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The phase transition in amphiphilic monolayers: isotherms in the cluster variation method

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Abstract. The liquid-expanded (LE)–liquid-condensed (LC) phase transition in monolayers of amphiphilic molecules is investigated in the pair approximation of the cluster variation method. The model analysed is the model proposed by Firpo *et al* which can be mapped into the Blume–Emery–Griffiths Hamiltonian. The signatures of the LE–LC transition are searched for as break points on the isotherms of the surface pressure–molecular area diagram. The results obtained in the pair approximation are improved with respect to those obtained in the Bragg–Williams approximation for a set of typical energy and entropy parameters in the case of pentadecanoic acid. In particular, the LE–LC phase transition is shown to be weakly first order. A comparison with experimental results gives satisfactory agreement.

1. Introduction

The so-called liquid-expanded (LE)–liquid-condensed (LC) phase transition is one of several phase transitions occurring in monolayers of simple amphiphilic molecules at the air–water interface. The origin of these monomolecular layers can be easily understood by considering that the elongated molecules generally present a hydrophobic end (a hydrocarbon chain) and a hydrophilic end (an acid or alcohol radical, for example). The most common experimental study of these phases is carried out by investigating the surface pressure–molecular area isotherm. The signature of the phase transition is a break point on the isotherm. Much experimental work has been done on these systems [1], but the nature of the LE–LC transition has been a long-standing controversy. Indeed the isotherm does not exhibit a plateau which is as clearly horizontal as that of the gas–liquid transition. A number of experimental factors can influence the results, preventing simple interpretation [2]. First, some experimental data suggested a second-order transition [3]. Subsequent measurements performed on carefully purified amphiphilics indicate that the transition is first order [4]. These results are reinforced by the conventional surface potential method [5], optical second-harmonic generation studies [6], fluorescence microscopy [2, 7, 8] and electron microscopy [9]. A variety of techniques have been used to analyse these systems. Their viscoelastic behaviour has been investigated by means of light-scattering experiments [10]. Infrared–visible sum-frequency vibrational spectroscopy has been employed to monitor the molecular orientation at different surface densities [11]. The structural properties and elasticity of amphiphilic monolayers have been analysed using x-ray reflectivity [8, 12].

On the theoretical side, some models have been proposed in order to describe this interesting phenomenon. A review of the first theoretical contributions has been given in [13]. Recently some new theoretical efforts have been made to describe amphiphilic

monolayers [14–17]. In this paper we refer to a model proposed some years ago by Firpo, Legre, Bois and Baret (FLBB) [18] which accounts for many of the fundamental properties of these systems. The model was firstly studied in the Bragg–Williams approximation, giving a satisfactory qualitative description. The break points on the isotherms, as calculated in that approximation, were in fair agreement with many experimental measurements, and the transition was obtained as second order. Subsequently, Legre *et al* [19], after mapping the FLBB model into a spin-1 Blume–Emery–Griffiths (BEG) model [20], have investigated the properties of the system with a Migdal–Kadanoff approximate position-space renormalization group. They have obtained the LE–LC transition, without finding the break points on the isotherms. The difference was attributed to long-range attractive interactions not considered in the model, which are implicit in the mean-field treatments of two-dimensional systems [19]. Subsequently, Legre *et al* [21] have studied the same model by introducing stresses of mean-field type in the Migdal–Kadanoff decimation procedure, obtaining the compressibility jump.

In this paper we analyse the FLBB model in the pair approximation of the cluster variation method (CVM) [22, 23]. Particular attention is devoted to the study of the isotherms, and to the localization of the break points. The CVM is generally very accurate in determining the critical parameters of systems. Its application to this amphiphilic system is particularly purposeful owing to two important characteristics of the method. First, since the CVM is a generalization of the mean-field approximation, it is certainly interesting to investigate the behaviour of the system with a slightly complex but more accurate approximation such as the pair approximation, where some correlations are taken into account. This enables one to verify better whether the model has the features peculiar to describing the LE–LC transition and implicitly to include long-range attractive interactions between unshielded molecular dipoles not considered in it. It should be remembered that in the case of $1/r^3$ attractive interactions the marginal dimension for which Landau theory applies is two [24]. Second, the formulation of the CVM that we apply is particularly convenient for analysing the pressure dependence of the order parameters, thus leading to a natural investigation of the order of the transition. The CVM is well suited to studying first-order transitions (in which, starting from the disordered phase, the transition occurs before the fluctuations have increased too much) [25] and our calculations indicate that the LE–LC phase transition is weakly first order. Moreover our approach gives results in better agreement with experimental data.

