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THERMODYNAMICS OF SMECTIC MIXTURES

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Résumé. — P. G. de Gennes discute le diagramme de phases thermodynamique d'un mélange de substances ayant des phases smectiques A et C à l'aide du développement de l'enthalpie libre suivant :

$$F(T, x, \varphi) = F_0(T, x) + \frac{1}{2} a(T, x) \varphi^2 + \frac{1}{4} b(T, x) \varphi^4 + \dots$$

où x est la fraction molaire du deuxième constituant et φ le paramètre décrivant la brisure de symétrie (*angle d'obliquité*). Il conclut que la transition de phase est du second ordre si b est positif lorsque $a(T, x)$ change de signe, la condition d'annulation de $a(T, x)$ définissant une limite de phase le long d'une ligne unique $x_0(T)$. Cette conclusion est erronée : la transition qui en découle est du premier ordre, à moins que ne soit aussi satisfaite la condition

$$\partial^2 F_0 / \partial x^2 > \frac{1}{2b} \left(\frac{da}{dx} \right)^2.$$

Si cette condition n'est pas satisfaite, il y a dans le diagramme un domaine de coexistence des phases A et C, limité par des lignes de part et d'autre de $x_0(T)$, ce qui constitue une spinodale plutôt qu'une limite de phase.

Abstract. — P. G. de Gennes discusses the thermodynamic phase diagram of a mixture of substances generating smectic A and C phases with the aid of the expansion of free enthalpy :

$$F(T, x, \varphi) = F_0(T, x) + \frac{1}{2} a(T, x) \varphi^2 + \frac{1}{4} b(T, x) \varphi^4 + \dots$$

where x is mole fraction of second component, φ the symmetry-breaking parameter (*tilt angle*), and concludes that the phase transition is one of second order, if b is positive where $a(T, x)$ changes sign, which locates the single-line phase boundary $x_0(T)$. This is erroneous : the transition so arising is of first order unless in addition

$$\partial^2 F_0 / \partial x^2 > \frac{1}{2b} \left(\frac{da}{dx} \right)^2.$$

and, without satisfaction of this condition there is a coexistence range in the phase diagram delimited by lines on either side of $x_0(T)$, which is a spinodal rather than a phase-boundary.

P. G. de Gennes (*The Physics of Liquid Crystals* (Clarendon Press), 1974, p. 277) treats the thermodynamics of the addition of a C-smectogen to an A-smectogen as follows. The free enthalpy F is considered as a function of temperature, T , composition, x (the mole-fraction of the second component) and a symmetry-breaking parameter φ . φ , identified in a model of the smectic phases as *the tilt of the mole-*

cules, is considered to be a continuously variable quantity, equal to 0 in the smectic-A phase, and $\neq 0$ in smectic C. Its most essential property is that an axis of infinite rotation symmetry in smectic-A ensures that $F(-\varphi) = F(\varphi)$. Hence odd terms are absent from the series development :

$$F(T, x, \varphi) = F_0(T, x) + \frac{1}{2} a(T, x) \varphi^2 + \frac{1}{4} b(T, x) \varphi^4 + \dots \quad (1)$$

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At constant x and T , this has stationary values at

$$0 = \partial F / \partial \varphi = a(T, x) \varphi + b(T, x) \varphi^3 + \dots \quad (2)$$

which are minima or maxima according to the sign (+ or -) of

$$\partial^2 F / \partial \varphi^2 = a(T, x) + 3 b(T, x) \varphi^2 + \dots \quad (3)$$

Thus, if $a > 0$ there is a minimum at $\varphi = 0$, making A the stable phase. If a changes sign $\varphi = 0$ becomes a maximum of F , and, provided $b > 0$ there are now minima of F (φ still being small) at

$$\varphi = \pm (-a/b)^{1/2}. \quad (4)$$

De Gennes deduces that when $b > 0$ the phase change occurs as one of second order at the condition $a(T, x) = 0$, represented by a single line in the (x, T) phase diagram. On the other hand, when $b < 0$, one must go to higher terms in (1) to find a minimum of F which occurs at finite φ giving rise to a first order transition with two lines in the (x, T) phase diagram, between which the phases coexist.

This argument pays insufficient attention to the freedom of a two-component system to become inhomogeneous in composition, breaking into phases with greater and smaller values of x .

Let $F_\varphi(T, x)$ denote the value of F minimized with respect to φ at constant x and T . Let us have $b > 0$, and $a \geq 0$ according as $x \leq x_0(T)$, so that $x_0(T)$ is de Gennes' 2nd order transition condition. Then

$$x < x_0 : F_\varphi(T, x) = F_0(T, x) \quad (5)$$

$$x > x_0 : F_\varphi(T, x) < F_0(T, x). \quad (6)$$

Close to x_0 , so that φ is small and we may neglect higher terms in (1), we have by use of (4) :

$$x \gtrsim x_0 : F_\varphi(T, x) = F_0(T, x) - a^2/4b. \quad (7)$$

Separation into phases of different composition will occur if, for some x , $d^2 F_\varphi / dx^2 < 0$. This condition may be brought about at higher x and φ by the effect of other terms but for x just above x_0 (where a is infinitesimal) we have :

$$d^2 F_\varphi / dx^2 = d^2 F_0 / dx^2 - \frac{1}{2b} \left(\frac{da}{dx} \right)^2 \quad (8)$$

so that to de Gennes' conditions for a second order transition must be added another necessary condition

$$\partial^2 F_0 / \partial x^2 > \frac{1}{2b} \left(\frac{da}{dx} \right)^2. \quad (9)$$

If this is not satisfied, we need information about the other coefficients, and at other values of x than $x_0(T)$ and its immediate neighbourhood : phases will coexist with compositions defined by a double tangent to $F_\varphi(x)$, one with $x < x_0$ and the other with x above the range in which $d^2 F_\varphi / dx^2 < 0$. $\partial^2 F_\varphi / \partial x^2$ changes sign at $x_0(T)$, since $\partial^2 F_0 / \partial x^2$ must be positive or else we should be involved with a different problem — phase separation independent of tilt. Thus $x_0(T)$ when (9) is not satisfied is the spinodal rather than the phase boundary.

First order smectic A-smectic C phase transitions of the kind indicated by de Gennes, as arising if $b < 0$ when $a(T, x)$ changes sign, are a somewhat unrelated phenomenon. They signify that higher terms in (1) give rise at constant T to minima of $F(T, x)$ occurring at finite φ which for some x (which is not necessarily that for the mixture whose stability we are testing) are lower than $F_0(T, x)$. Change of sign of $a(T, x)$ is not necessarily involved for any x .