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Phase diagrams for a model of a lipid monolayer

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Abstract. A microscopic model of a lipid monolayer is proposed. It includes, within a single scheme, the following factors which are considered to be essential in phase transitions in lipid systems: formation of gauche rotamers, interactions between polar heads, interactions between hydrocarbon chains (depending on their conformation) and changes in the energy of the system due to a directional ordering of the chains. Phase diagrams are constructed and discussed and it is shown how the phase diagrams are modified by alterations of these parameters and the length of the hydrocarbon chains.

Key words: Lipid monolayers, phase transitions, Ising model

1. Introduction

In recent years there has been considerable interest in phase transitions of lipid monolayers. In addition to the fact that such systems are intrinsically interesting, they are closely related to biological membranes for which they often serve as models. Whilst the types of phases encountered in lipid monolayers are well known, there is less agreement as to the character of the driving force for the transitions between them. The commonly accepted model seems to be the phase diagram of Albrecht et al. (1978), where the following phases are distinguished: low density (gaseous), isotropic and anisotropic liquids and two crystalline phases with tilted and untilted chains. It is believed that the important factors in the observed phase transitions are: formation of the gauche ± rotamers, interactions between polar heads, van der Waals type attraction between hydrocarbon chains, excluded volume interactions, anisotropy in the chain orientation and, in bilayers, interactions between the two monolayers. One of the aims of a theoretical approach is to reproduce this phase diagram and to estimate the role played by each interaction. So far the main attempts have been directed to explaining the transition between fluid and crystalline phases. The two are often referred to as the liquid extended (LE) and liquid condensed (LC) phases, and the transition is called the main transition. The results of Albrecht et al. (1978), as well as theoretical studies by Caillé and Ågren (1975), Firpo et al. (1981), and Baret et al. (1982a), indicate the presence of a phase called either anisotropic liquid or nematic. It is characterised by anisotropic distribution of the projections of the chain axis on the plane of the substrate and its origin is in the repulsive hard core and attractive intermolecular interactions (Caillé and Ågren 1975).

Theoretical models are usually based on just a few of the above listed mechanisms, apart from the van der Waals interactions which are nearly always present. The models fall roughly into two categories – linking the main transition with the excluded volume effects or with the changes in the conformational states of the hydrocarbon chains (for details and references see excellent reviews by Bell et al. (1981), Nagle (1980), and Caillé et al. 1980). Zuckermann et al. (1982) considered both factors, using a combination of two different models. The Marseille group linked the main transition with either the cooperative character of interactions between kinks made of gauche ± rotamers (Firpo et al. 1984) or with changes of the rotational symmetry of the system (Baret et al. 1982b). Interactions between polar heads are quite often neglected, one of the exceptions being Baret et al. (1982b). Also the effect of the length of a hydrocarbon chain is rarely considered, although Marčelja (1974) and Caillé (1974, 1980) investigated how melting of a chain depends on its length.

In this paper we shall consider several types of interactions present in a lipid monolayer and, using the spin-1 Ising Hamiltonian, derive the phase diagram for the system. We shall also determine how the length of a hydrocarbon chain affects the phase diagram and in particular the value of the main transition temperature.

2. Model and calculations

Let us assume that our lipids are fatty acids, such as myristic or palmitic acid and that they have a hydrophilic polar head with a single, saturated hydrocarbon chain attached to it. The latter is composed of several, say N, carbons, However, only a certain part of them, say n, farthest from the polar group, may be subject to an excitation from a trans to a gauche conformation. Therefore e.g. in palmitic acid, where $N = 15$, the first 15-n $C-C$ bonds will form a rigid part and rotamers will appear in the last n bonds. This assumption is well corroborated by the results of Marčelia (1974) and Caillé (1974). The rigid part is always, in our model, tilted to the plane of the polar heads, and we assume that it can be oriented roughly along two, mutually perpendicular, directions. This will enable us to reproduce the isotropic and anisotropic phases. A similar assumption has been made by Firpo et al. (1981). We shall consider the following factors:

1. Long-range interactions between polar heads, characterised by a constant J_1. They are independent of conformation or orientation of the two interacting chains and are the main factor in the condensation process.