The paper is organized as follows. In section 2 we present the model by reviewing the main steps in its original construction and we show how it is related to the BEG model. We also discuss the choice of a suitable ensemble to be used in the CVM approach. In section 3 we develop the free-energy calculation in the CVM approach and the necessary tools to draw isotherms. In section 4 we present the isotherms and the main results of our calculations and we make comparisons with experiments. Finally, in section 5 we make some conclusive remarks.

2. The model

Let us begin with short review of the model. It is a lattice three-state (spin-1) model to account for the basic properties of monolayers of simple amphiphilic molecules (having a single polar group and a single hydrocarbon chain) near the LE–LC transition. These states simulate the molecular states (of different helicities) corresponding to a chain with a kink in the plus state (+1) and to a chain with a kink in the minus state (−1). These kinks are intrachain defects in the configuration *gauche*(+)–*trans-gauche*(−) in the plus state and

gauche(-)-*trans-gauche*(+) in the minus state. Associated with these molecular states are the number operators N_+ and N_- . The vacancies are the third state (0), with the associated number operator N_0 . In a lattice spin-1 system these states correspond to the eigenvalues $S_i = +1$ (plus state), 0 (vacancies), -1 (minus state) of the z component of a spin-1 operator at the lattice site i . Let us introduce the occupation-number operators at site i , as is usual in a lattice gas approach, as the Kronecker deltas $\delta(S_i, 1) = \frac{1}{2}(S_i^2 + S_i)$ for a plus state, $\delta(S_i, -1) = \frac{1}{2}(S_i^2 - S_i)$ for a minus state, and $\delta(S_i, 0) = 1 - S_i^2$ for a vacancy. From these quantities we can form the following number operators for the pairs of molecules (at nearest-neighbour sites):

$$N_{++} = \sum_{\langle ij \rangle} \delta(S_i, 1)\delta(S_j, 1) \quad (2.1)$$

$$N_{--} = \sum_{\langle ij \rangle} \delta(S_i, -1)\delta(S_j, -1) \quad (2.2)$$

$$N_{+-} + N_{-+} = \sum_{\langle ij \rangle} [\delta(S_i, 1)\delta(S_j, -1) + \delta(S_i, -1)\delta(S_j, 1)]. \quad (2.3)$$

Moreover we have

$$N = N_+ + N_- = \sum_{i=1}^{N'} [\delta(S_i, 1) + \delta(S_i, -1)] = \sum_{i=1}^{N'} S_i^2 \quad (2.4)$$

$$N_0 = \sum_{i=1}^{N'} \delta(S_i, 0) = N' - N \quad (2.5)$$

where N is the number of molecules, N' is the number of lattice sites and $\langle ij \rangle$ indicates summation of the nearest neighbours. The FLBB Hamiltonian of the system is [18]

$$H = -|\omega|(N_{++} + N_{+-} + N_{-+} + N_{--}) - |\Delta\omega|(N_{++}^{(j)} + N_{--}^{(j)}) + \Delta E(N_+ + N_-) \quad (2.6)$$

where $|\omega|$ denotes the attractive interaction energy between nearest-neighbour molecules, $|\Delta\omega|$ is an additional attractive interaction energy to be associated with those nearest-neighbour molecules in the same state which partially overlap, giving a decrease in area per molecule, ΔE is the excitation energy of the kink in the (+1) and (-1) states, and $N_{++}^{(j)}$ and $N_{--}^{(j)}$ are the numbers of ++ and -- nested pairs, respectively.

