Four particle cluster approximation for the Maier–Saupe model of the isotropic–nematic phase transition

R. Van der Haegen,[a] J. Debruyne, R. Luyckx,[b] and H. N. W. Lekkerkerker

Fakulteit Wetenschappen, Vrije Universiteit Brussel, B-1050 Brussel, Belgium
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The cluster variation theory for the Maier–Saupe model of the isotropic–nematic phase transition is extended to the four-particle level. As in the case of the Heisenberg ferromagnet, the irregularities of the three-particle cluster approximation applied to cubic lattices, where there are no triangles of nearest neighbors, disappear. The extension from three- to four-particle clusters yields improved values of all quantities, characteristic for the phase transition.

I. INTRODUCTION

In previous work,[1] we have applied the cluster variation method to the Maier–Saupe model for the isotropic-nematic phase transition in the three-particle approximation, in order to investigate the shortcomings of a mean-field description,[2] which are twofold:

(i) The difference between the critical temperature T_c of the first order transition and the temperature T_c^* at which the liquid phase becomes absolutely unstable is measured to be about 1 K for MBBA[3] ($T_c = 318$ K), whereas a mean-field treatment leads to a theoretical value

$$T_c - T_c^* \cong 30 \text{ K} .$$

(ii) Other characteristic quantities of the phase transition are the averages of the second and the fourth Legendre polynomials $P_2(\cos\theta)$ and $P_4(\cos\theta)$ over the orientational distribution function $f(\theta)$, where θ is the angle between the long axis of the molecules and the director n. Although the values of $\langle P_2(\cos\theta)\rangle$ predicted by this theory are in reasonable agreement with experimental data, the calculated values of $\langle P_4(\cos\theta)\rangle$ are considerably higher than the experimental ones.[4,5]

The improvement which we obtain by using the variational cluster expansion method results from the introduction of higher order correlations between the interacting molecules. The conclusion of this work was that for lattices where a pair of nearest neighbors has common nearest neighbors the three-particle cluster approximation leads to an encouraging improvement over the two-particle cluster approximation (which is identical to the earlier developed constant-coupling treatment), whereas if this is not the case no progress results. The same tendency has been observed in the magnetic case.[6] The cluster variation theory has been applied to the Heisenberg ferromagnet up to the four-spin approximation by Ballensiefen and Wagner,[7] who showed that the irregularities of the three-spin approximation for cubic lattices disappear when the method is extended to four-spin clusters. Naturally, one expects to encounter the same qualitative behavior in the case of the Maier–Saupe model for the isotropic–nematic phase transition.

In Sec. II, we present the development of the cluster variation theory, together with its essential features as applied to the Maier–Saupe model, up to the four-particle level. The next section contains a discussion of the results obtained within this approximation. Finally, we give some concluding remarks.

II. FOUR-PARTICLE CLUSTER VARIATION METHOD

Here, we restrict ourselves to the simplest intermolecular potential that gives the possibility of nematic ordering. Further, the assumption of nearest neighbor interaction is made, so that we can use the rotationally invariant Maier–Saupe Hamiltonian

$$H = -J \sum_{(i,j)} P_2(\mathbf{a}_i \cdot \mathbf{a}_j) \tag{1}$$

where J is a positive constant, the summation is over all interacting pairs of molecules and $\mathbf{a}_i$ is a unit vector pointing in the direction of the long axis of molecule i.

The use of a variation parameter $\overline{S}$ in the cluster variation theory yields a series expansion of the free energy per particle.

$$f = f_{(0)} + f'_{(2)} + f'_{(3)} + f'_{(4)} + \cdots . \tag{2}$$

The zeroth order term of this expansion corresponds to the mean-field approximation

$$-\beta f_{(0)} = \tfrac{1}{2}\gamma J\beta\overline{S}^2 + \ln Z_1 . \tag{3}$$

The additional contributions of two-particle and three-particle clusters to the free energy are calculated by direct application of the cluster theory. Using Hamiltonian (1), one obtains the following expressions for the free energy per molecule in the two-particle and three-particle cluster approximation

$$-\beta f_{(2)} = -\beta(f_{(0)} + f'_{(2)}) = \tfrac{1}{2}\gamma \ln Z_I - (\gamma - 1)\ln Z_1 \tag{4}$$

$$-\beta f_{(3)} = -\beta(f_{(0)} + f'_{(2)} + f'_{(3)}) = \frac{\gamma\gamma_1}{3!}\ln Z_\Delta - \tfrac{1}{2}\gamma(\gamma - \gamma_1 - 1)\ln Z_\Lambda$$

$$+ \tfrac{1}{2}\gamma(\gamma_1 - 2\gamma + 3)\ln Z_I + \tfrac{1}{2}(\gamma - 1)(\gamma - 2)\ln Z_1 , \tag{5}$$

where γ is the number of nearest neighbors and γ_1 is the number of common nearest neighbors of a pair of nearest neighbors. Further

