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Phase transitions in monolayers at air/water and oil/water interfaces

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Abstract. Real-space renormalisation group methods are used to study a two-dimensional lattice fluid model on a triangular lattice with application to phospholipid monolayers at air/water and oil/water interfaces. The phase diagram and pressure–area isotherms are calculated for various strengths of the couplings between neighbouring molecules. The choice of an overall attractive interaction energy between nearest-neighbours yields, in a certain temperature range, two phase transitions along the isotherms. These are interpreted to be a first-order vapour–liquid transition and a continuous transition between two types of liquid phase. With an overall repulsive interaction the first-order transition is absent. The nature of the continuous liquid–liquid transition is examined in detail.

1. Introduction

In recent years much work has been devoted to an examination of the phase properties of natural membranes. It has also been recognised that lipids isolated from membranes display phase properties similar in many respects to those of the parent membrane. This has led to a study of lipid monolayer and multilayer systems as models for membranes. In general it is found that phase transitions of pure lipid systems are somewhat sharper than those associated with real membranes. This is not surprising since it may be expected that in membranes the cooperative effects of the interactions between lipids will be disturbed by the wide distribution of chain lengths, the presence of double bonds or branching in the chains and the interactions with the non-lipid species. Monolayers provide a particularly effective means of investigating lipid phase properties as the number density can be easily controlled and accurately measured at a given surface pressure. In this introduction we shall not attempt a complete survey of previous experimental and theoretical work but shall simply draw attention to some references which seem relevant to the present paper. A more detailed discussion can be found in a recent review by Bell *et al* (1981).

Monolayers of amphipathic molecules at air/water interfaces, where each molecule has a headgroup with an affinity to water and an attached carbon chain, have been known for many years to display interesting phase properties (Adam and Jessop 1926, Nutting and Harkins 1939, Adam 1941, Harkins 1943, 1952). On certain pressure–area

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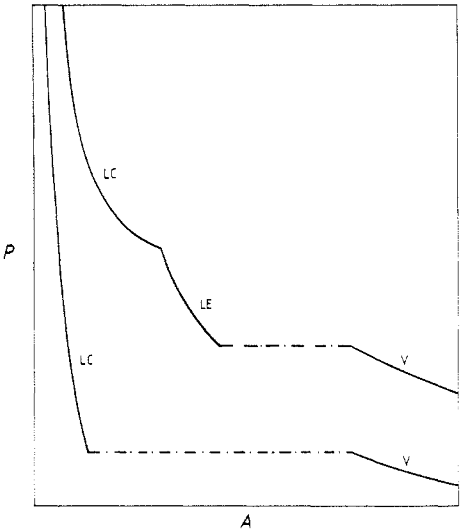


Figure 1. Schematic representation of the pressure–area isotherm behaviour of lipid monolayers at the air/water interface: LC is the liquid condensed phase, LE is the liquid expanded phase and V is the vapour phase.

isotherms a first-order vapour–liquid transition, with a discontinuity in density, is observed with a second type of transition occurring at lower areas as shown schematically in figure 1. This second transition is continuous in the sense that there is no density gap and it appears on the isotherm as an apparently abrupt change of slope. The phases on either side of this continuous transition are often termed liquid-expanded (LE) and liquid-condensed (LC). At lower temperatures it frequently happens that only the vapour–liquid transition can be seen on the isotherm. According to Phillips and Chapman (1968) these phenomena are found, for certain chain lengths, in phospholipid monolayers at the air/water interface. For phospholipid monolayers at the oil/water interface there are no vapour–liquid transitions but the continuous LE–LC transitions still occur (Taylor *et al* 1973, Tan *et al* 1976, Pethica *et al* 1976).