An intrachain entropy ΔS_t can be associated with the molecular states (+1) and (-1), whose defect is free to move along the chain:

$$\Delta S_t = \Delta S[(N_+ + N_-) - \alpha(N_{++}^{(j)} + N_{--}^{(j)})] \quad (2.7)$$

where ΔS is the internal entropy for (+1) and (-1) states and α is a positive coefficient which describes phenomenologically the entropy lost from a nested pair of molecules in the same state. Moreover the total area of the monolayer can be written as

$$A = 2\sigma_0(N_+ + N_-) + \nu\sigma_0N_0 - \sigma_0(N_{++}^{(j)} + N_{--}^{(j)}) \quad (2.8)$$

where the first term is the area of the states (+1) and (-1) ($2\sigma_0$ is the area of an isolated molecule), the second term is the vacancy area (ν is an adjustable parameter) and the

third term accounts for the area reduction due to packing of the kinks. Denoting by Π the surface pressure and by T the absolute temperature, we consider the thermodynamic potential [18, 19]

$$H_H = H - T \Delta S_i + \Pi A \quad (2.9)$$

which, utilizing (2.1)–(2.5), can be written in the form of the spin-1 BEG Hamiltonian [20]

$$H_H = -J \sum_{\langle ij \rangle} S_i S_j - K \sum_{\langle ij \rangle} S_i^2 S_j^2 + D \sum_i S_i^2 + M N'. \quad (2.10)$$

In (2.10) the following quantities have been introduced:

$$\begin{aligned} J &= (|\Delta\omega| + \Pi\sigma_0 - \alpha T \Delta S)/z & K &= J + |\omega| \\ D &= \Pi\sigma_0(2 - \nu) + \Delta E - T \Delta S & M &= \nu \Pi\sigma_0 \end{aligned} \quad (2.11)$$

z denoting the lattice coordination number. Moreover the assumption $N_{++}^{(j)} + N_{--}^{(j)} = (2/z)(N_{++} + N_{--})$ has been made [18]. The chemical potential μ is then given by

$$\mu = \frac{G}{N} \quad G = \langle H_H \rangle - TS \quad (2.12)$$

where G is the Gibbs free energy, the symbol $\langle \rangle$ means ensemble average and S denotes the entropy of the system (without the intrachain entropy included in $\langle H_H \rangle$). The ensemble considered in (2.12) is the ' T - Π - N ' ensemble. Taking into account that, according to (2.10), H_H has been expressed as a spin-1 Hamiltonian characterized by the dynamical variables S_i ($i = 1 \dots N'$) obeying relation (2.4), it is more convenient to utilize an ensemble ' T - Π - μ ' in which the number N' of lattice sites is fixed and not the number N of molecules [19]. This is possible in view of the thermodynamic limit. In this context we introduce the 'free energy'

$$\Psi = G - \mu \langle N \rangle \quad N = \langle N \rangle \quad (2.13)$$

and, according to (2.12), the equation of state of the system is

$$\Psi(T, \Pi, \mu) = 0. \quad (2.14)$$

From (2.12), (2.13) and (2.4) we can write

$$\Psi = \langle H^* \rangle - TS \quad H^* = H_H - \mu \sum_{i=1}^{N'} S_i^2 \quad (2.15)$$

and H^* is again a BEG Hamiltonian. The problem is now reduced to the determination of the 'free energy' Ψ associated with the spin-1 'Hamiltonian' H^* . With this aim we shall utilize the CVM in the pair approximation.

3. The cluster variation approach

The CVM is based on an approximate expression of the entropy of the system as a sum of suitably weighted cluster entropies relative to a set Γ of maximal clusters and of all their subclusters [23]:

$$S = \sum_{\alpha \in \Gamma} a_{\alpha} N_{\alpha} S_{\alpha} \quad S_{\alpha} = -k_B \text{Tr}(\rho_{\alpha} \ln \rho_{\alpha}). \quad (3.1)$$

In (3.1) N_{α} is the total number of clusters of the α kind and a_{α} is a counting factor, which is easily calculated using the Moebius function [23]. S_{α} is the entropy associated with the cluster α and ρ_{α} is the reduced density matrix for the cluster α , which has to be determined by the minimum-free-energy requirement subject to the constraints

$$\text{Tr} \rho_{\alpha} = 1 \quad \rho_{\alpha} = \text{Tr}_{\omega \setminus \alpha} \rho_{\omega} \quad \omega > \alpha. \quad (3.2)$$

($\text{Tr}_{\omega \setminus \alpha}$ means the partial trace.)