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

$$Z_I = \int d\mathbf{a}_1 \int d\mathbf{a}_2 \exp\beta J\{(\gamma-1)\overline{S}[P_2(a_{1z})+P_2(a_{2z})]+P_2(\mathbf{a}_1\cdot\mathbf{a}_2)\} \, ,$$

$$Z_\Lambda = \int d\mathbf{a}_1 \int d\mathbf{a}_2 \int d\mathbf{a}_3 \exp\beta J\{(\gamma-1)\overline{S}[P_2(a_{1z})+P_2(a_{3z})]+(\gamma-2)\overline{S}P_2(a_{2z})+P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+P_2(\mathbf{a}_2\cdot\mathbf{a}_3)\} \, ,$$

and

$$Z_\Delta = \int d\mathbf{a}_1 \int d\mathbf{a}_2 \int d\mathbf{a}_3 \exp\beta J\{(\gamma-2)\overline{S}[P_2(a_{1z})+P_2(a_{2z})+P_2(a_{3z})]+P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+P_2(\mathbf{a}_2\cdot\mathbf{a}_3)+P_2(\mathbf{a}_3\cdot\mathbf{a}_1)\} \, ,$$

where the subscripts I, Λ, and Δ refer to the type of diagram that gives rise to that particular contribution.

The variation parameter $\overline{S}$ is determined by minimizing the free energy; $\partial f/\partial\overline{S}=0$. This yields a consistency relation for $\overline{S}$, which is satisfied by $\overline{S}=0$ (isotropic phase) for all temperatures. In Fig. 1, we sketch the behavior of the other solutions of this equation as a function of temperature.

The behavior of the free energy as a function of $\overline{S}$, which is presented in Fig. 2 for a few characteristic temperatures, is the same for each level of the cluster approximation. It is clear from Fig. 2 that the first-order transition between isotropic and nematic phase ($\overline{S}\neq 0$) takes place at the temperature T_c for which the two minima that occur in the free energy function are equally deep. The isotropic phase becomes absolutely unstable with respect to nematic ordering below a certain temperature T_c^*, which is therefore determined by the condition $(\partial^2 f/\partial\overline{S}^2)_{\overline{S}=0}=0$.

Since the fourth term in the free energy expansion was already evaluated for the case of the Heisenberg ferromagnet[7] we simply made the transcription to the isotropic–nematic phase transition. Adding the total contribution of all pure four-vertex diagrams $f'_{(4)}$ to the three-vertex free energy $f_{(3)}$ gives for the free energy per molecule in the four-particle cluster approximation

$$-\beta f_{(4)} = -\beta(f_{(3)}+f'_{(4)}) = \nu_1 \ln Z_{\boxtimes} + \nu_2 \ln Z_{\boxtimes} + \nu_3 \ln Z_{\Box}$$
$$+ \nu_4 \ln Z_{\boxtimes} + \nu_5 \ln Z_{\sqcup} + \nu_6 \ln Z_{\swarrow} - a\ln Z_\Delta - b\ln Z_\Lambda + c\ln Z_I - d\ln Z_1 \tag{6}$$

with

$$Z_{\boxtimes} = \iiiint d\mathbf{a}^4 \exp\beta J\{(\gamma-3)\overline{S}[P_2(a_{1z})+P_2(a_{2z})+P_2(a_{3z})+P_2(a_{4z})]$$
$$+P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+P_2(\mathbf{a}_2\cdot\mathbf{a}_3)+P_2(\mathbf{a}_3\cdot\mathbf{a}_4)+P_2(\mathbf{a}_4\cdot\mathbf{a}_1)+P_2(\mathbf{a}_1\cdot\mathbf{a}_3)+P_2(\mathbf{a}_2\cdot\mathbf{a}_4)\} \, ,$$

$$Z_{\boxtimes} = \iiiint d\mathbf{a}^4 \exp\beta J\{(\gamma-2)\overline{S}[P_2(a_{2z})+P_2(a_{4z})]+(\gamma-3)\overline{S}[P_2(a_{1z})+P_2(a_{3z})]$$
$$+P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+P_2(\mathbf{a}_2\cdot\mathbf{a}_3)+P_2(\mathbf{a}_3\cdot\mathbf{a}_4)+P_2(\mathbf{a}_4\cdot\mathbf{a}_1)+P_2(\mathbf{a}_1\cdot\mathbf{a}_3)\} \, ,$$