2. Short-range interactions between the n most distant, from the polar head, carbons within each chain. This is a part of a single chain energy coming from summation over $C-C$ bond energies as modified by their neighbours, and may be regarded as a microscopic analogue of the energy (E_{int}) introduced by Marčelja (1974). The interaction is one-dimensional, with a constant J_2, and as such cannot lead to a new transition, and hence change the form of the phase diagram. It can, however, change the critical parameters, such as transition temperature or pressure. This is what has been found (see e.g. Caillé et al. 1980) as a result of changing the length of hydrocarbon chains. Also Marčelja (1974) showed that, for a single chain, the order parameter has a jump as a function of the temperature, which indicates the existence of interactions between rotamers of the same chain.

3. Long-range (van der Waals like) attraction between chains. Interaction constant is J_3 for chains in the all-*trans* conformation, and decreases with increasing number of rotamers in either of the chains, as a result of geometrical changes.

4. Long-range interactions between chains (interaction constant J_4) – ordering the chains anisotropically and responsible for the transition from isotropic to anisotropic phases.

As is usually the case, we assume that the substrate is modelled by a planar lattice of V sites on which the polar heads are located. This can be conveniently described by the following Hamiltonian (divided here by $\beta = (k_B T)^{-1}$) where k_B is the Boltzmann constant and T is the temperature):

$$\begin{aligned} -\beta\mathscr{H} = {} & J_1 \sum_{\lambda,\nu} S_\lambda^2 S_\nu^2 + J_2 \sum_{\lambda=1}^{V} S_\lambda^2 \left(\sum_{i=1}^{n-1} \sigma_i \sigma_{i+1} \right) \\ & + J_3 \sum_{\lambda,\nu} S_\lambda^2 \left(\sum_{\substack{i=1 \\ i\in\lambda}}^{n} \sigma_i \right) S_\nu^2 \left(\sum_{\substack{j=1 \\ j\in\nu}}^{n} \sigma_j \right) \\ & + J_4 \sum_{\lambda,\nu} S_\lambda S_\nu + \mu \sum_{\lambda=1}^{V} S_\lambda^2 . \end{aligned} \tag{1}$$

$S_\lambda = 0, \pm 1$ and means that at the lattice site λ there is no hydrocarbon chain ($S_\lambda = 0$) or that it is oriented in one of the permissible directions ($S_\lambda = \pm 1$). $\sigma_i = +1$ ($i \in \lambda$) if the $C-C$ link (i-th from the end of a chain at the site λ) is in the trans, and $\sigma_i = -1$ if it is in the gauche state. μ is the chemical potential.

To derive the phase diagram we shall use the molecular field approximation (MFA) for the long-range interactions, whereas the short-range ones will be calculated exactly. A similar approach has already been used in describing magnetic lattice gas (Dudek and Pekalski 1984). Within the spirit of the MFA, we introduce three unknown averages, for the three interactions 1, 3, 4, to be determined later from the stability conditions for the free energy. We have therefore

$$n^{-1} \langle S_\lambda^2 \sum_{\substack{i=1 \\ i\in\lambda}}^{n} \sigma_i \rangle = m, \tag{2}$$

$$\langle S_\lambda^2 \rangle = \varrho, \tag{3}$$

$$\langle S_\lambda \rangle = q. \tag{4}$$

$\langle \ldots \rangle$ means a statistical (grand canonical) average with the Hamiltonian (1). According to the definition, m measures the average amount of rotamers in the last n $C-C$ links of a hydrocarbon chain. $m = 1$ means that an average chain is in the all-trans (ground) state. A smaller value of m corresponds to the appearance of the gauche rotamers. The main (melting) transition is in our model associated with m equal to zero. The second parameter, ϱ, is the average density of the polar heads and its change (discontinuous, as it will turn out) is connected with the liquid-gas transition. Finally, q is a measure of directional anisotropy of the hydrocarbon chains. If $q = 1$ then all the chains are tilted roughly along the same direction and the system is anisotropic to the highest degree. If $q = 0$, their directions are scattered and the system is isotropic. Although MFA is a crude approximation, there are some indications (Caillé et al. 1980) that it works reasonably well in lipid and biological systems. With Eqs. (2)–(4) our