There has been a considerable amount of theoretical work on lattice models, attempting to explain the above behaviour. These theories divide into two main groups. The first group is based on the idea that each carbon chain disorders from the all-trans conformation, in which it is perpendicular to the interface and the carbon atoms are coplanar, to a random conformation. This transition is cooperative and the internally disordered chains occupy a larger area. Theories based on this idea (Nagle 1973, 1975, 1976, Marčelja 1974, Scott 1974, 1975) predict that the LE–LC transition is first order. The second group of theories regard the LE–LC transition as occurring as a result of molecules in their all-trans configuration assuming a form of long-range orientational order. The earliest calculation of this kind is due to Kirkwood (1943). He assumed that the headgroups formed a regular two-dimensional lattice parallel to the interfacial plane with the carbon chains all in the all-trans conformation perpendicular to the plane. His mean-field theory predicted a continuous transition but did not provide a means of obtaining isotherm behaviour. In order to do this it is necessary to introduce vacant sites on the lattice. Bell *et al* (1978) (hereafter referred to as BMT) used the simplest form of lattice model which incorporates both vacancies and orientational effects, by treating the monolayer as a dilute spin-½ Ising model. Mean-field calculations for their model predict both first-order liquid–vapour and continuous LE–LC transitions.

The present paper examines the model of BMT using real-space renormalisation group (RSRG) methods. Mean-field methods always yield classical values for critical exponents at continuous transitions, while RSRG methods, although also approximate, are able to give exponents in better agreement with known exact results for certain exactly soluble models (for a review see Niemeijer and van Leeuwen 1976). Although BMT, as indicated above, regarded their model as a diluted spin-½ Ising model, this is equivalent to the representation of the model as a spin-1 Ising model with the spin variable $S = \pm 1$ corresponding to the orientational state of the molecule and $S = 0$ corresponding to a vacant site. This is the formalism which we adopt. While monolayers are observed experimentally in a limited range of absolute temperature, models can be studied at all temperatures down to 0 K. BMT considered only the temperature range appropriate to monolayers but, particularly for repulsive intermolecular interactions, there are low-temperature phenomena which are interesting for their own sake. We include these in our results.

We describe the model and method of calculation in § 2. In § 3 the results for the phase diagrams and isotherm behaviour are presented and our conclusions are given in § 4.

2. The model

We consider a triangular lattice divided into three equivalent sublattices A, B and C. Each lattice site is either vacant or occupied by a headgroup. We suppose that a molecule

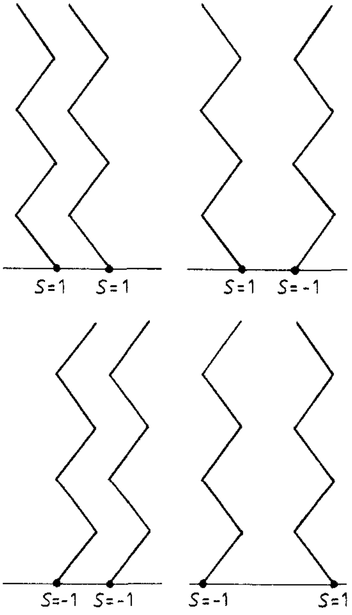


Figure 2. The four possible states of a pair of neighbouring molecules labelled with their values of the variable S_i. A pair of molecules both in the same state interacts with an energy $-(\varepsilon + \theta)$ and a pair of molecules in different states interacts with an energy $-(\varepsilon - \theta)$.

with its headgroup on a lattice site is in one of two states. These two states are coplanar and are distinguished by the conformations of the carbon chains (figure 2). It can be seen that these states transform into each other under a rotation of 180° about an axis through the headgroup and perpendicular to the interface. They can therefore be regarded as two orientational states of the molecule. At each lattice site we have a variable S_i which can take the value 0, ± 1 corresponding respectively to the site being vacant or occupied by a molecule in one of its two orientational states. A pair of molecules on adjacent sites has an energy $-(\varepsilon + \theta)$ if they are both in the same state and $-(\varepsilon - \theta)$ if they are in different states (θ corresponds to the parameter J of BMT). The mean density of molecules is controlled by using the grand canonical distribution with chemical potential μ as an independent variable. In terms of the variables S_i the Hamiltonian of the system is given by

