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INFLUENCE OF FLUCTUATIONS ON THE ORDER PARAMETERS IN NEMATIC MIXTURES

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Abstract NMR measurements and computer simulations suggest that the component order parameters of nematic mixtures differ less from each other than proposed by mean field theories. Using a simple resticted orientation model for the nematogenes and going beyond the mean field approximation one may explain the observed behaviour of the order parameters.

INTRODUCTION

In the framework of the mean field approximation (MFA) some essential features of the phase transition nematic-isotropic are well understood. Nevertheless, there are some discrepancies between the mean field treatment of nematic mixtures and the measured relation between the component order parameters S_1 and S_2 of the constituents. According to MFA this relation can be parameterized as[1]

$$S_1 = f(y), \quad S_2 = f(r \cdot y), \quad f(y) = \frac{d}{dy} \ln \int_0^1 \exp[y \cdot P_2(\xi)] d\xi \qquad (1)$$

($r^2 = T_2 / T_1$, clearing point ratio). To discuss this relation it is not necessary to know the order parameters as a function of temperature. In fact, relation (1) does not depend on the composition of the mixture! This could be a hint that the MFA fails qualitatively to explain the order parameter relation $S_1(S_2)$. To confirm this idea we imagine a mixture with a low concentration of component 2 which has a considerably higher transition temperature than the (host) component 1 (r is large). According to (1) a moderate value of S_1 corresponds to a component order parameter S_2 tending to 1 since $f(y \to \infty) \to 1$. This is a direct consequence of the mean field picture which considers a molecule of component 2 in the

effective "field" of the other molecules. From a microscopic point of view the molecule 2 should be affected by the orientational fluctuations of the host molecules resulting in a decreased value of its order parameter. Thus, the order parameters of both components differ much less from each other than predicted by the MFA. To confirm this consideration we compare the MFA result (1) with some experimental and computer simulation data (Fig.1). The ^{13}C-NMR measurements where performed by Grande et al.[2] whereas the Monte Carlo results are taken from Hashim et al.[3] It is obvious that the MFA cannot explain neither the experimental nor the simulation data.

THE MODEL

In this section a restricted orientation lattice model is introduced which simply permits non mean field calculations. We assume that the axially symmetric non-polar rigid molecules are living on a simple cubic 3-dimensional lattice. The allowed orientations of the molecules are restricted to the x , y and z axis of the lattice. The intermolecular potential V is supposed to be a function of $\vec{r}_{ij}$ and Θ_{ij}, where $\vec{r}_{ij}$ is the interparticle distance vector in the principal axis frame of molecule i; Θ_{ij} is the angle between the long axis of both molecules. Taking into account only the nearest neighbour (nn) interactions one obtains four invariant pair configurations which are shown in the scheme below.

(a) V=-J (b) V=0 (c) V=0 (d) V=0

The energy of configuration (a) is -J and the energies of configurations (b) - (c) are assumed to be zero. One can extend the model and take four different interaction constants for all configurations. Now we introduce "spin" variables s_i = 1,2,3 for the three possible orientations of a molecule at lattice site i, the values R_{ij} = 1,2,3 label the direction of the link between the two sites

i and j. As a result the Hamiltonian of the model reads

$$H = -J \sum_{<ij>} (1 - \delta_{s_i R_{ij}}) \delta_{s_i s_j} \quad . \tag{2}$$

(<ij> denotes nn pair summation) The extension of this model to a binary mixture with quenched disorder yields the Hamiltonian

$$H^{mix} = - \sum_{<ij>} J_{n_i n_j} (1 - \delta_{s_i R_{ij}}) \delta_{s_i s_j} \quad . \tag{3}$$

J_{11}, J_{22}, $J_{12} = J_{21} = \sqrt{J_{11} J_{22}}$ (geometric mean rule) are the interaction parameters between the two kinds of molecules, the randomly chosen numbers n_i are equal to 1 or 2 if a lattice site is occupied by a molecule of component 1 or 2. Since model (2) is very similar to the 3-state Potts model (besides the δ_{sR}-term) it is of some interest to investigate its properties in the pure nematogenic case. For comparison we employed a cluster variation (CV) technique and performed Monte Carlo simulations of the model.

THE CLUSTER APPROXIMATION

In order to get corrections to the mean field picture the approximation scheme of the cluster variation method is utilized[4,5], restricted to the pair approximation[5]. The entropy Σ and internal energy U of the system (2) are given by

$$\Sigma/kN = 5 \sum_{\alpha=1,3} p_\alpha \ln p_\alpha - \sum_{\alpha,\beta,\gamma=1,3} p^{(\gamma)}_{\alpha\beta} \ln p^{(\gamma)}_{\alpha\beta} \tag{4a}$$

$$U/JN = - \sum_{\alpha,\beta=1,3} (1 - \delta_{\alpha\beta}) p^{(\beta)}_{\alpha\alpha} \quad , \tag{4b}$$