Hamiltonian becomes

$$-\beta \mathscr{H}_{\mathrm{MFA}} = \sum_{\lambda=1}^{V} \left(-A_0 + A_1 S_\lambda^2 + A_2 S_\lambda + S_\lambda^2 \mathscr{H}^*\right) \quad (5)$$

with

$$A_0 = J_1 \varrho^2 + J_3 (\mathrm{mn})^2 + J_4 q^2,$$
$$A_1 = 2 J_1 \varrho + \mu, \quad (6)$$
$$A_2 = 2 J_4 q,$$

and $\mathscr{H}^*$ is the part of the Hamiltonian coming from the short-range interactions

$$\mathscr{H}^* = \sum_{i=1}^{n-1} J_2 \sigma_i \sigma_{i+1} + 2 J_3 \mathrm{mn} \sum_{i=1}^{n} \sigma_i . \quad (7)$$

As is easily seen, $\mathscr{H}^*$ is the Hamiltonian of the one-dimensional Ising model in an external "field" $2 J_3 m$. This part can be calculated exactly (see Appendix). Denoting the contribution from (7) to the total partition function, Z_G, by Z_n, we have

$$Z_G = Tr_S \exp(-\beta \mathscr{H}_{\mathrm{MFA}})$$
$$= 2 \exp(-A_0)(1 + \exp(A_1) Z_n \cosh A_2). \quad (8)$$

Hence, the free energy per lattice site, f, is

$$f = -\lim V^{-1} \beta^{-1} \ln Z_G$$
$$= \beta^{-1}(A_0 - \ln 2 - \ln(1 + \exp(A_1) Z_n \cosh A_2). \quad (9)$$

Out of the three stability conditions

$$\partial f / \partial m = 0, \quad \partial f / \partial \varrho = 0, \quad \partial f / \partial q = 0, \quad (10)$$

one is used to eliminate the chemical potential and two others to determine the unknown averages – m and q. Density ϱ is regarded as an external parameter. It is obvious that the equation determining m must depend on the number, n, of active $C - C$ links of a hydrocarbon chain. The calculations are simple but lengthy, and are outlined in the Appendix. It is customary to use $v = \varrho^{-1}$ instead of ϱ. v is simply connected with a, the area per lipid, $v = a/a_0$, where a_0 is the smallest area, taken in the following to be 20 Å². As is usually the case, see e.g. Nagle (1980), the sequences for odd and even n have different initial terms. We have decided to use the odd (longer) sequence and therefore we present results for $n = 1$, 3, 5.

$$n = 1 \quad m_1 = v^{-1} \tanh C_1 \quad (11.1)$$

$$n = 3 \quad m_3 = (3v)^{-1} \frac{3 e^{2J_2} \sinh 3C_3 + (2 + e^{-2J_2}) \sinh C_3}{\exp(2J_2) \cosh 3C_3 + (2 + \exp(-2J_2)) \cosh C_3} \quad (11.2)$$

$$n = 5 \quad m_5 = (5v)^{-1} \frac{3 \exp(4J_2) \sinh 5C_5 + 3A \sinh 3C_5 + B \sinh C_5}{\exp(4J_2) \cosh 5C_5 + A \cosh 3C_5 + B \cosh C_5} \quad (11.3)$$

with

$$A = 3 + 2\exp(2J_2);$$
$$B = A + \exp(-4J_2)(1 + 4\exp(2J_2)) \quad (12)$$

and

$$C_k = 2 k J_3 m_k \quad \text{for} \quad k = 1, 3, 5. \quad (13)$$

From the remaining two stability conditions (10) we get

$$q = v^{-1} \tanh(2 J_4 q) \quad (14)$$

and

$$\varrho = D/(D+1) \quad (15)$$

with

$$D = Z_n \exp(A_1) \cosh A_2 . \quad (16)$$

After eliminating μ we get the free energy, f, for our (lattice gas) model, or the (lateral) pressure π, to which it is equal (Huang 1963), as

$$\pi a_0 = \mathrm{MC}\{-J_3 \mathrm{mn}^2 - J_1 q^2 + \beta^{-1} \ln(v/(v-1))$$
$$+ \beta^{-1} \ln 2\}. \quad (17)$$