$$H = \sum_{\Delta} H_{\Delta} \tag{1a}$$

with

$$\begin{aligned} H_{\Delta} = {} & -\tfrac{1}{6}\mu(S_{\mathrm{A}}^2 + S_{\mathrm{B}}^2 + S_{\mathrm{C}}^2) - \tfrac{1}{2}\theta(S_{\mathrm{A}}S_{\mathrm{B}} + S_{\mathrm{B}}S_{\mathrm{C}} + S_{\mathrm{C}}S_{\mathrm{A}}) \\ & -\tfrac{1}{2}\varepsilon(S_{\mathrm{A}}^2S_{\mathrm{B}}^2 + S_{\mathrm{B}}^2S_{\mathrm{C}}^2 + S_{\mathrm{C}}^2S_{\mathrm{A}}^2) \end{aligned} \tag{1b}$$

where the summation is over all elementary triangles of the lattice and $S_{\alpha}(\alpha = \mathrm{A, B, C})$ denotes the state of the molecule on the site on sublattice α in triangle Δ.

We use a block-spin transformation similar to that employed by Schick *et al* (1977) in their study of the spin-$\frac{1}{2}$ Ising model and Schick and Griffiths (1977) for the three-state Potts model. An initial cluster of nine sites is chosen such that three sites belong to each

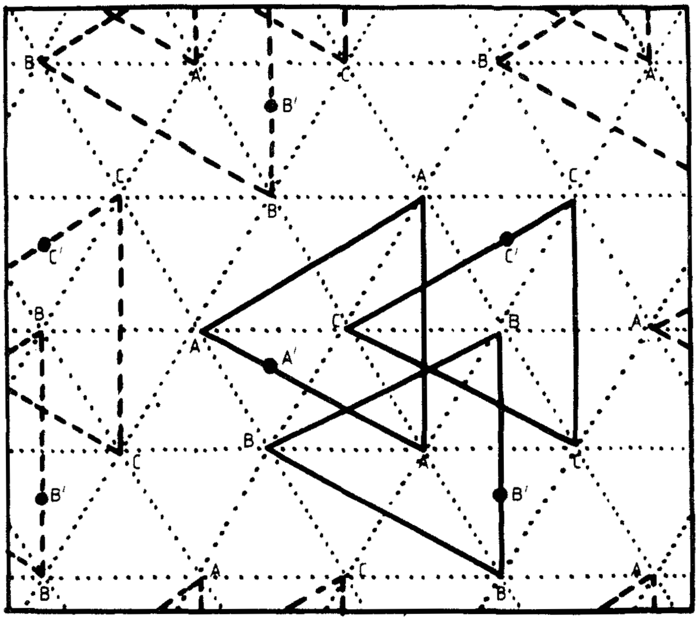


Figure 3. The nine-site cluster of sites with periodic boundary conditions. The spin-state at the site α' of the renormalised lattice is determined by the spin-states at the three α sites ($\alpha = \mathrm{A, B, C}$).

of the three sublattices and periodic boundary conditions are imposed (see figure 3). Application of the renormalisation group transformation reduces the nine-site cluster to a cluster of three sites, one belonging to each of the three sublattices. This corresponds to an increase in length scale by a factor $\sqrt{3}$. The spin state on the renormalised α' site ($\alpha = \mathrm{A, B, C}$) is determined by the spin-states on the three α sites in the nine-site cluster using a weight function. Our results are presented for one particular choice of weight function. If two or three spins on the α sublattice are in the same state then the renormalised spin at α' is assigned to this state. If the three spins are all different then the renormalised spin has a probability of one-third of being in any one of the three spin states. In any RSRG calculation all couplings which are generated by the recurrence relations must be included even if they are not present in the initial Hamiltonian. The Hamiltonian given by equations (1), is invariant under spin inversion and divisible into terms containing the spins on the elementary triangles of the lattice. The recurrence relations will generate all distinct even degree symmetric polynomials in the spins S_A, S_B and S_C. These consist of the three terms given in equation (1*b*) plus the two three-spin terms $S_A S_B S_C\,(S_A + S_B + S_C)$ and $S_A^2 S_B^2 S_C^2$, and we have altogether a five-dimensional space of coupling constants (Southern and Lavis 1980). A special case of the spin-1 Ising model is the three-state Potts model with symmetry group $\mathscr{S}_3$ on the three spin states. The Hamiltonian for this model on a triangular lattice corresponds to the Hamiltonian of the spin-1 Ising model with particular linear relationships between the coupling constants (Young and Lavis 1979). We are in this case left with a space of two independent coupling constants. The weight function we have chosen is that utilised by Schick and Griffiths (1977) to treat the three-state Potts model and the two-parameter subspace of the model is therefore invariant under the operation of our recurrence relations.

