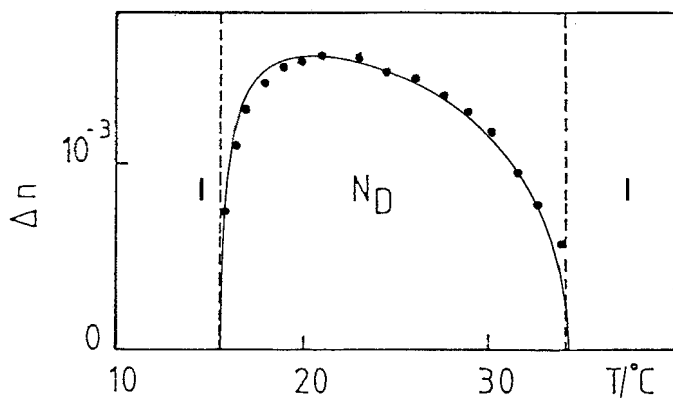

Figure 2. Order parameter y_1 versus temperature for $\xi = -0.52$ and $d = 0.2425$. Theoretical curve (solid line) and experimental data from [7] (dots).
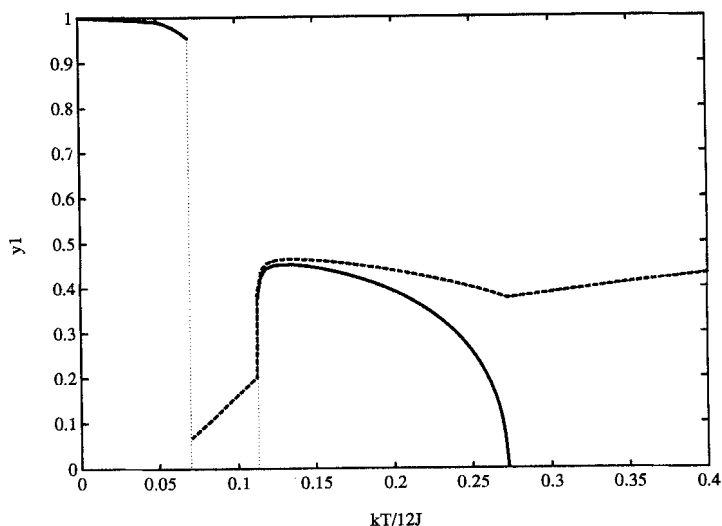
Figure 3. Order parameters y_1 (solid line) and y_2 (broken line) versus temperature for $\xi = -0.52$ and $d = 0.238$.

results with the experimental data. In figure 1 the phase diagram is shown for $\xi = -0.52$ both in the tetrahedron (thick line) and in the pair approximation (thin line). This diagram exhibits first order phase transitions (broken lines), second order phase transitions (solid lines) and a tricritical point T. Improving approximation, the second order transition line undergoes a remarkable variation, while the first order one is nearly unchanged. We can identify two kinds of reentrant behaviour according to the value of d. For values of d just larger than 0.24 we have a nematic–isotropic reentrant phase. The behaviour of the order parameter y_1 versus temperature (solid line) is given in figure 2 for $d = 0.2425$. In the same figure the experimental data (dots) obtained by Galerne et al. [7] are reproduced. It is worth noting that the agreement is good. A problem occurs with respect to the order of the transition: while the low temperature transition (isotropic–nematic) can be of first order (see figure 1), the successive more high temperature transition (nematic–isotropic) is of second order. This fact apparently is in contrast with the experimental results. The phase diagram of figure 1 shows another remarkable feature. For values of d just lower than 0.24 the system exhibits the sequence nematic–isotropic–nematic–isotropic phase when the temperature increases from zero. Figure 3 gives the behaviour of the order parameters y_1 and y_2 in this case ($d = 0.238$). A first order nematic–isotropic phase transition is followed by a reentrant behaviour characterized by a first order phase transition (low temperature) and a second order phase transition (high temperature). It is worthwhile to observe that a phenomenon of this type has been already pointed out in thermotropic liquid crystals, where a succession of smectic–nematic–smectic–nematic phases has been registered [14].

3. Conclusion

In summary, the model proposed in this paper has several interesting features as it concerns reentrant behaviour in liquid crystals, even if some problems exist. Work is in progress to improve the model in order to overcome this.

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