In the pair approximation adopted here, the maximal cluster is a nearest-neighbour pair and the free energy f per site can be expressed as [26]

$$f = \frac{\Psi}{N'} = \frac{\langle H^* \rangle}{N'} + k_B T \left[\frac{1}{2} z \text{Tr}(\rho_p \ln \rho_p) + (1 - z) \text{Tr}(\rho_s \ln \rho_s) \right] \quad (3.3)$$

where ρ_s and ρ_p denote the site and pair density matrices, respectively, and k_B is the Boltzmann constant.

In order to work with only independent variables it is useful to introduce the order parameters

$$y_1 = \langle S_i \rangle \quad y_2 = \langle S_i^2 \rangle \quad (3.4)$$

and the nearest-neighbour two-site correlation functions

$$y_3 = \langle S_i S_j \rangle \quad y_4 = \langle S_i S_j^2 \rangle \quad y_5 = \langle S_i^2 S_j^2 \rangle. \quad (3.5)$$

$\langle H^* \rangle$ can be written in terms of y_i ($i = 1, \dots, 5$) as

$$\frac{\langle H^* \rangle}{N'} = -\frac{1}{2} z J y_3 - \frac{1}{2} z K y_5 + D' y_2 + M \quad D' = D - \mu. \quad (3.6)$$

Analogously the elements of site and pair density matrices (which turn out to be diagonal) can be written in terms of y_i :

$$\rho_{s1} = \frac{1}{2}(y_2 + y_1) \quad \rho_{s2} = 1 - y_2 \quad \rho_{s3} = \frac{1}{2}(y_2 - y_1) \quad (3.7)$$

and

$$\begin{aligned} \rho_{p1} &= \frac{1}{4}(y_3 + y_5 + 2y_4) & \rho_{p9} &= \frac{1}{4}(y_3 + y_5 - 2y_4) \\ \rho_{p2} &= \rho_{p4} = \frac{1}{2}(y_2 - y_5 + y_1 - y_4) & \rho_{p6} &= \rho_{p8} = \frac{1}{2}(y_2 - y_5 - y_1 + y_4) \\ \rho_{p3} &= \rho_{p7} = \frac{1}{4}(y_5 - y_3) & \rho_{p5} &= 1 + y_5 - 2y_2 \end{aligned} \quad (3.8)$$

which satisfies the constraints (3.2). The minimization of the free energy with respect to y_i ($y = 1, \dots, 5$) requires the solution of five non-linear algebraic equations

$$\frac{\partial f}{\partial y_i} = 0 \quad i = 1, \dots, 5. \quad (3.9)$$

This system can be solved explicitly for the correlation functions, obtaining [26]

$$y_3 = \frac{\omega(B+R) - 2}{W} \quad y_4 = \frac{\omega(B-R)}{W} \quad y_5 = \frac{\omega(B+R) + 2}{W} \quad (3.10)$$

where

$$\begin{aligned} B &= [(y_2 + y_1)/(y_2 - y_1)]^\eta & R &= 1/B & V &= [2(1 - y_2)/(y_2 - y_1)]^\eta \\ C &= [2(1 - y_2)/(y_2 + y_1)]^\eta & W &= 2\epsilon(C + V) + \gamma CV + \omega(B + R) + 2 \\ \eta &= (z - 1)/z & \epsilon &= \exp[\beta(J - K + D'/z)] & \gamma &= \exp[\beta(J - K + 2D'/z)] \\ \omega &= \exp(2\beta J) & \beta &= 1/k_B T. \end{aligned} \quad (3.11)$$

In addition the order parameters y_1 and y_2 satisfy the equations

$$y_1 = \frac{\epsilon(V - C) + \omega(B - R)}{W} \quad y_2 = \frac{\epsilon(V + C) + \omega(B + R) + 2}{W} \quad (3.12)$$

which can be solved numerically by iteration. By insertion of these solutions in (3.6)–(3.8) and (3.3) and using (2.14), the state equation of the system is determined. From (2.14), given the values of T and Π it is possible to determine the chemical potential μ and to draw the Π - μ isotherms.

