

Nature of nematic–smectic-*A* phase transition in liquid crystals

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The unusual behavior of thermodynamic quantities near an *N-A* transition is explained. The absence of a jump in the heat capacity for large widths of the nematic zone and the anomalously narrow width of the nematic zone corresponding to the tricritical point on the *N-A* transition curve are due to the weakness of the modulation of the density of the substance by the smectic “wave.”

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1. Research in recent years has shown that the physical picture of the nematic–smectic-*A* (*N-A*) transition must be considerably modified by the inclusion of the large anisotropy of the correlation function and the role of dislocations and by fluctuation spreading of the long-range order in the smectic phase (see, for example, Ref. 1). Unfortunately, existing experimental results often do not permit clarifying the extent to which the observed differences from the predicted “classical” approach² are related to physical phenomenon and the extent to which they are due to secondary distorting factors. In addition, the published data are sometimes so contradictory that they cast doubt on the possibility of a universal interpretation.

In this paper, based on an analysis of the existing experimental information and a qualitative analysis using the Landau–de Gennes theory, we explain the unusual behavior of the thermodynamic quantities near a *N-A* transition. In addition, we explain the increase in the entropy of the *N-I* transition (nematic–isotropic liquid) when the width of the nematic zone decreases.

2. Numerous experiments, performed on different substances using differential scanning calorimeters (DSC), NMR, and methods for determining the anisotropy of the index of refraction and magnetic susceptibility and specific volume (see, for example, Refs. 3 and 4) indicate that the jumps in the entropy, nematic order parameter, and volume disappear on the *N-A* transition curve, i.e., a tricritical point appears when the width of the nematic zone is equal to $\Delta = 1 - (T_{NA}/T_{NI}) = 0.1-0.15$. It is simultaneously noted that these values are close to the predicted positions of the tricritical point following from McMillan's model⁵ and models related to it.⁶ It is well known (see, for example, Ref. 7), however, that the DSC method is a considerably nonequilibrium method and cannot correctly separate the pretransitional (fluctuation) effects in the anomaly of the heat capacity from a diffuse δ function, which is related to the latent heat of the transition. Recent precision (and more equilibrium) calorimetric experiments on a number of substances⁸ showed that the heat of the transition is virtually absent up to values $\Delta \sim 10^{-2}$. An appreciable heat of transition ($\Delta S/R = 0.05$ and $\Delta S/R = 0.2$, respectively) and a truly tricritical behavior of the heat capacity

(critical index $\alpha = 0.5$) were observed only in two cases with $\Delta = 1.7 \times 10^{-2}$ (Ref. 9) and more reliably with $\Delta = 3.5 \times 10^{-3}$ (Ref. 10). When the width of the nematic zone increases, α decreases from ~ 0.3 at $\Delta \approx 0.02$ to $\alpha \sim 0$ at $\Delta \approx 0.06$ (the crossover from the tricritical behavior to "helium" behavior). At the same time the amplitude of the singular part of the heat capacity decreases catastrophically, so that the anomaly virtually disappears for $\Delta \approx 0.1$. It may be concluded that the disappearance of peaks in DSC thermograms indicates that the fluctuation part of the heat capacity decreases (beyond the range of sensitivity of the method), rather than the disappearance of the heat of transition. Thus the tricritical point appears on the N - A transition curve with a width of the nematic zone an order of magnitude smaller ($\Delta_0 \sim 10^{-2}$) than predicted by models based on the self-consistent-field approximation.^{5,6}

