Vol. A53 (1978) ACTA PHYSICA POLONICA No 2

METASTABLE AND UNSTABLE STATES AT THE NEMATIC-ISOTROPIC TRANSITION IN THE MEAN-FIELD LATTICE MODEL[*, **]

By J. Stecki

Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw[***]

(Received March 18, 1977)

The course of the free energy and of the isotherms of pressure vs density near the first order nematic isotropic transition is examined in detail for the mean field lattice model in the Bethe approximation. It is shown how it so happens that no continuous pressure density isotherms with Van-der-Waals loops may exist in this case for a first-order phase transition between phases of different symmetry.

1. *Introduction*

In the transition region between liquid and vapor, the Van der Waals loop separates the regions of stable vapor from stable liquid. The isotherm of pressure p vs density $n = N/V$ contains two metastable portions and an unstable portion inbetween but it is nevertheless continuous. The transition between the disordered isotropic and ordered uniaxial phases is also of the first order but the phases are of different symmetry [1] and therefore the course of the free energy and its derivatives must be examined anew. In this note we record briefly the behaviour of the simplest possible mean field model, namely the lattice model in the Bethe approximation.

2. *Working equations*

In this model [2–4] the molecules are simulated by an occupied row of r consecutive sites. Lattice sites may be either occupied or empty. No multiple occupation is allowed. For instance, a simple cubic lattice in $d = 3$ dimensions will allow 3 distinct orientations

---

[*] Dedicated to Professor Kazimierz Gumiński on the occasion of his 70-th birthday.

[**] This work has been supported by the Institute of Physical Chemistry of the Polish Academy of Sciences, coordinating the interdepartmental research program 03.10.01.

[***] Address: Instytut Chemii Fizycznej PAN, Kasprzaka 44/52, 01-224 Warszawa, Poland.

and the molecules are labelled according to their orientation. Thus in a system of V sites with density $n = N/V$ and volume fraction $\theta = rN/V$ the distribution of N molecules between orientations $\alpha = 1, 2, 3$ is specified by giving the fractions $x_\alpha = N_\alpha/N$ with $\sum x_\alpha = 1$. For uniaxial ordering one of the x's is large, say x_d, and all others are equal

$$x_\alpha = x_1 \quad \text{for} \quad \alpha \neq d, \quad x_1 = \frac{1-x_d}{d-1}. \tag{1}$$

In the isotropic phase, all x's are equal, $x_d = 1/d$. The free energy of the system is considered to be a given function

$$F = F(T, V, N, \{x_\alpha\}) = N(T, n, \{x_\alpha\}) \tag{2}$$

and the set $\{x_\alpha\}$ is so chosen as to minimize F at constant T, V, N or f at constant T, n. The model can be solved in the Bethe approximation [2–4] also with attractive "isotropic" segment-segment interaction [4]; the basic features are clear already in the athermal model corresponding to a hard-core interaction between elongated molecules. Then

$$\beta f n = \sum n_\alpha \log n_\alpha - \sum s_\alpha \log s_\alpha + (1-\theta)\log(1-\theta), \tag{3}$$

where $n_\alpha = nx_\alpha$, $s_\alpha = 1 - an_\alpha$, $a = r-1$, $\alpha = 1 \ldots, d$. The isotropic phase at $x_\alpha = d^{-1}$ has a positive pressure

$$\beta p = n^2 \left(\frac{\partial \beta f}{\partial n}\right)_{T,\{x\}} \tag{4}$$

and a positive coefficient $\partial p/\partial n$ at all densities. At a given density, βf is also a function of $\{x_\alpha\}$, which can be visualized as a multidimensional surface. To consider only uniaxial ordering one examines a one-dimensional cut along the line where all x's except x_d are equal to each other, as indicated by Eqs. (1). Along this line

$$\left(\frac{\partial(\beta f)}{\partial x_d}\right)_{T,\mathrm{uniax}} = \beta\mu_d - \beta\mu_1, \tag{5}$$

where μ_α is the chemical potential of the component α defined in the usual manner

$$\mu_\alpha = \left(\frac{\partial F}{\partial N_\alpha}\right)_{T,V,N_\alpha'}. \tag{6}$$

Variations of f with x_d, are limited to curves of three types shown in Fig. 1. Each of them has a minimum (or maximum) at $x_d = 1/d$ corresponding to the isotropic phase, infinite and positive first and higher derivative at $x_\alpha = 1$ corresponding to the logarithmic divergence of the chemical potential μ_1. Curves of similar type of free energy vs order parameter were considered e.g. by de Gennes [5] and Landau [6].

The second derivative f''_{xx} at $x = d^{-1}$ is positive at lower densities but at densities higher than $\theta_{00} = d/(r-1)$ it is negative. For $\theta_{00} < \theta$ the isotropic phase is absolutely unstable (with regard to variations in x). However, it still has positive pressure and compressibility. It is only the (isotropic) orientational distribution that became unstable.