where p_α is the probability to find a molecule in state α and $p^{(\gamma)}_{\alpha\beta}$ is the probability to find a molecule in state α and in γ direction a molecule in state β. In the uniaxial nematic phase the director is assumed to be aligned with the z axis (α=3); hence $p_1 = p_2 = (1-p_3)/2$, $S = \langle P_2(\cos(\theta)) \rangle = (3p_3 - 1)/2$. Taking into account the symmetries of the system, the probabilities $p^{(\gamma)}_{\alpha\beta}$ may be parameter-

izied by 6 variables. Minimizing the free energy $F = U-\Sigma T$ one yields 6 coupled equations which , in part, can be solved analytically. One obtains ($J = k = 1$) $T_{ni} = 1.205$, $S(T_{ni}) = 0.525$, the latent heat $\Delta U = 0.25$ and the entropy jump $\Delta\Sigma = 0.207$ (MFA: $T_{ni} = 1.44$, $S(T_{ni}) = 0.500$, $\Delta U = 0.333$, $\Delta\Sigma = 0.231$). The transition temperatures and the jumps of configurational entropy and internal energy are reduced in comparison with MFA results. From a rough Monte Carlo simulation of the model (Fig.2) it is obvious that the cluster approximation yields a satisfactory improvement of MFA. Further, the rescaled transition temperatures of the 3-state Potts model[6,7] are well above the corresponding temperatures of (2). So, the thermodynamics of (2) is more affected by fluctuations and one expects similar consequences in the case of binary mixtures.

THE MODEL MIXTURE

Now, the considerations above are extended to the case of Hamiltonian (3). For dilute mixtures the probability q_3 to find a molecule of the minority component (component 2) in the z direction is given by (neglecting nnn correlations)

$$q_3 = \sum_{\{s_i\}_{nn}} \left[\prod_{i=1,6} p_{s_i}\right] \frac{\exp[-E(3,\{s_i\}_{nn})/kT]}{\sum_{s=1,3} \exp[-E(s,\{s_i\}_{nn})/kT]} \quad , \quad S_2 = (3q_3 - 1)/2 \quad , \quad (5)$$

where $E(s,\{s_i\}_{nn}) \propto J_{12}$ is the energy of a molecule in state s surrounded by the six nn molecules of component 1 in the states $s_1, \ldots, s_6$. The p_α may be calculated from the pair approximation mentioned above. The validity of (5) is restricted to the case of small J_{12} ($r < 1$), otherwise nnn correlations become important. In Fig.1 the results of a Monte Carlo simulation of (3) and the solution of (5) are compared.

Finally we note that the simple approximation (5) is sufficient to explain the order parameter differences in binary nematic mixtures whereas the MFA fails qualitatively. Furthermore we mention the

importance of the dependence of the intermolecular potential V on the vector $\vec{r}_{12}$ which led to the model (2),(3). In comparison with the 3-state Potts model this model exhibits an increased sensitivity to fluctuations.

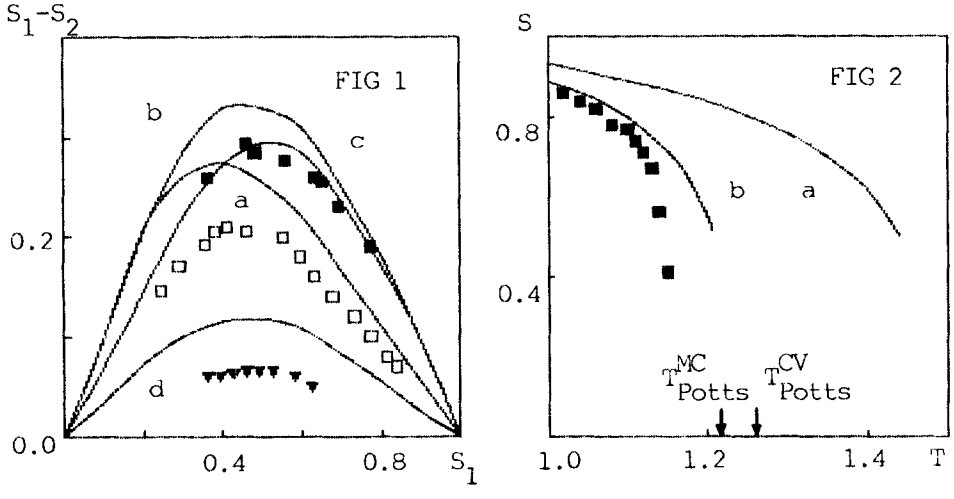


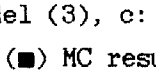
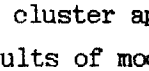
FIGURE 1 Order parameter difference S_1-S_2 versus S_1(r=2), a: MFA (1), b: MFA of model (3), c: cluster approximation (5), (□) MC results of Ref.3, (■) MC results of model (3), (▼) experimental data[2] for 25% C_6H_{13}-  -CN, 75% C_5H_{11}-  -CN (r=1.33), d: MFA for r=1.33

FIGURE 2 Order parameter S versus T for model (2), a: MFA, b: CV method, (■) MC data, T^{MC}_{Potts}, T^{CV}_{Potts} corresponding (rescaled) transition temperatures of the 3-state Potts model[6,7]

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