

A THEORY OF MONOLAYER PHASE TRANSITIONS

Th.W. RUIJGROK

*Institute for Theoretical Physics, Princetonplein 5, P.O. Box 80006, 3508 TA Utrecht,
The Netherlands*

K. SOKALSKI

Instytut Fizyki, Uniwersytet Jagielloński, Reymonta 4, 30-059, Kraków, Poland

Received 11 August 1988

We present the exact calculation of the equation of state for a simple model describing the phase transitions occurring in lipid monolayers. The model is of the van der Waals type, but with the density dependent attraction replaced by a long range interaction of another kind. For the size of the molecular hard cores we choose a function which increases with the internal energy of the p possible states of the molecule. As a result of this choice we find $p - 1$ first order phase transitions between the liquid and the solid state of the monolayer.

1. Description of the model

In recent experiments Pallas and Pethica [1] have resolved a long standing controversy by showing that the phase changes observed in some lipid monolayers are first order phase-transitions.

Subsequently Nagle [2] performed some new calculations on his model of 1973, which “is now in much better agreement with experiment”. In this theory, which is analogous to the dimer model once solved by Kasteleijn [3], much emphasis is put on the effect of the excluded volume of neighbouring chains and the motion of lipid heads in a plane is not considered at all.

It is the purpose of the present paper to investigate just this degree of freedom in the framework of a van der Waals-like theory.

The model we now want to present is different from Nagle’s, because the assumptions about the underlying mechanism are formulated in another way.

Consider N identical lipid molecules of mass m , the heads of which are moving in a plane, with the flexible hydrocarbon chains sticking out on one side. Let there be p possible states of each chain and let J_s ($s = 1, 2, 3, \dots, p$) be the energy of such an internal state. Any microscopic state of the whole

system is now given by fixing the two-dimensional momentum vector of each molecule, the position of its head in the plane and its internal configuration labeled by s . If N_s is the number of molecules in state s , the total number is given by

$$N = \sum_{s=1}^p N_s. \quad (1)$$

In the spirit of all mean field theories we will now assume that each molecule interacts with every other molecule with a strength which is inversely proportional to the number of particles and depends only on the internal states of the two particles considered. The total potential energy therefore takes the form

$$V = \frac{1}{N} \sum_{s,s'=1}^p J_{ss'} N_s N_{s'} + \sum_{s=1}^p N_s J_s, \quad (2)$$

where J_s and $J_{ss'}$ are constants independent of a , which is the area per particle. We could have included an attractive long range interaction à la van der Waals, by adding a term of the form $\tilde{V} = -N\tilde{J}a_0/a$, where a_0 is some excluded area. We will refrain from doing so, because the gas-liquid transition caused by this term occurs in a density region which is outside our present interest.

After integration over the momenta the canonical partition function of this system becomes

$$Z_N = \lambda_T^{-2N} \sum'_{\{N_s\}} \frac{e^{-\beta V(N_1, \dots, N_p)}}{N_1! \dots N_p!} Q(\{N_s\}), \quad (3)$$

where the thermal wavelength is $\lambda_T = 2\pi\hbar/\sqrt{2\pi mkT}$ and the prime indicates that the summation over each N_s from 0 to N is restricted by the condition (1). The configurational integral is written as

$$Q(\{N_s\}) = \int \prod_{s=1}^p \mathbf{d}\mathbf{r}_{N_s}^s, \quad (4)$$

where the asterisk indicates that the coordinates of each particle are to be integrated over the whole area $A = Na$ of the monolayer, but in such a way that overlaps are excluded. This integral cannot be calculated exactly, but will be approximated by assuming that each particle in a state s is surrounded by an area $a_{ss'}$, which cannot be entered by a particle in a state s' . If, moreover, the effect of overlap of these areas is neglected, we easily obtain the following

expression for the configurational integral:

$$Q(\{N_s\}) = \prod_{s=1}^p \left[Na - \sum_{s'=1}^p N_{s'} a_{ss'} \right]^{N_s}. \quad (5)$$