The phase diagram is determined by iterating the recurrence relations for the coupling constants (see Southern and Lavis 1979 for a more detailed discussion). A trajectory which begins at a point where the behaviour is not critical will iterate to a sink which characterises the phase. These regions are separated by the critical regions which form domains of attraction for the critical fixed points. Once these fixed points have been located the recurrence relations can be linearised about the fixed points and the eigenvalues λ_i of the linear equations can be calculated. The critical exponents y_i are related to the eigenvalues by $\lambda_i = b^{y_i}$, where b is the scale factor which is equal to $\sqrt{3}$ in the present calculation.

3. Isotherm behaviour

As in the work of BMT we confine our attention to the case $\theta > 0$, and in this case there are four possible stable ground states labelled C_1, C_2, C_3 and C_4 in figure 4. The state C_1 is the ground state corresponding to the vapour phase V, the state C_2 is the ground state corresponding to the liquid condensed phase LC in which each site is occupied by a molecule in the same orientation and the state C_4 is the ground state corresponding to the phase HC in which the molecules, all in the same orientation, form a honeycomb arrangement on two of the three sublattices. The state C_3 is one in which every elementary triangle contains exactly one molecule in either configuration. This phase does not exhibit long-range order at any non-zero temperature. In terms of the renormalisation procedure this means that the fixed point associated with the phase is not a sink. The diagram which would correspond to figure 4 for a temperature fractionally above zero would have the whole of the region occupied by C_3 in figure 4 as part of the stability

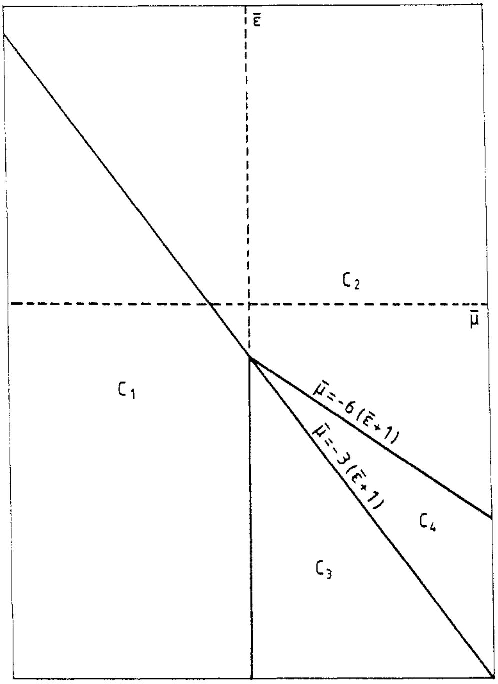


Figure 4. The zero temperature phase diagram for $\theta > 0$ in terms of the variables $\bar{\varepsilon} = \varepsilon/\theta$ and $\bar{\mu} = \mu/\theta$.

region of C_1. In addition to these low-temperature phases there also exists a high-temperature disordered phase which is the liquid-expanded (LE) phase.