$$Z_{\Box} = \iiiint d\mathbf{a}^4 \exp\beta J\{(\gamma-2)\overline{S}[P_2(a_{1z})+P_2(a_{2z})+P_2(a_{3z})+P_2(a_{4z})]+P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+P_2(\mathbf{a}_2\cdot\mathbf{a}_3)+P_2(\mathbf{a}_3\cdot\mathbf{a}_4)+P_2(\mathbf{a}_4\cdot\mathbf{a}_1)\} \, ,$$

$$Z_{\boxtimes} = \iiiint d\mathbf{a}^4 \exp\beta J\{(\gamma-1)\overline{S}P_2(a_{4z})+(\gamma-2)\overline{S}[P_2(a_{2z})+P_2(a_{3z})]$$
$$+(\gamma-3)\overline{S}P_2(a_{1z})+P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+P_2(\mathbf{a}_1\cdot\mathbf{a}_3)+P_2(\mathbf{a}_1\cdot\mathbf{a}_4)+P_2(\mathbf{a}_2\cdot\mathbf{a}_3)\} \, ,$$

$$Z_{\sqcup} = \iiiint d\mathbf{a}^4 \exp\beta J\{(\gamma-1)\overline{S}[P_2(a_{1z})+P_2(a_{4z})]+(\gamma-2)\overline{S}[P_2(a_{2z})+P_2(a_{3z})]+P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+P_2(\mathbf{a}_2\cdot\mathbf{a}_3)+P_2(\mathbf{a}_3\cdot\mathbf{a}_4)\} \, ,$$

and

$$Z_{\swarrow} = \iiiint d\mathbf{a}^4 \exp\beta J\{(\gamma-1)\overline{S}[P_2(a_{2z})+P_2(a_{3z})+P_2(a_{4z})]+(\gamma-3)\overline{S}P_2(a_{1z})+P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+P_2(\mathbf{a}_1\cdot\mathbf{a}_3)+P_2(\mathbf{a}_1\cdot\mathbf{a}_4)\} \, .$$

The coefficients ν_i, a, b, c, and d are listed for various lattices in Table I, together with the number of nearest neighbors and common nearest neighbors. Again, the subscripts refer to the contribution of the corresponding type of diagram.

Minimizing $-\beta f_{(4)}$ with respect to the variation parameter yields

$$\nu_1(\gamma-3)\left\langle\sum_{i=1}^{4}P_2(a_{iz})\right\rangle_{\boxtimes} + \nu_2\langle(\gamma-2)[P_2(a_{2z})+P_2(a_{4z})]+(\gamma-3)[P_2(a_{1z})+P_2(a_{3z})]\rangle_{\boxtimes} + \nu_3(\gamma-2)\left\langle\sum_{i=1}^{4}P_2(a_{iz})\right\rangle_{\Box}$$

$$+\nu_4\langle(\gamma-1)P_2(a_{4z})+(\gamma-2)[P_2(a_{2z})+P_2(a_{3z})]+(\gamma-3)P_2(a_{1z})\rangle_{\boxtimes} + \nu_5\langle(\gamma-1)[P_2(a_{1z})+P_2(a_{4z})]+(\gamma-2)[P_2(a_{2z})+P_2(a_{iz})]\rangle_{\sqcup}$$

$$+\nu_6\left\langle(\gamma-1)\left[\sum_{i=2}^{4}P_2(a_{iz})\right]+(\gamma-3)P_2(a_{1z})\right\rangle_{\swarrow} - a(\gamma-2)\left\langle\sum_{i=1}^{3}P_2(a_{iz})\right\rangle_\Delta - b\langle(\gamma-1)[P_2(a_{1z})+P_2(a_{3z})]$$

$$+ (\gamma - 2) P_2(a_{1z}) \rangle_\Lambda + c(\gamma - 1) \langle P_2(a_{1z}) + P_2(a_{2z}) \rangle_I - d\gamma \langle P_2(a_{1z}) \rangle_1 = 0 \ . \tag{7}$$

where $\langle \cdots \rangle_1$ denotes an average over the one-particle orientational distribution function