The model is now completely specified by choosing the parameters J_s , $J_{ss'}$ and $a_{ss'}$. In a harmonic oscillator model for the hydrocarbon chain it would not be unreasonable to take J_s to be linear in s . In analogy and for computational convenience we will take $J_{ss'}$ to be bilinear in s and s' . Consequently we define dimensionless constants K and K' by

$$\beta J_s = Ks \quad \text{and} \quad \beta J_{ss'} = K'ss'. \quad (6)$$

The excluded volume $a_{ss'}$ is not determined by the size of the heads of the lipid molecules, but rather by the states of the tails. We will assume that $a_{ss'}$ only depends on the total internal energy of the two molecules and therefore adopt the following simple expression:

$$\alpha_{ss'} = K''a(s + s')^\alpha. \quad (7)$$

The factor a is included in order to make K'' dimensionless. It is important, however, to remember that $a_{ss'}$ is independent of the area per particle, so that K'' is inversely proportional to a . From now on we will treat K'' as an independent variable and call it the (dimensionless) density. For the exponent α we will choose either $\alpha = 1$ or $\alpha = 2$ and refer to these two choices as model I and model II respectively. Upon substitution into eq. (3) the partition function can now be written as

$$Z_N = \left(\frac{a}{\lambda_T^2} \right)^N \sum_{f_1, \dots, f_p} e^{Ng(f_1, \dots, f_p)}, \quad (8)$$

where the following abbreviations have been introduced:

$$f_s = \frac{N_s}{N} \quad \text{with} \quad \sum_{s=1}^p f_s = 1,$$

$$g(f_1, \dots, f_p) = 1 - K \sum_s s f_s - K' \left(\sum_s s f_s \right)^2 - \sum_s f_s \log \frac{f_s}{1 - K'' X_s^\alpha}, \quad (9)$$

$$X_s^\alpha = \sum_{s'} (s + s')^\alpha f_{s'}. \quad \text{is a polynomial in } s \text{ of order } \alpha.$$

The partition function of eq. (8) is now calculated in the standard way by

replacing the sum by the largest term. We should therefore determine the non-negative numbers f_1, \dots, f_p in such a way that $g(f_1, \dots, f_p)$ is maximal, but under the condition $\sum_s f_s = 1$. The usual way of doing this is by solving f_1, \dots, f_p from $\partial g / \partial f_{s'} = \lambda - 1$ ($s' = 1, \dots, p$), where the Lagrange multiplier λ is to be found from the normalisation condition. This leads to

$$\psi_{s'} = -\lambda - Ks' - 2K's' \sum_{s=1}^p s f_s - K'' \sum_{s=1}^p (s + s')^\alpha e^{\psi_s} \quad (s' = 1, \dots, p) \quad (10)$$

in which

$$\psi_s \equiv \log \frac{f_s}{1 - K'' X_s^\alpha} . \quad (11)$$

This equation looks formidable, but on closer inspection it is seen that $\psi_s = P_1^\alpha(s)$ is a polynomial in s of order α . From eq. (11) it then follows that f_s is of the form $f_s = P_2^\alpha(s) e^{P_1^\alpha(s)}$, where also $P_2^\alpha(s)$ is a polynomial in s of order α . Eq. (10) is therefore reduced to a few (highly nonlinear) equations for the coefficients in the two polynomials $P_1^\alpha(s)$ and $P_2^\alpha(s)$. With sufficient care they can and were solved with high accuracy.

In order to check whether the solution found in this way really gave the maximum of $g(f_1, \dots, f_p)$, we compared it with the result obtained by applying the simplex method of Nelder and Mead [4], as described in Numerical Recipes [5]. In most cases the agreement was perfect. In some regions of the density K'' , however, it turned out that the solution of eq. (10) gave the correct (simplex) result only after some of the f_s -values had been set equal to zero. This phenomenon and also its physical meaning will be explained in the next section.

The equation of state is obtained from $p = (1/\beta N) \partial \log Z_N / \partial a$ by taking the largest term in eq. (8) and using the expression for $g(f_1, \dots, f_p)$ as given in eq. (9). We obtain

$$\beta p = \frac{1}{a} + \sum_s \frac{\partial g}{\partial f_s} \frac{\partial f_s}{\partial a} + \frac{\partial g}{\partial K''} \frac{dK''}{da} , \quad (12)$$

from which it is seen that the a -dependence of g occurs not only through the solutions f_s of the equations

$$\frac{\partial g}{\partial f_s} = \lambda - 1 \quad (s = 1, \dots, p) , \quad (13)$$

but also through the explicit dependence on K'' as it occurs in eq. (9). Because of eq. (13) and because $\sum_s f_s = 1$, the second term on the right-hand side of eq. (12) vanishes. Since K'' is proportional to the density $dK''/da = -K''/a$, so that after calculating $\partial g/\partial K''$ from eq. (9), we find

$$p^* \equiv \frac{pK''a}{kT} = K'' \left[1 - K'' \sum_s \frac{f_s}{K'' - 1/X_s^\alpha} \right]. \quad (14)$$

The results of the computations based on the above formulae will be reported in the next section.