The use of the mean field approximation caused the appearance of unphysical van der Waals loops in the isotherms at first-order transitions. The correct tie lines were obtained from the Maxwell construction (MC in Eq. (17)).

Solving Eqs. (11), (14) and (17) permits the construction of the (π, v) isotherms. Some of them exhibit flat parts (after the Maxwell construction) which are associated with first-order transitions, others have cusps – identified as second-order ones. From that data the phase diagrams in the (π, T) plane are constructed. Some of the isotherms, showing first and second order transitions are shown in Fig. 1.

3. Results and discussion

Results for $n = 1, 3, 5$ and a particular choice of J's are presented in Fig. 2a–c. These values are consistent with those commonly used (e.g. Baret and Firpo 1983; Zuckermann et al. 1982) and yield all the phases permitted by the model. The sequence of phase diagrams illustrates well the effect of the length of the hydrocarbon chains on the number and location of possible phases.

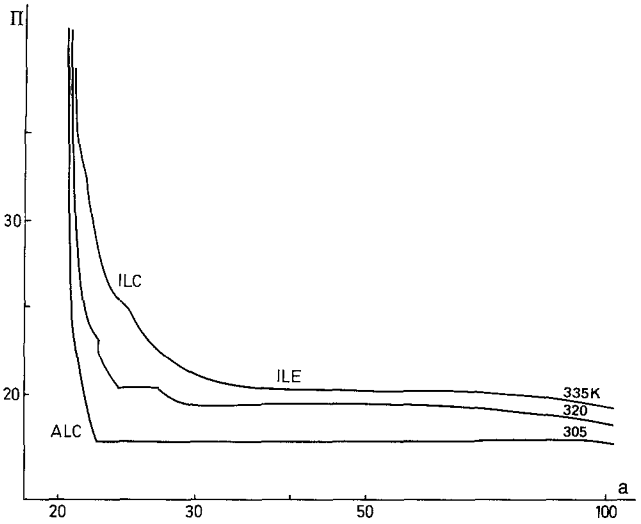

Fig. 1. Isotherms pressure, π, versus area per lipid, a, at different temperatures, showing first (flat parts) and continuous or second order (cusps) transitions. The J parameters have the following values: $J_1 = 9 \cdot 10^{-14}$ ergs, $J_2 = 2 \cdot 10^{-14}$ ergs, $J_3 = 4 \cdot 10^{-15}$ ergs, $J_4 = 2.5 \cdot 10^{-14}$ ergs. $n = 5$, area in Å^2, pressure in dynes/cm

For $n = 1$ we have $\mu = 0$ at all (except very low) temperatures, which means that the liquid condensed phase, i.e. the phase where most of the $C - C$ links on an average hydrocarbon chain are in the trans (ground) conformation, is practically never reached. There is only a first-order transition (broken line in Fig. 2) from a gaseous (G) to isotropic liquid extended (ILE) phase and then a second-order transition (solid line) to the anisotropic liquid extended phase (ALE), in which there is a preferred direction for the average orientation of the hydrocarbon chains.

When there are three active $C - C$ links per hydrocarbon chain, a new phase appears – anisotropic liquid condensed (ALC), separated from ALE by a line of second-order transitions. The transition line known form the previous figure is unchanged.