The area per molecule given by $\sigma = \langle A \rangle / N$ can be determined by the relation [19]

$$\sigma = \left. \frac{\partial \mu}{\partial \Pi} \right|_T \quad (3.13)$$

or more directly, using the definition (2.8) and (2.1)–(2.5), (3.4) and (3.5), by

$$\sigma = \sigma_0 \{ 2 - \nu + [\nu - \frac{1}{2}(y_5 + y_3)] / y_2 \}. \quad (3.14)$$

We now have the Π - σ isotherms.

The procedure developed here for the CVM pair approximation can be easily extended in order to achieve a more accurate determination of the free energy [27], e.g. assuming as maximal cluster a square for a square lattice. In this case, however, the calculation is much more complex and often the results do not change appreciably with respect to those obtained in the pair approximation, which already takes into account some correlations. We remember that the CVM when utilized in the site approximation corresponds to the mean-field approach.

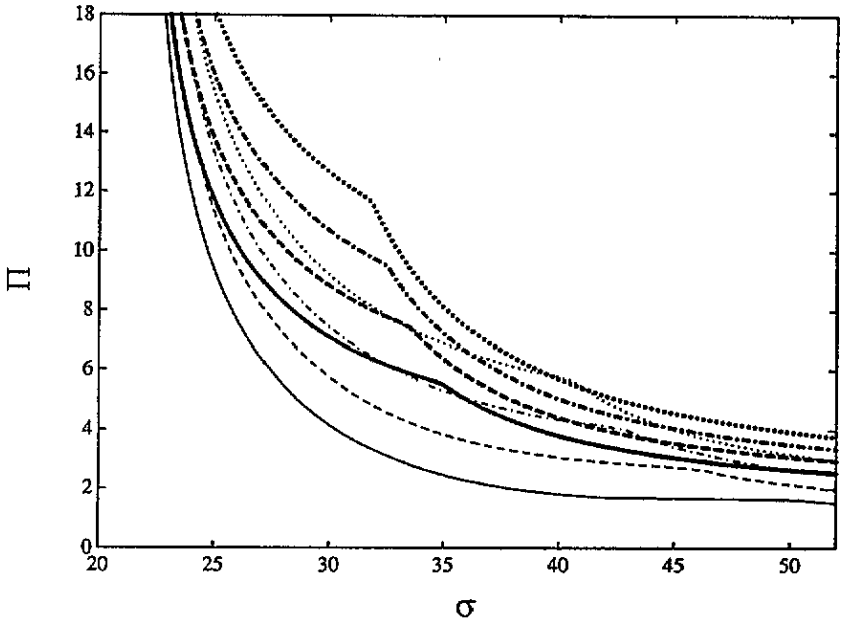


Figure 1. Π (mN m^{-1})- σ (\AA^2) isotherms in the CVM (thick lines) and in the mean-field approximation (thin lines): —, —, $T = 289$ K; - - -, - - -, $T = 296$ K; — · —, — · —, $T = 303$ K; ·····, ·····, $T = 310$ K.

4. Isotherms and order parameters

In the previous section we have identified a procedure to evaluate the Π - σ isotherms. Let us now determine these isotherms having in mind a specific substance: pentadecanoic acid. For this system, FLBB [18] have proposed the following values for the model parameters:

$$\begin{aligned} |\omega| = 216 & & |\Delta\omega| = 1565 & & \Delta E = 500 & & \Delta S = 3.5 \\ \sigma_0 = 22 & & \nu = 2 & & \alpha = 1.2 & & \end{aligned} \quad (4.1)$$

(energy parameters are in $k_B = 1$ units, σ_0 are in squared ångströms and ν and α are dimensionless).

In order to compare our results with those of FLBB we have performed calculations for the square lattice using the values (4.1). Figure 1 shows the Π - σ isotherms obtained in the CVM pair approximation (thick lines) and the corresponding isotherms evaluated in the mean-field treatment of FLBB (thin lines). In both the approximations there is a break point on each of the isotherms, indicating the LE-LC transition. However, the CVM pair approach gives different positions of these break points, in better agreement with the experimental values. For instance, for the isotherm at $T = 296$ K, the experimental break point—in units of millinewtons per metre for pressure and squared ångströms for molecular area—is $(\Pi, \sigma) = (5, 32)$ from the results of Winch and Earnshaw (as quoted in [8]) (determined by interpolating the experimental values at $T = 295.56$ K and at $T = 296.66$ K) and $(\Pi, \sigma) = (\simeq 5.8, 33-34)$ by using the data reported in [2]. Our calculations give $(\Pi, \sigma) = (7.5, 33.4)$, while the results of FLBB indicate that $(\Pi, \sigma) = (2.8, 45.6)$. For $T = 303$ K the experimental data collected in [2] give $(\Pi, \sigma) = (\simeq 13.5, 28-29)$, our