A numerical study of the trajectory flows allows the construction of the phase diagram in the temperature–chemical-potential plane for any initial choice of $\bar{\varepsilon} = \varepsilon/\theta$. The method by which, in RSRG calculations, the free energy f per lattice site (in units of $k_{\mathrm{B}}T$) and its derivatives are derived is described by Niemeijer and van Leeuwen (1976) (see also Southern and Lavis 1980). In the case of the present model (using the grand canonical distribution) the pressure P of the system is given by

$$PA_0 = -k_{\mathrm{B}}Tf \tag{2}$$

where A_0 is the area per lattice site. The area A per molecule is given by

$$A = (\partial P/\partial\mu)_T^{-1}. \tag{3}$$

Isotherms at fixed values of the reduced temperature $k_{\mathrm{B}}T/\theta$ can therefore be obtained in the plane of reduced pressure PA_0/θ against reduced area A/A_0 for various values of $\bar{\varepsilon}$.

For large positive $\bar{\varepsilon}$ a continuous transition exists between the LC and LE phases. The transition terminates at a critical end-line point. This end-line point is the meeting point of the continuous LE–LC transition and two first-order transitions, one between the vapour and the LC phase at low temperatures and one between the vapour and the LE phase at higher temperatures. The vapour–LE transition terminates at a critical end-point. We are therefore able to obtain, for decreasing temperature, isotherms which