For $n = 5$ our phase diagram changes significantly, apart from the G–ILE transition which remains unaffected. Interactions between carbon groups within a chain are now sufficient (because of their number – their strength remains the same) to change the sequence of phases. Now the hydrocarbon chains may stay in the non-melted state (majority of the $C - C$ links in the *trans* conformation) till much higher temperature, above that at which the system becomes anisotropic. Because of the exchange of the location of the $m = 0$ and $q = 0$ lines, the ILC phase appears in the place of the ALE phase. Transitions between phases, i.e. their character (first or second-order), as well as their location on the (π, T) plane are, in general, determined by the values of the J's.

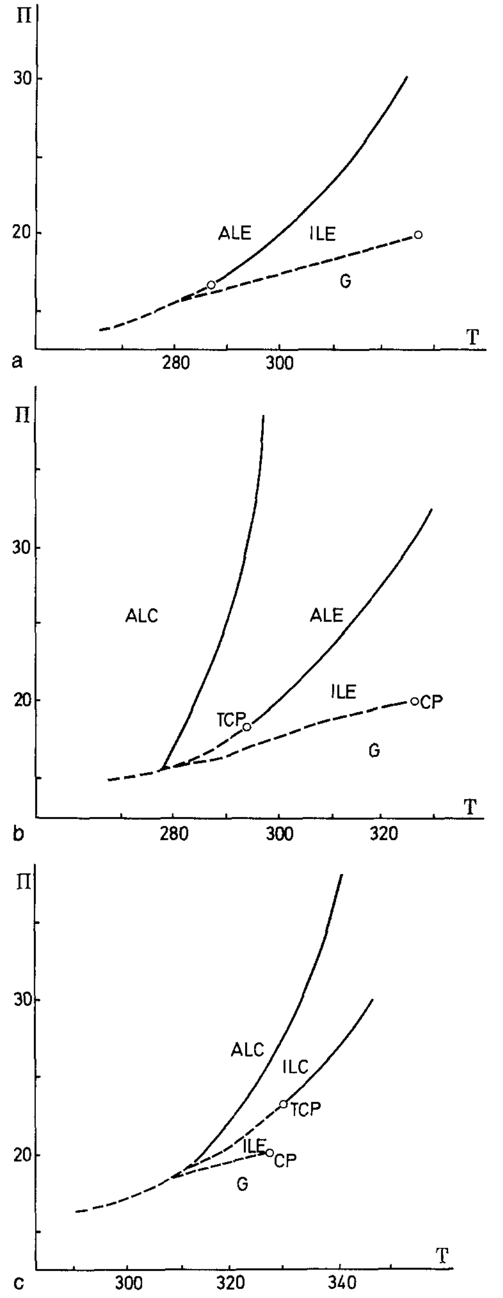

Fig. 2 a–c. Phase diagrams in the lateral pressure – temperature (π, T) plane. Solid lines indicate continuous, *broken ones* – first order transitions. The phases are denoted in the usual way: G: gaseous; *ILE*: isotropic liquid expanded ($m = 0$, $q = 0$); *ALE*: anisotropic liquid expanded ($m = 0$, $q \neq 0$); *ILC*: isotropic liquid condensed ($m \neq 0$, $q = 0$); *ALC*: anisotropic liquid condensed ($m \neq 0$, $q \neq 0$). *CP* is the critical and *TCP* the tricritical point. Values for the J parameters as in Fig. 1. Pressure is in dyne/cm, temperature in K. **a** $n = 1$, $m = 0$ in all shown plane; **b** $n = 3$; **c** $n = 5$

Instead of presenting numerous figures illustrating the iunfluence of the values of particular J's on the phase diagram, we have decided to describe it qualitatively. This seems justified since the whole approach has a rather qualitative character. The discussion presented below will be illustrated by examples for $n = 5$.