calculations result in $(\Pi, \sigma) = (9.5, 32.4)$ and the mean-field approximation [18] gives $(\Pi, \sigma) = (4.1, 42.5)$.

In order to investigate the characteristics of the LE-LC transition, it is useful to analyse the behaviour of the order parameter y_1 . By definition (3.4), $y_1 \neq 0$ corresponds to the situation in which one of the two molecular states is more populated and therefore the area per molecule is smaller as molecules in the same state can partially overlap; in other words the LC phase is characterized by $y_1 \neq 0$, whereas the LE phase is characterized by $y_1 = 0$. Figure 2 gives y_1 versus Π for the temperature values in figure 1. As we can observe, the LE-LC transition is weakly first order according to the more recent experiments [4-7]. Figure 3 shows the behaviour of y_2, y_3, y_4, y_5 versus Π in the typical case $T = 303$ K. The order of the transition is the main difference between our results and those of FLBB [18]; it is first order in our work and second order in their work. This is a further improvement obtained in the CVM pair approximation with respect to the mean-field treatment.

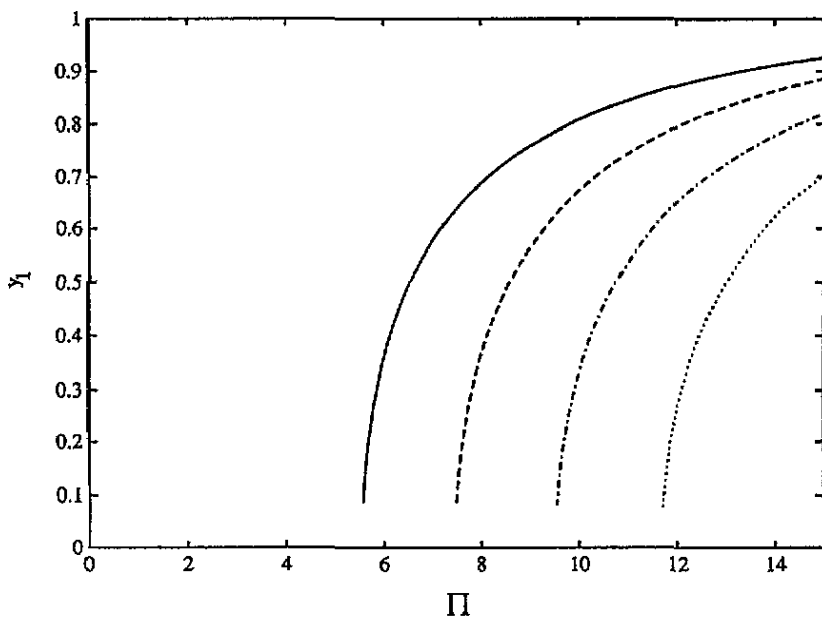


Figure 2. Behaviour of the order parameter y_1 versus Π (mN m^{-1}) for the isotherms in figure 1: —, $T = 289$ K; ---, $T = 296$ K; - · -, $T = 303$ K; ·····, $T = 310$ K.

By using the parameter values (4.1) we have compared our results with some recent experiments. The data in figure 4 have been extracted from [2] and show the experimental isotherms of Harkins *et al* [3], of Pallas and Pethica [4] and of Moore *et al* [2] at $T = 298.16$ K. The dashed line is our result. In figure 5 we give the data of Guyot-Sionnest *et al* [11] at $T = 301.66$ K and our data (dashed line). In order to make a more complete comparison, taking into account that the parameter values (4.1) were proposed by FLBB on the basis of the experimental data in [28], which, as shown by [2, 4], underestimate the gas-liquid critical temperature, we have made a new choice of the parameters, i.e.