The mesophase will exist at $x_d = x^*$, the local minimum of f, and at high θ it will be stable. The minimum x^* will wander with density, so that the pressure is equal to

$$\beta p = \beta n^2[f'_n + f'_x(dx/dn)] = n^2 \beta f'_n, \tag{7}$$

but

$$\frac{\partial(\beta p)}{\partial n} = \frac{\partial}{\partial n}(n^2 \beta f'_n) + n^2 \beta f''_{xn}(dx^*/dn) \tag{8}$$

and

$$dx/dn = -\frac{f_{xn}}{f''_{xx}}. \tag{9}$$

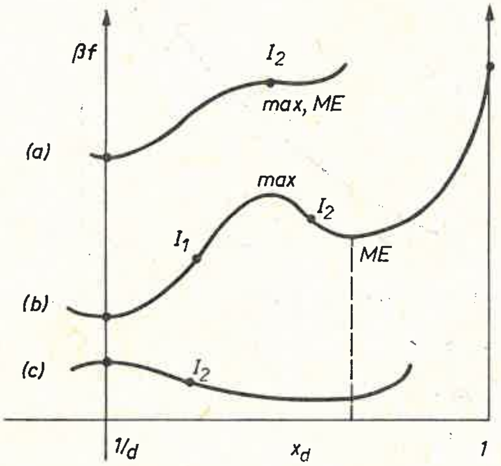

Fig. 1. Free energy βf vs composition variable x_d

If the mesophase is to be stable or metastable it is the full density derivative that must be positive and not only the derivative at constant x.

The first order phase transition may be located by the equality of the chemical potentials and pressures of the isotropic phase at $T, n', x_d = d^{-1}$ and of the mesophase at $T, n'', x_d = x^*(T, n'')$.

There is no reason why the free energy should take equal values in coexisting phases; at the transition, points like I and N belonging to two different curves of type (*b*) of Fig. 1 will represent coexisting phases. The insert in Fig. 3 represents a typical Van der Waals isotherm containing the well known continuous loop. We shall draw now the corresponding $p-n$ isotherm for the other case, represented in Fig. 2. The line marked "iso" represents the pressure, or βp, of the isotropic phase; the line marked "meso" represents the pressure $\beta p(n, x^*(n))$ of the ordered uniaxial phase. Since $f'_x = 0$, the expression is common for both cases.

$$\exp(\beta p) = S_1^{d-1} S_\alpha / (1-\theta). \tag{10}$$

The first order transition occurs at I_T-N_T, with pressure p_T and densities θ_0 and θ^*. At these points not only pressures but also chemical potentials are equal. The portion of the line "iso" between θ_0 and θ_{00} represents the metastable states of the isotropic phase; the last portion for $\theta_{00} < \theta < 1$ represents the unstable isotropic phase. At the high-density side, the mesophase is stable; as we lower the density, the free energy curve $f(x_d)$ goes over from case (*c*) to case (*b*) (Fig. 1). The equilibrium composition x^* decreases with a decrease of density, $dx^*/d\theta > 0$ since $f''_{xx} > 0$ at $x = x^*$ and $f''_{xn} < 0$. Then two things happen, at first sight independently. At some density the derivative dp/dn ceases to be positive; from then on the mesophase is absolutely unstable mechanically (see point S in Fig. 3). The second event, in our model occurring always at an even lower density, is

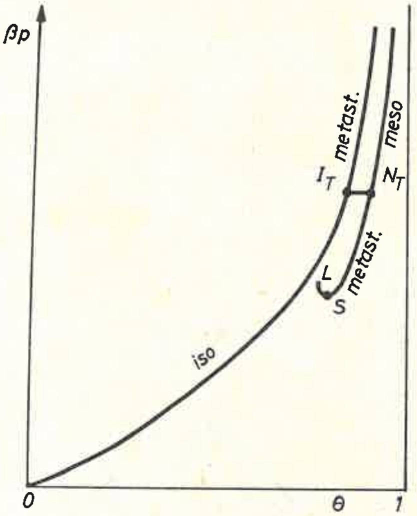

Fig. 2. A typical diagram of pressure βp vs density for an athermal (or supercritical) system

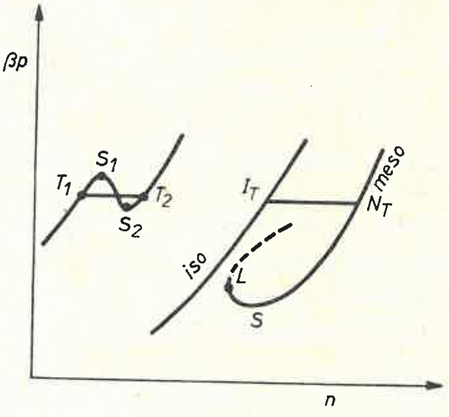

Fig. 3. The region about the transition with the metastable and unstable states. The insert shows a continuous isotherm joining phases of the same symmetry

the disappearance of the minimum ME in (*b*), Fig. 1, and with it of any possibility of a mesophase metastable or unstable. The condition $f'_x = 0$ or

$$x_1 S_1^a = X_d S_d^a \tag{11}$$

leads to an algebraic equation which has 3 solutions at $d^{-1} < x_d < 1$. As we lower the density, two solutions, marked MA and ME come to coincide with each other and with the inflexion point I_2; the "last" point x_L^* of the curve $x^*(n)$ is a solution of

$$f'_x = f''_{xx} = 0. \tag{12}$$

For lower θ the two roots are complex. This density θ_L^* is marked in Fig. 3. As we approach the phase at θ_L^*, x_L^*, dx^*/dn becomes infinite because f''_{xx} vanishes. The unstable meso isotherm *p-n* ends with an infinite (negative) slope, at the last point marked L in Fig. 3. There is no possible connection between the mesoline and the isoline in this figure.