J_1 governs the polar head organisation and hence the location of lipids and their density. Influences

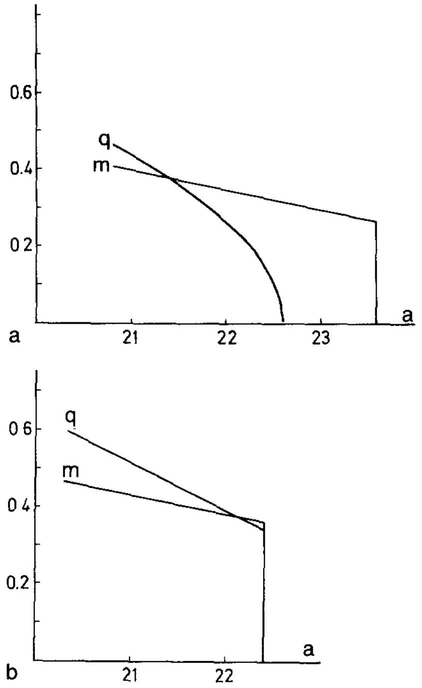

Fig. 3 a and b. Change of m and q with density (area per lipid). Same values of the parameters as in Fig. 1. $n = 5$. Area in Å^2. **a** $T = 320$ K; **b** $T = 310$ K

mainly the G–LE transition, which is first-order. For large values of J_1 or low temperatures, the jump in the density at the transition is so large that the system goes directly from the gaseous to the ALC phase, as illustrated in Fig. 1 for the lowest temperature. As one would expect, an increase in J_1 moves the critical point to higher temperatures and lowers the transition line on the (π, T) diagram.

J_2 and J_3-forces responsible for the appearance of rotamers. They influence the $m = 0$ (main transition) line. Depending on their values the transition can be of first or second-order. An increase in J will, in general, shift the tri-critical point to a higher temperature, hence the transition will be longer of the first-order. J_2 acts within a chain, J_3 between them. Of the two, J_3, as a long-range interaction, is more "influential". An increase from 4 to 6 ($\cdot 10^{-15}$ ergs) lowers the LE–LC line below the LE–G one. An increase of J_2 by the same amount, shifts the lines but does not merge transitions. J_2 can, however, produce other effects. Changing its value from 2.8 to 3 ($\cdot 10^{-15}$ ergs) results in the appearance of a temperature, T_0, below which the transition line $m = 0$ is above the $q = 0$ one, on the (π, T) diagram. For $T > T_0$ the order is reversed. This may mean that for larger J_2 the hydrocarbon chains become more rigid, which manifests itself more clearly at higher temperatures.

J_4 determines the degree of anisotropy of the hydrocarbon chains. Again the transition can be of first or second-order character, depending on the value of J_4. An increase of J_4 lowers the $q = 0$ transition line and moves the tri-critical point to higher temperatures.

It should be noted that the phase diagram, as shown in Fig. 2c, is not the only one possible when $n = 5$. By changing the parameters J we can have a diagram with another topology, e.g. a single line of first-order transitions (G–ALC) which at a tri-critical point will change into a second-order transition (ILE–ALC). It is also possible to merge the first-order transitions (ILE–ILC and ILC–ALC) into a single one ILE–ALC.

It is also interesting to see how m and q change with a (volume per lipid) and at what values of m and q the system passes, in a first-order transition, to a new phase. This is shown in Fig. 3 a and b for the same set of parameters as in Fig. 1 and two different temperatures. Obviously, in each case both m and q diminish with increasing volume, but at sufficiently high temperatures q drops much faster than m does. This means that the mechanism leading to a directional ordering of the hydrocarbon chains is more sensitive to changes in the density than is the melting of the chains.

4. Conclusions

Using the spin-1 Ising model (lattice gas system), we have constructed a microscopic model which, within a single framework, contains most of the factors influencing phase diagrams in lipid systems. Some of these factors (polar head or van der Waals interactions) were already considered within a microscopic approach, while others were treated phenomenologically. For this model we have constructed phase diagrams in the (π, T) plane and compared thermal behaviour of two parameters – one connected with the number of rotamers and the second with anisotropic orientation of the chains.

Lipid chains are represented here by a series of $C - C$ links, of which only the n outermost are active, i.e. subject to conformational changes. The calculations were performed for n up to 5. The non-active part of the hydrocarbon chain is assumed to be rigid, i.e. always in the all-trans conformation, but tilted to the plane of polar heads located at the sites of a two-dimensional lattice. Its exact form is, because of the approximation used, not relevant here. It has been shown how the form of the phase diagram depends on the number, n, of links and on the values of the parameters.