$$\begin{aligned}
 |\omega| &= 220 & |\Delta\omega| &= 1580 & \Delta E &= 500 & \Delta S &= 3.5 \\
 \sigma_0 &= 21 & \nu &= 2 & \alpha &= 1.21.
 \end{aligned}
 \tag{4.2}$$

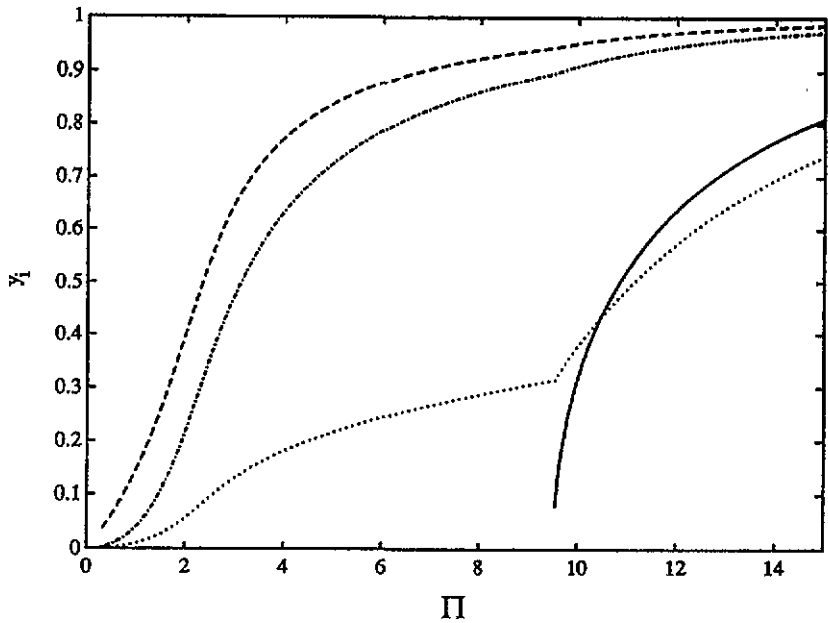


Figure 3. Correlations versus Π (mN m^{-1}) at $T = 303$ K: ---, y_2 ; ·····, y_3 ; —, y_4 ; - · - ·, y_5 .

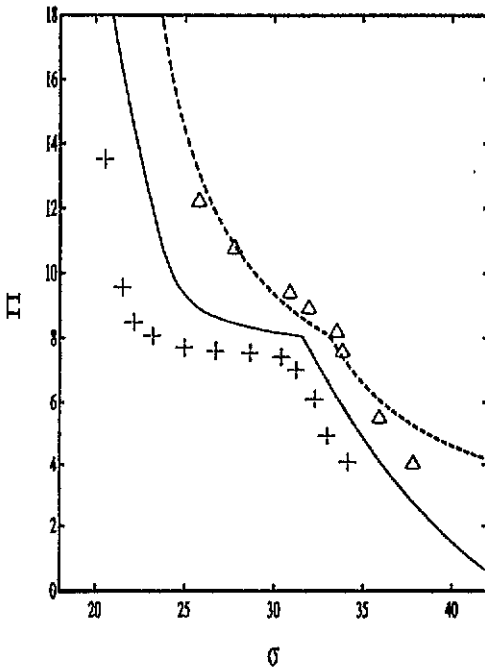


Figure 4. The cvm Π (mN m^{-1})- σ (\AA^2) isotherm (---) compared with the data of Harkins *et al* [3] (Δ), of Pallas and Pethica [4] (+) and of Moore *et al* [2] (—), utilizing the parameter values (4.1). $T = 298.16$ K.

This choice of parameters follows the same criteria utilized by FLBB [18], but now using the more accurate experimental data given in [2]. The remaining arbitrariness in the selection of these parameters is useful to obtain good estimates for the break points. We