2. Results

From eq. (14) it is seen that when the density K'' increases and passes one of the values $K_s^\alpha \equiv 1/X_s^\alpha$ ($s = 1, \dots, p$), the pressure would jump from $+\infty$ to $-\infty$, if not f_s , which also depends on K'' , simultaneously would go to zero too. On further increase of K'' we found that this f_s maintained its zero value. Since K_s^α increases when s becomes smaller, the next number to become zero at $K'' = K_{s-1}^\alpha$ is f_{s-1} . This process is repeated until at $s=2$ we have $f_1 = 1$ and $f_s = 0$ for $s > 1$. From this distribution we obtain $K_2^\alpha = 3^{-\alpha}$ and $K_1^\alpha = 2^{-\alpha}$. The other critical densities depend on the temperature and on the density. It can be shown, however, that

$$\lim_{T \rightarrow 0} K_s^\alpha = (s+1)^{-\alpha} \quad \text{for } s = 1, \dots, p. \quad (15)$$

In the density region $3^{-\alpha} \leq K'' \leq 2^{-\alpha}$ it now follows from eq. (14) that the pressure is given by

$$p^* = \frac{K''}{1 - 2^\alpha K''}. \quad (16)$$

K'' cannot grow beyond $2^{-\alpha}$, so that this is the hard core limit of the density.

The case of very low temperature can be treated analytically because then K and K' become dominant in eq. (9) and we must choose f_1, \dots, f_p such that

$$g(f_1, \dots, f_p) = -K \sum_s s f_s - K' \left(\sum_s s f_s \right)^2 \quad (17)$$

is as large as possible, under the condition $\sum_s f_s = 1$. The solution is $f_1 = 1$ and $f_s = 0$ for $s > 1$. This shows that for very low temperature the pressure is again given by eq. (16) but now for all densities below $2^{-\alpha}$.

The picture which emerges from the above considerations is that on compression the mutual exclusion of the hydrocarbon chains lowers the population of the higher excited states, until eventually all lipids are in the same all-trans state.

The disappearance of an excited state, each time the density passes through a critical value, is most pronounced at high temperatures. For this reason we will first study eqs. (10) and (11) for the case where the terms with K and K' can be neglected. If K_p^α is the smallest critical density which is still larger than K'' , we are allowed, after we had confirmed it by comparison with the simplex method, to put $f_s = 0$ for $s > p'$. This means that effectively we can replace p in eq. (10) by p' .

In order to investigate what kind of phase transitions will occur we calculate from eq. (8) the free energy per particle, divided by kT and obtain

$$\hat{f} = \beta f = \hat{f}_0 + 1 - g(f_1, \dots, f_p), \quad (18)$$

where $\hat{f}_0 = -\log(a/\lambda_T^2) - 1$. In fig. 1 we show $\hat{f} - \hat{f}_0$ as a function of the area per particle. We have taken model I ($\alpha = 1$) for infinite temperature and $p = 3$. The critical values at $1/K_2^\alpha = 3$ and at $1/K_3^\alpha$ are indicated by vertical dashed lines. This figure is made up of three continuous lines. The upper part is obtained by putting $f_1 = 1$ and $f_2 = f_3 = 0$, the middle part by putting $f_3 = 0$ and solving the equations with $p = 2$, while the lower part (with $1/K'' > 1/K_3^\alpha$) is

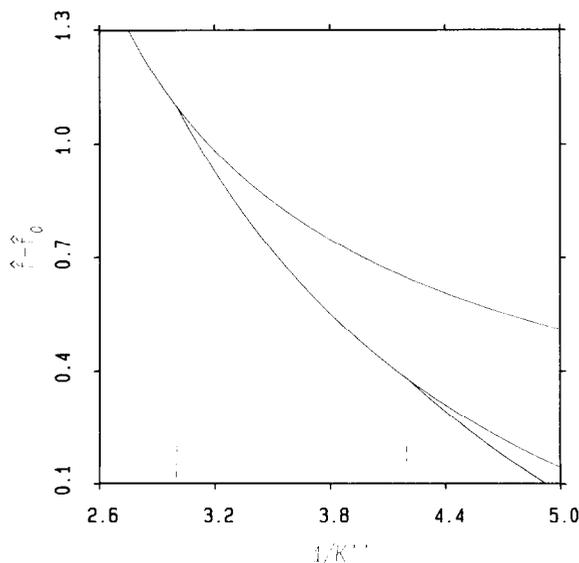


Fig. 1. Plot of $\hat{f} - \hat{f}_0$ versus the area per particle for $p = 3$, $\beta = 1/kT = 0$ and $\alpha = 1$.