The phase diagram for $n = 5$ reproduces correctly the majority of experimentally observed phases in lipid systems (Albrecht et al. 1978). The role of particular interactions has been discussed. It seems that the interactions between polar heads, although the strongest, do not play a crucial role, except in determining the density of lipids. In contrast – the interactions between the chains – which in this model depend on the conformations of the chains – are very important, despite their small numerical value. Quite generally, it may also be noticed that by changing the values of any of the J's, the phase diagram is affected in the following way – an increase of a J will push downwards the respective line and it may, if it happens close to the tri-critical point, change the character of the transition – from second to first-order.

It is also possible to estimate (very roughly because n is small), the influence of n on the value of T_M (melting temperature). Using the two reliable points ($n = 3$ and $n = 5$), one can extrapolate it to $n = \infty$. It gives $T_M(\infty)$ from 500 K for $\pi = 20$ dyne/cm to 580 K for $\pi = 30$ dyne/cm, in fair agreement with the predictions of Nagle (1980) yielding 511 K for polyethylene.

Certainly the model presented above is a simple one and it contains four adjustable parameters (the J's) which are associated with four different and independent interactions. The number could be reduced but only at the price of imposing additional (artificial) relations among them. It is however reassuring that for reasonable values the choice of J's leading to the phase diagram in Fig. 2c, is unique. The method we have used (MFA) is a crude one. Therefore the agreement of each particular result with more refined theories or experiment, does not completely validate the model. It is nevertheless encouraging that the phase diagrams, dependence on the length of the hydrocarbon chains, different sensitivity of q and m on density are, qualitatively at least, correct.

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Appendix

Here we shall derive the equation for the order parameter, m, in the simplest non-trivial case, i.e. for $n = 3$. For higher n values the calculations follow the same lines.

The three-spin (in a chain) partition function Z_3 is given by

$$\begin{aligned} Z_3 &= Tr_\sigma \exp\{J_2(\sigma_1\sigma_2+\sigma_2\sigma_3)+6J_3 m(\sigma_1+\sigma_2+\sigma_3)\} \\ &= Tr_\sigma \exp\{J_2(\sigma_1+\sigma_3)\sigma_2+C_3(\sigma_1+\sigma_2+\sigma_3)\} \\ &= Tr_\sigma(\cosh J_2+\sigma_1\sigma_2\sinh J_2) \\ &\quad\cdot(\cosh J_2+\sigma_2\sigma_3\sinh J_2) \\ &\quad\cdot(\cosh C_3+\sigma_1\sinh C_3)(\cosh C_3+\sigma_2\sinh C_3) \\ &\quad\cdot(\cosh C_3+\sigma_3\sinh C_3). \end{aligned} \tag{A.1}$$

The only terms which, after taking the trace, will contribute, are those where the σ's are squared. Hence

$$\begin{aligned} Z_3 &= \cosh^3 C_3\cosh^2 J_2 \\ &\quad+\cosh C_3\sinh^2 C_3(\sinh^2 J_2+2\sinh J_2\cosh J_2) \\ &= 1/4\,[\cosh 3C_3\exp(2J_2) \\ &\quad+\cosh C_3(2+\exp(-2J_2))]. \end{aligned} \tag{A.2}$$

From $\partial f_3/\partial\varrho = 0$ and using Eq. (9), we can determine the chemical potential μ (see also Eq. (15)):

$$e^{A_1} = \frac{\varrho}{1-\varrho}(Z_3\cosh A_2)^{-1}. \tag{A.3}$$

From $\partial f_3/\partial m = 0$ we get

$$3m = \varrho\,[3\cosh 3C_3\,e^{2J_2}+\sinh C_3(2+e^{-2J_2})]Z_3^{-1}. \tag{A.4}$$

Inserting (A.3) into (A.4) we arrive at (11.2).

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