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

and similarly, $\langle \cdots \rangle_{\text{diagram}}$ means the average over a more-particle distribution for which Z_{diagram} is the normalization constant. As always, $\bar{S} = 0$ satisfies the consistency relation (7) and the nontrivial solutions have qualitatively the same functional form as the one presented in Fig. 1. The free energy in the four-particle cluster approximation shows the behavior pictured by Fig. 2. At this level, the temperature T_c^* is determined by solving the equation

$$\nu_1(\gamma - 3)^2 \left\langle \left[\sum_{i=1}^{4} P_2(a_{iz}) \right]^2 \right\rangle_{\boxtimes (\bar{S}=0)} + \nu_2 \langle \{(\gamma - 2)[P_2(a_{2z}) + P_2(a_{4z})] + (\gamma - 3)[P_2(a_{1z}) + P_2(a_{3z})]\}^2 \rangle_{\boxtimes (\bar{S}=0)}$$

$$+ \nu_3(\gamma - 2)^2 \left\langle \left[\sum_{i=1}^{4} P_2(a_{iz}) \right]^2 \right\rangle_{\Box (\bar{S}=0)} + \nu_4 \langle \{(\gamma - 1)P_2(a_{4z}) + (\gamma - 2)[P_2(a_{2z}) + P_2(a_{3z})] + (\gamma - 3)P_2(a_{1z})\}^2 \rangle_{\asymp (\bar{S}=0)}$$

$$+ \nu_5 \langle \{(\gamma - 1)[P_2(a_{1z}) + P_2(a_{4z})] + (\gamma - 2)[P_2(a_{2z}) + P_2(a_{3z})]\}^2 \rangle_{\sqcup (\bar{S}=0)} + \nu_6 \left\langle \left\{(\gamma - 1)\left[\sum_{i=2}^{4} P_2(a_{iz}) \right] + (\gamma - 3)P_2(a_{1z})\right\}^2 \right\rangle_{\vee (\bar{S}=0)}$$

$$- a(\gamma - 2)^2 \left\langle \left[\sum_{i=1}^{3} P_2(a_{iz}) \right]^2 \right\rangle_{\triangle (\bar{S}=0)} - b \langle \{(\gamma - 1)[P_2(a_{1z}) + P_2(a_{3z})] + (\gamma - 2)P_2(a_{2z})\}^2 \rangle_{\Lambda (\bar{S}=0)}$$

$$+ c(\gamma - 1)^2 \langle [P_2(a_{1z}) + P_2(a_{2z})]^2 \rangle_{I (\bar{S}=0)} = \tfrac{1}{5} d\gamma^2 \ . \tag{8}$$

III. RESULTS AND DISCUSSION

We have applied the four-particle cluster approximation to the Maier–Saupe model system for the lattices, listed in Table I. The calculation of the integrals, appearing in the consistency equations, was done by using the quadrature formula of Gauss. The use of 16 Gauss points per integration variable gave an accuracy of 1 part in 10^4 or better. The consistency points were located with a predictor–corrector method.

The values obtained for the transition temperature for the various lattices are listed in Table II, together with the results of previous calculations (three-particle cluster approximation), constant coupling approximation[8] and the mean field treatment. Taking higher order clusters into account yields a monotonically decreasing
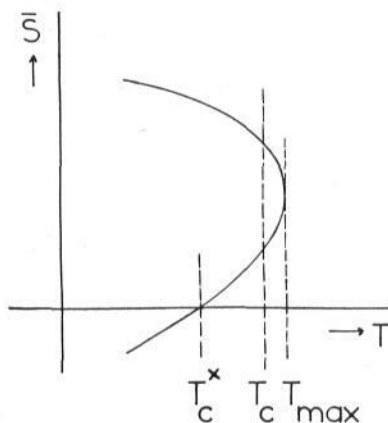
critical temperature for the hl and fcc lattice. The discontinuity in T_c for the sc and bcc lattice, in going from the two-particle to the three-particle cluster approximation, disappears in going one step further. The decrease obtained by going from three- to four-particle clusters yields for the sc lattice a temperature T_c which lies very closely to the value of 0.186, calculated with the Monte Carlo method.[9]

Theoretical values of $(T_c - T_c^*)/T_c$ are presented in Table III for successive approximations. We see that
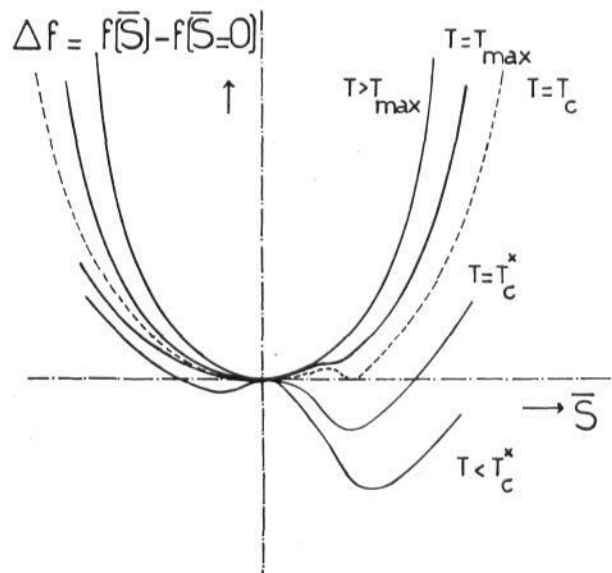

FIG. 1. Qualitative representation of the behavior of the variation parameter $\bar{S}$ as a function of temperature.