In Fig. 3 we show an enlarged portion of Fig. 2; the dashed line is included for illustration — it gives the pressures at the unstable locus of $f'_x = 0$ marked max in Fig. 1.

The striking feature of the figure is its lack of symmetry. Whereas the point S may be associated with the spinodal curve, which in the usual case is the locus of $\partial p/\partial n = 0$ separating the (mechanically) metastable and unstable states, no such other point appears — the isotropic phase is mechanically stable for all pressures and densities. The unstability of the orientational distribution appears in the meso phase after other possibilities have been exhausted — the first order phase transition and the mechanical unstability next — and the isotherm is singular at this point with a negative infinite derivative. The unstability of the isotropic orientational distribution is not to be seen at all on the isotherm of the isophase; that f''_{xx} changes sign from positive to negative is a separate piece of information.

The interesting question is then how it was possible to observe Van-der-Waals loops in Monte Carlo simulations of first-order phase transitions between phases of different symmetry — it seems that the very existence of either one of them is to be justified separately. For the nematic-isotropic transition discussed here, the number of points reported by Vielliard-Baron [7] would be much too small to support an idea that the continuous loop exists. If one choses for simulation a system of average density just slightly smaller that θ_L^*, the result might depend (as it might elsewhere) on the input orientational distribution before the true equilibrium corresponding to the isotropic phase is reached.

An important point is that for the states outside the "local equilibrium" $\mu_1 = \mu_2 = \ldots = \mu_d$ or $f'_x = 0$ the pressure is not really defined because $\beta p = n^2(\partial \beta f/\partial n)_x$ becomes now

$$\beta p = n^2 \left[\left(\frac{\partial \beta f}{\partial n} \right)_{x,T} + \frac{\partial \beta f}{\partial x} \times \frac{dx}{dn} \right]$$

and the derivative dx/dn is not *uniquely* specified. In other words, consider the free energy to be a functional of the orientational one-particle distribution function $n_1(\boldsymbol{r}, \boldsymbol{\omega})$. When varying the volume, the work *pdV* will depend on how $n_1(\boldsymbol{r}, \boldsymbol{\omega})$ itself is going to vary with the change of the average density. For two states — iso and meso — this variation is uniquely specified: $n_1(\boldsymbol{r}, \boldsymbol{\omega})$ at each density is to minimize the free energy. In our discrete model this is simulated by two values taken by $x_d = d^{-1}$ or $x^*(n)$. In other states the change of n_1 with n is unspecified and the pressure $p = -\partial F/\partial V$ cannot be defined without this specification.

To illustrate these results we quote several numbers calculated from Eq. (1) for $r = 4, d = 3$. Here $\theta_{00} = 1$, i.e. the isophase is always stable or metastable. The coordinates of the transition are $\theta_{\rm iso} = 0.87943$, $\theta = 0.902$, $\beta p = 1.3707$, $x^* = 0.84085$. The coordinates of the point S are $\theta = 0.8788$. $\beta p = 1.264$ and $x^* = 0.735$. The coordinates of the point L are $\theta_L^* = 0.877455 \pm 0.000005$, $x_L^* = 0.698$, $\beta p = 1.274 \div 1.275$. The isotropic phase has a pressure of this magnitude at $\theta = 0.866$. It does not seem to be necessary that the points L and S lie to the left of the iso density at the transition, but they do so for $r = 4$, $d = 3$.

Introduction of the temperature through the segment-segment attractive interaction acting besides the hard-core volume exclusion does not alter the qualitative picture presented here.

This paper is dedicated to Professor K. Gumiński to whom so many theoretical chemists owe so much. Also the present author profited in the past from the advice, and encouragement and discussions with Professor Gumiński, which are gratefully acknowledged on this occasion.

REFERENCES

[1] L. D. Landau, E. M. Lifshitz, *Statistical Physics*, Pergamon Press 1958.

[2] E. A. di Marzio, *J. Chem. Phys.* **35**, 658 (1961); M. A. Cotter, D. A. Martire, *Mol. Cryst. Liquid Cryst.* **7**, 501 (1969).

[3] R. Alben, *Mol. Cryst. Liquid Cryst.* **13**, 193 (1971).

[4] J. Stecki, *J. Chem. Phys.* **67**, 948 (1977).

[5] P. G. de Gennes, *Physics of Liquid Crystals*, Oxford 1974.

[6] L. Landau, *Collected Papers*, p. 193, Gordon and Breach, New York 1965.

[7] J. Vielliard-Baron, *J. Chem. Phys.* **56**, 4729 (1972); *J. Phys.* (France) **30**, (Suppl. C4) 22 (1969).