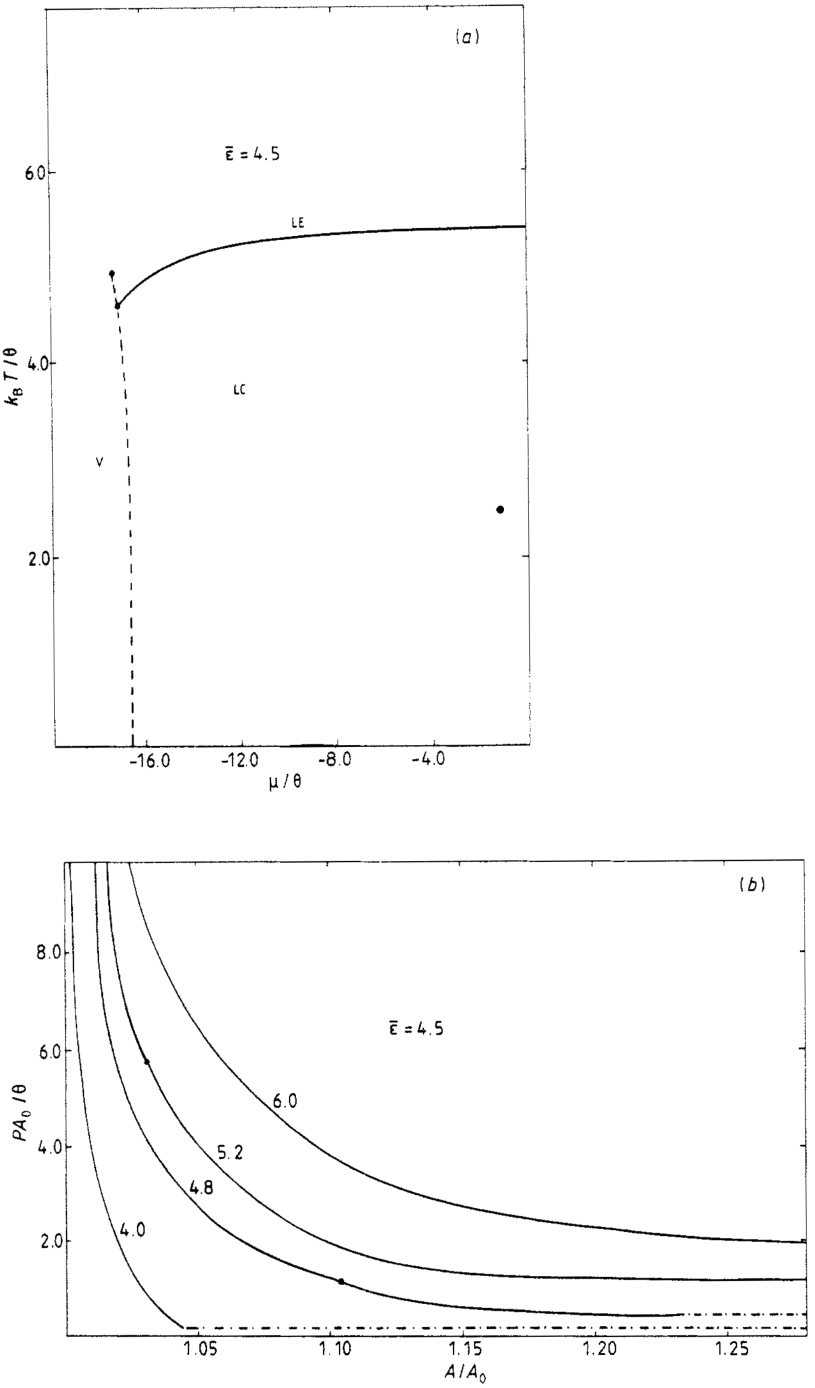


Figure 5. For $\bar{\varepsilon} = 4.5$ (*a*) is the phase diagram in the k_BT/θ, μ/θ plane. The first-order transitions are indicated by broken lines and the higher-order transition by a continuous line. (*b*) gives the isotherms, labelled with their values of k_BT/θ, in the pressure–area plane. The higher-order transitions are marked by dots and the first-order transitions are represented by chain curves.

exhibit: (i) no transitions; (ii) only a first-order vapour–LE transition; (iii) both a first-order vapour–LE transition and a continuous LE–LC transition; and (iv) only a first-order vapour–LC transition. As the value of $\bar{\varepsilon}$ is lowered the critical end-point temperature decreases and we have a range of temperatures for which isotherms have only an LE–LC transition (figure 5*a*). At $\bar{\varepsilon} = 3.0$ the critical end-point and the critical end-line point coalesce to give a tricritical point. In the range $-1.0 \leqslant \bar{\varepsilon} \leqslant 3.0$ the behaviour of the system is similar to that of the ferromagnetic Blume–Capel model (Blume 1966, Capel 1966) with at most one phase transition occurring on any isotherm; either a first-order vapour–LC transition, at low temperatures, or a continuous LE–LC transition at higher temperatures. As $\bar{\varepsilon}$ approaches -1.0 the tricritical point approaches zero temperature and below this value there are no first-order transitions. However, at low temperatures the honeycomb (HC) phase corresponding to the ground-state C_4 is now present (figure 6(*a*)). There is a continuous transition between the HC and LC phases and the three phases LE, LC and HC meet at a multicritical point at zero temperature.

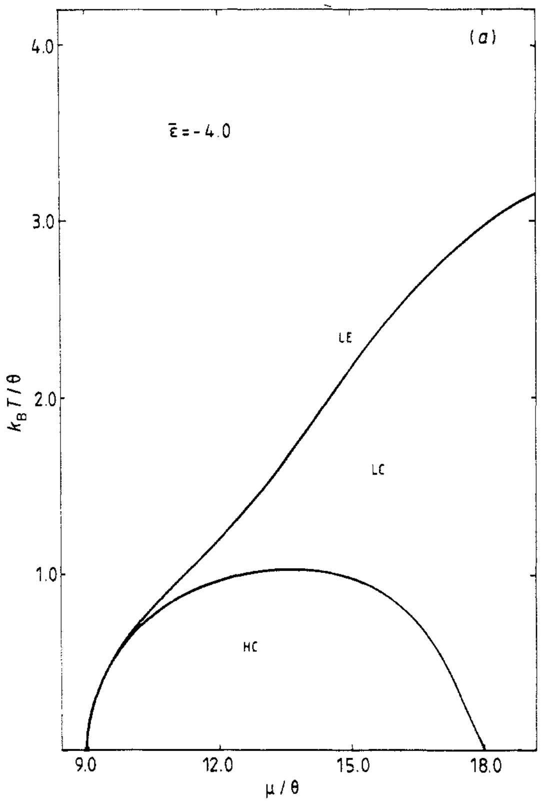
We shall not examine all these cases in detail since we are primarily concerned with the LC–LE transition which occur for all values of $\bar{\varepsilon}$. As indicated above, figures 5(*a*) and 6(*a*) are representative examples of phase diagrams in the reduced-temperature–chemical-potential plane, being respectively for the values $\bar{\varepsilon} = 4.5$ and -4.0. The relevant exponents for the fixed points which control the transitions in these two cases are listed in table 1. The phase diagram in figure 5(*a*) exhibits behaviour similar to that expected for lipid monolayers at the air/water interface. Figure 6(*a*) shows a phase diagram more appropriate to lipid monolayers at the oil/water interface. Figures 5(*b*) and 6(*b*) show isotherms in the pressure–area plane for the same two cases. These latter figures differ not only in that, unlike 5(*b*), figure 6(*b*) has no first-order transitions, but also because, for $\bar{\varepsilon} < -1.0$, crossings occur between the isotherms. This means that there is a region in which the coefficient of thermal expansion is negative. This phenomenon arises from the existence of the low-density HC phase. There does not appear to be any experimental evidence for the existence of this additional phase in lipid monolayers at an oil/water interface in the temperature range of observations, although isotherm crossing does occur in certain monolayer systems where molecules have extended configurations (Bell and Dunne 1978, 1979).