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

TABLE I. Values of ν_i, a, b, c, and d for various lattices, together with their nearest neighbors and common nearest neighbors. hl: hexagonal layer lattice; sc: simple cubic lattice; bcc: body centered cubic, fcc: face centered cubic.

	hl	sc	bcc	fcc
γ	6	6	8	12
γ_1	2	0	0	4
ν_1	...	...	...	2
ν_2	3	...	...	24
ν_3	...	3	12	3
ν_4	12	...	...	120
ν_5	27	63	148	282
ν_6	2	20	56	44
a	16	0	0	168
b	81	183	484	954
c	63	108	312	816
d	10	10	35	165

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

	hl	sc	bcc	fcc
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
Four-particle cluster	0.1768	0.1903	0.1985	0.2034

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

	hl	sc	bcc	fcc
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
Four-particle cluster	0.0235	0.0383	0.0395	0.0451

TABLE IV. Values of $\langle p_2(\cos\theta)\rangle_c$ for various lattices.

	hl	sc	bcc	fcc
Meanfield	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
Four-particle cluster	0.2740	0.3471	0.3504	0.3597

TABLE V. Values of $\langle p_4(\cos\theta)\rangle_c$ for various lattices.

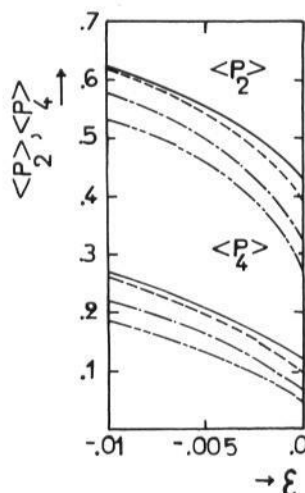|	hl	sc	bcc	fcc
Mean field	0.1199	0.1199	0.1199	0.1199
Two-particle cluster	0.0972	0.0972	0.1033	0.1091
Three-particle cluster	0.0664	0.0985	0.1041	0.0871
Four-particle cluster	0.0492	0.0784	0.0799	0.0841

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 hl lattice. Mean-field approximation (—), two-particle cluster (– – – –), three-particle (– · – · – ·), and four-particle cluster approximation (– – – — – – –).

the four-particle cluster theory leads to a valuable improvement over the three-particle approach in each of the examined lattices. However, the value for the sc lattice is still much larger than the value 0.007 ± 0.004, predicted by recent Monte Carlo calculations.[9] Again, we notice the disappearance of the irregularity of the three-particle cluster approximation in the lattices with no common nearest neighbors.

In Tables IV and V we give the values for $\langle P_2(\cos\theta)\rangle$ (order parameter) and $\langle P_4(\cos\theta)\rangle$, taken at the critical temperature (index c). The development of the values for the order parameter, predicted by successive approximations, is much like that in the case of the transition temperature. The result obtained for $\langle P_2(\cos\theta)\rangle_c$ nearly reaches the Monte Carlo value (0.333 ± 0.009) for the sc lattice.[9] Notice that, for the sc and bcc lattice, the decrease for the value of $\langle P_4(\cos\theta)\rangle_c$ in going from the mean field approximation to the two-particle cluster approximation is even slightly smaller than the decrease in going from three- to four-particle clusters. In Fig. 3, we present the variation of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ as a function of the reduced temperature $\epsilon = (T - T_c)/T_c$.

IV. CONCLUDING REMARKS

We conclude that the extension of the cluster variation method from three- to four-particle clusters leads to improved values for all quantities, characteristic for the phase transition within the Maier–Saupe model. Actually, the values obtained for T_c and $\langle P_2(\cos\theta)\rangle_c$ are very close to the results of the Monte Carlo method for the sc lattice. Even though an important improvement results by extending the cluster theory, the quantity $(T_c - T_c^*)/T_c$ is still considerably larger than the Monte Carlo value in the same lattice. Further, the discontinuity for lattices with no common nearest neighbors in the three-particle cluster approximation disappears by extension of the method.

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