calculated from the full equations (10) and (11) with $p = 3$. It is clear that $\hat{f} - \hat{f}_0$ and therefore also the free energy f is not a convex function of the area per particle, as it should. The correct free energy is obtained by taking the convex hull of the curve, which involves the double tangent construction of Maxwell. Numerically this construction could be calculated to very high accuracy, as is shown in table I. Between the tangent points the pressure is constant. The distance between these points in the area per particle scale is denoted by d_s in table I. It is seen that this distance approaches a constant value for increasing s .

For model II this distance was found to increase linearly with s .

The distribution function f_s was calculated as a function of the density K'' . After the Maxwell-construction, however, these f_s were not well-defined in the two-phase regions. We therefore show in fig. 2 f_s not as a function of K'' , but as a function of the pressure p^* ; hence the discontinuities. The figure illustrates the successive vanishing of f_s with increasing pressure, until eventually only $f_1 = 1$ remains. A full measurement of the distribution functions $f_s(p^*)$ may be out of the question. An experimental determination of the first two moments, i.e., of $\sigma_1(p^*) = \sum_s s f_s$ and $\sigma_2(p^*) = \sum_s s^2 f_s$, may however be feasible because they are connected with the average excluded area. For this reason we have included these functions in fig. 3.

In fig. 4 we present p^* as a function of the area per particle for $p = 5$ and $\alpha = 1$. The lower curve corresponds to $T = 0$, the upper to $T = \infty$. For finite temperatures the isotherms fall in between these two extremes. They have been calculated, but are not shown here. The lengths of the flat parts in each isotherm are equal, but reduce to zero when the temperature decreases. This behaviour is completely different from the well known gas-liquid transition: low and high temperatures seem to be reversed and for each transition region the coexistence curve is turned upside down. The origin of this behaviour lies

Table I

Critical densities K_s'' at infinite temperature. The densities at the left and right endpoints of each two-phase region are denoted by $K_s''(\text{L})$ and $K_s''(\text{R})$ with $\alpha = 1$. The lengths of these regions in the area scale are d_s .

| s | K_s'' | $K_s''(\text{L})$ | $K_s''(\text{R})$ | d_s |
|-----|---------------|-------------------|-------------------|--------|
| 2 | $\frac{1}{3}$ | 0.317765 | 0.347987 | 0.2733 |
| 3 | 0.23814453 | 0.229960 | 0.246450 | 0.2910 |
| 4 | 0.18409100 | 0.178778 | 0.188821 | 0.2975 |
| 5 | 0.14980654 | 0.146819 | 0.153526 | 0.2976 |
| 6 | 0.12621647 | 0.123768 | 0.128545 | 0.3003 |
| 7 | 0.10901737 | 0.107152 | 0.110724 | 0.3011 |
| 8 | 0.095930815 | 0.0946901 | 0.0974627 | 0.3004 |
| 9 | 0.085629000 | 0.0845435 | 0.0867543 | 0.3014 |
| 10 | 0.077344313 | 0.0764185 | 0.0782225 | 0.3018 |

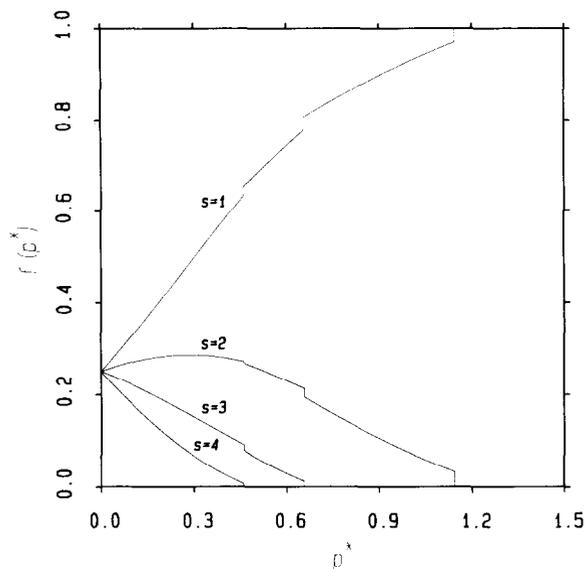


Fig. 2. Plot of the distributions f_i versus the scaled pressure p^* for $p = 4$, $\beta = 1/kT = 0$ and $\alpha = 1$.