In the range of temperatures for which the LE–LC transition occurs the isotherms do not clearly exhibit this transition as a discontinuity of slope in contrast to the experimental results (figure 1) and those results obtained in the mean-field calculations of BMT. In order to understand this behaviour it is useful to examine the situation using scaling theory. The slope of the isotherms in the pressure–area plane can be expressed in the form

$$(\partial P/\partial A)_T = -1/A\kappa_T \qquad (4)$$

Table 1. Fixed points and relevant critical exponents

Type	Phases involved	Relevant exponents
First-order point	V–LC	2.0
First-order point	V–LE	2.0
Critical point	LE–LC	0.638
Critical point	LC–HC	0.956
Critical end-point	V–LE	1.761, 0.697
Critical end-line point	V–LE–LC	2.0, 0.638
Multicritical point	LE–LC–HC	0.738, 0.469



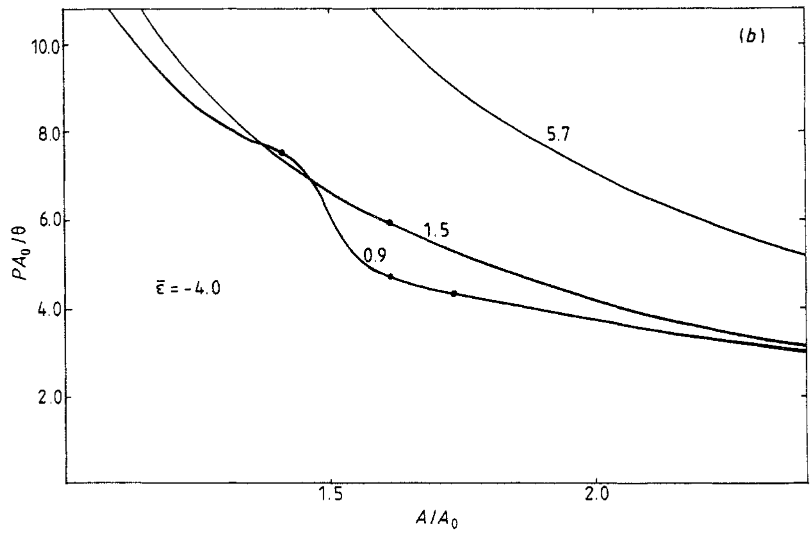


Figure 6. For $\bar{\varepsilon}=-4.0$ (a) is the phase diagram in the k_BT/θ, μ/θ plane. Higher-order transitions are indicated by continuous lines. (b) gives the isotherms, labelled with their values of k_BT/θ, in the pressure–area plane. The higher-order transitions are marked by dots.