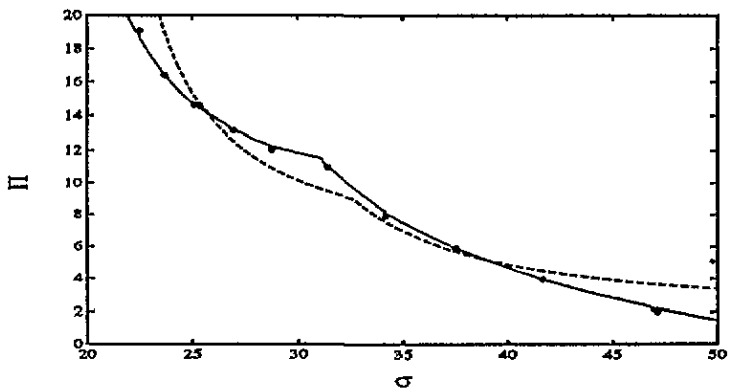


Figure 5. The CVM Π (mN m^{-1})- σ (\AA^2) isotherm (---) compared with the data of Guyot-Sionnest *et al* [11] (—●—), utilizing the parameter values (4.1). $T = 301.66$ K.

obtain break points closer to the experimental values as shown in figures 6 and 7 which correspond to figures 4 and 5, respectively. The global agreement is fairly satisfactory. Better confirmation of the validity of the model could be obtained from utilization of the CVM at a higher level of approximation, which properly includes more correlations.

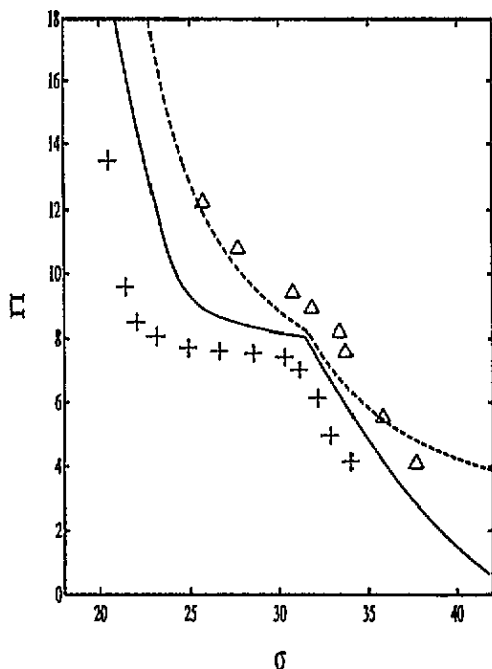


Figure 6. As in figure 4, utilizing the parameter values (4.2).

5. Concluding remarks

Using the FLBB model, which was proposed to describe the LE-LC transition in amphiphilic monolayers at the air-water interface, we have determined the surface pressure-molecular

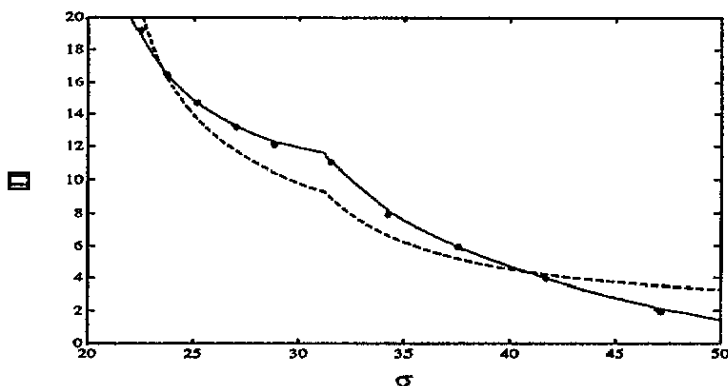


Figure 7. As in figure 5, utilizing the parameter values (4.2).

area isotherms and found the expected break point at the LE-LC transition. An accurate analysis of the order parameters introduced in our procedure has shown a weakly first-order transition agreeing with the more recent experiments. Our investigation has been performed in the pair approximation of the CVM which allows us to take some correlations correctly into account. The good applicability of a generalized mean-field methodology to a two-dimensional system can be related to the presence in the real system of long-range attractive interactions, which reduce the upper critical dimension. At the same time the model seems to possess the basic features to describe the LE-LC transition, as suggested by the improvement obtained in the CVM pair approximation with respect to the Bragg-Williams approach. The presence of a first-order transition is the main difference between our results and those of FLBB. Moreover, for a set of significant temperatures, also the quantitative agreement with experimental data is improved.

The results obtained here confirm the validity of the FLBB model and encourage further investigation employing the CVM at a higher level of approximation. Work is in progress along this line.

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