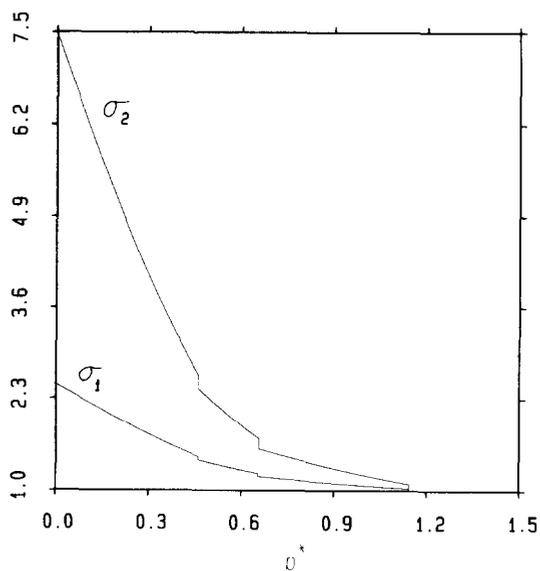


Fig. 3. Plot of the first two moments σ_1 and σ_2 versus the scaled pressure p^* for $p = 4$, $\beta = 1/kT = 0$ and $\alpha = 1$.

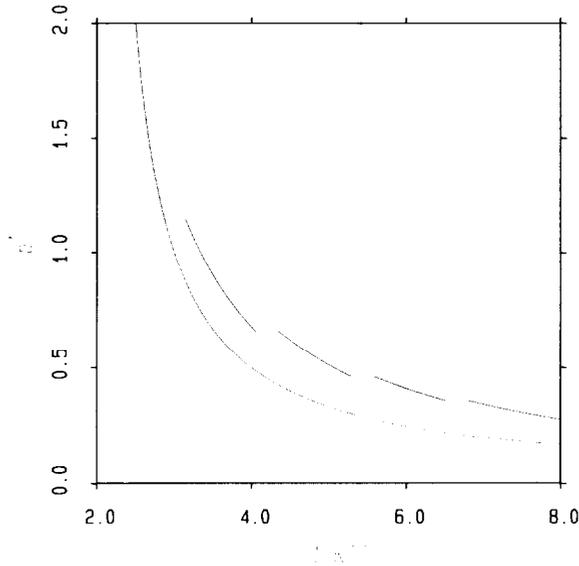


Fig. 4. Plot of the scaled pressure p^* versus the area per particle for $p = 5$ and $\alpha = 1$. The lower part is for zero temperature, the upper part for infinite temperature.

in the strong repulsion between two hydrocarbon chains as described by eq. (7).

In order to weaken this effect we have considered another model in which the excluded volume is given by

$$a_{ss'} = K'' a (\sqrt{s} + \sqrt{s'}). \quad (19)$$

All calculations were repeated with the following results. The flat parts in each isotherm were again largest at infinite temperature and zero for $T = 0$. The only effect of the weaker mutual repulsion is that with decreasing density the successive flat parts now get smaller. There is no critical temperature above which the two-phase regions would disappear.

The conclusion therefore is that for any temperature, no matter how large, the solidification process upon compression passes through a series of first order phase transitions, in each of which the highest remaining excited state of every molecule is suppressed, because the available free space is reduced.

Acknowledgement

One of the authors (K.S.) is grateful to the Institute of Theoretical Physics in Utrecht for the kind hospitality.

References

- [1] N.R. Pallas and B.A. Pethica, *Langmuir* 1 (1985) 509.
- [2] J.F. Nagle, *Faraday Discuss. Chem. Soc.* 81 (1986) 151.
- [3] P.W. Kasteleijn, *J. Math. Phys.* 4 (1963) 287.
- [4] J.A. Nelder and R. Mead, *Computer Journal* 7 (1965) 308.
- [5] W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, *Numerical Recipes* (Cambridge Univ. Press, Cambridge, 1988).