where κ_T is the compressibility. In the neighbourhood of a phase boundary controlled by a fixed point with one relevant exponent y the compressibility takes the form

$$\kappa_T = \kappa_T^{(0)} + B|\Delta\mu|^{(d-2y)/y} \tag{5}$$

where $\kappa_T^{(0)}$ is the non-singular contribution to the compressibility, B is an amplitude factor, $\Delta\mu$ is the difference of the chemical potential from its critical value and d is the spatial dimension (see e.g. Hankey and Stanley 1972 for a discussion of the scaling theory arguments which lead to this result). It has been shown by Nienhuis and Nauenberg (1975) that a necessary condition for a first-order phase transition at a boundary with relevant exponent y is that $y = d$. An extension of this argument leads to the result that at a continuous transition a necessary condition for a finite discontinuity in the compressibility corresponding to a discontinuity in slope on the isotherm is that $y = d/2$. This value of the exponent is that which is obtained by mean-field methods and we can in consequence understand the discontinuity in slope obtained by BMT at the LE–LC transition. In general the exponents are not expected to take their classical values, particularly in low-dimensional systems where fluctuations play a significant role, except when the intermolecular forces are of very long range. If $y > d/2$ the compressibility diverges at the transition (unless $B = 0$) and the slope of the isotherm is zero. On the other hand if $y < d/2$ the compressibility is dominated by its non-singular part and the isotherms will not necessarily indicate the presence of the transition by an anomaly of slope. In this latter case any difference of slope which occurs on an isotherm in a neighbourhood of the phase transition will arise from the influence of the change of phase on the non-singular part of the compressibility. There is some indication of an effect of this kind in figure 5(*b*). In our calculations two factors are responsible for the absence of any very strong indications of a transition: (i) the exponent obtained is $y = 0.638$ and thus we cannot obtain a divergent contribution to the compressibility: (ii) the fixed point governing the LE–LC transition lies in the pure spin-$\frac{1}{2}$ subspace of our model and with our choice of weight function the subspace is invariant under the operation of the recurrence relations. The relevant scaling field in terms of which the singular contribution to the compressibility can be expressed is given in terms of the left eigenvector associated with the relevant exponent (Niemeijer and van Leeuwen 1976). In our case, since the spin-$\frac{1}{2}$ subspace is invariant this vector lies in this subspace and consequently has no chemical potential component. This means that the amplitude factor B in equation (5) is identically zero. This latter difficulty can be eliminated by using a weight function for which the spin-$\frac{1}{2}$ subspace is no longer invariant. We have investigated such changes of the weight function but in no case have we been able to obtain an exponent greater than $d/2$.

4. Discussion

We have examined the behaviour of the simple orientational model of BMT using RSRG methods. Although the phase diagrams show the same general behaviour as observed by mean-field methods, the isotherm behaviour is significantly different at the continuous LE–LC transition. Our results indicate that the discontinuity in slope obtained by BMT is an artifact of mean-field methods. As we indicated in the introduction, lattice models seeking to reproduce the phase transition behaviour of phospholipid monolayers tend to fall into one of two groups: those which attempt an explanation for the phase transitions in terms of chain disorder from the all-trans conformation and those for which the explanation is attempted in terms of orientational ordering of the molecules which remain in the all-trans conformation. Our model is of course in the latter group. Its inadequacies are evident from our calculations, while models based purely on chain disorder have incorrectly predicted the LE–LC transition to be first order. It is clear that a more realistic model must contain elements from both these approaches. In real systems many of the carbon chains are likely to be extended along the interface at large areas and these may change to an upright configuration concurrently with the orientational ordering process. Unfortunately increasing the realism of the theory limits the methods which can be used to study it. A model with extended states or more than two orientational states for a lipid may exhibit a continuous transition with an exponent $y > d/2$, corresponding to a divergent compressibility, and a point on the isotherm at which the slope is zero. However, we do not in general expect a discontinuity in slope unless the intermolecular forces are very long-ranged. The comparison of the BMT results with those of the present paper points to the desirability of more detailed experimental information in the immediate neighbourhood of the LE–LC transition. In making this remark we are of course well aware of the difficulties involved in monolayer experiments and of the very considerable achievement represented by the accuracy of the experimental isotherms to which we have referred.

Acknowledgments

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