It is easy to see that the disappearance of the apparent jumps in the nematic order parameter and volume with $\Delta = 0.1$ – 0.15 is uniquely related to the disappearance of the anomaly in the heat capacity. The singular part of the thermodynamic potential near the N - A transition in zero-ordering field has the form $\delta\Phi \sim At^{2-\alpha}$, where A is the coefficient in the singular part of the heat capacity ($\delta c_p \sim At^{-\alpha}$), $t = (T - T_{NA})/T_{NA}$, and T_{NA} is a smooth function of pressure P , of the chemical potential μ (for the mixture) and of other "fields," including the field h of the conjugate nematic order parameter Q . For this reason, it is evident that the entropy, nematic order parameter, volume, and concentration (of the mixture) contain identical fluctuation parts: $\delta S \sim At^{1-\alpha}$, $\delta Q \sim A(dT_{NA}/dh)t^{1-\alpha}$, $\delta V \sim A(dT_{NA}/dP)t^{1-\alpha}$, $\delta x \sim A(dT_{NA}/d\mu)t^{1-\alpha}$, and anomalies in these quantities, perceived as diffuse jumps, disappear at the same time. The sharp decrease in the constant A is apparently attributable to the increase in the direct correlation length $\xi_0(A \sim \xi_{0\perp}^{-2} \xi_{0\parallel}^{-1})$.¹¹ Thus the direct correlation length in a direction perpendicular to the layer ($\xi_{0\perp}$) in bilayered smectics increases from 4 to 40 Å when Δ increases from 0.025 to 0.13. For this reason, the problem is the transition from short- to long-range action in smectics with an increase in the degree of orientational order. It would seem that the transition to long-range action must lead to a replacement of the singularity in the heat capacity (and other second derivatives of thermodynamic potential) of the type $t^{-\alpha}$ by a finite jump. The anomalies, however, disappear completely. We shall show that this behavior of the thermodynamic quantities and the anomalously narrow width of the nematic zone, corresponding to the tricritical point ($\Delta_0 \sim 10^{-2}$), have the same origin. The expansion of the thermodynamic potential near N - A transition, according to the Landau-de Gennes theory, has the form²

$$\frac{\Delta\Phi}{RT_{NA}} = \frac{1}{2} a_1 t_1 \psi^2 + \frac{1}{4} B_1 \psi^4 + \frac{1}{2} a_2 t_2 Q^2 + \frac{1}{4} B_2 Q^4 + \lambda Q \psi^2, \quad (1)$$

where $t_1 = t(\lambda = 0)$, $T_{NA}(\lambda = 0)$ is the temperature of the transition into the A phase in the absence of interaction between the orientational and smectic order, $t_2 \approx \Delta$ (with $T \approx T_{NA}$), the smectic order parameter ψ is referred to the density of the substance, while the interaction constant $\lambda = -(a_1/2T_{NA})(dT_{NA}/dQ)$.¹² The transition changes from second- to first-order transition when the condition $B_1 - (2\lambda^2/a_2\Delta) = 0$ is satisfied. Since the experimental value $\Delta_0 \sim 10^{-2}$ and assuming that $a_2 \sim B_1 \sim 1$, we obtain the estimate $\lambda \sim 10^{-1}$ for the interaction constant. From the results presented in Ref. 4

for CBNA, we have the estimate $(1/T_{NA})(dT_{NA}/dQ) \sim 1$. Thus it is necessary to admit the existence of one more small parameter $a_1 \sim 10^{-1}$, which determines the jump in the molar heat capacity $\Delta c_p/R = a_1^2/B_1$ and the value of the order parameter at $T=0$, K: $\psi_0 = (a_1/B_1)^{1/2}$. For the quantities of substances usually used in experiments ($\sim 10^{-3}$ mole), the jump in the molar heat capacity $\sim 10^{-2}R$ corresponds to the measured quantity $\sim 10^{-5}R$, which falls outside the range of sensitivity of existing techniques. The fact that the maximum value of the smectic order parameter ($\psi_0 \approx 0.3$) is smaller than unity corresponds to the intuitive idea of a comparatively weak modulation of the density of the substance by the smectic "wave." An analogous situation apparently arises with the smectic-A-smectic-C transition (the maximum angle of inclination of molecules $\theta = (0.3-0.4)\pi/2$). At the same time, for an $N-I$ transition $Q_0 = 1$, and the estimate presented above $a_2 \sim 1$ is correct.

3. The universal picture described above breaks down due to the small ($\leq 10^{-2}R$) jumps in entropy with $\Delta \geq 0.02$ observed in some quite accurate experiments. In this case, the transition temperature is observed to split from 10^{-2} to 10^{-1} K, which is caused by the presence of an impurity, while the critical index $\alpha \approx 0-0.3$ is less than the tricritical value $\alpha = 0.5$. Such an effect cannot be explained by the nonuniversality of the interaction constant only, since it is sometimes observed in substances in which according to other data there is a continuous transition.¹³ Impurities appear to be the most probable reason for the effect. We shall estimate the effect of equilibrium impurities on the nature of the transition near the tricritical point. The thermodynamic potential, which depends only on the smectic order parameter and the impurity concentration, is

$$\frac{\Delta \Phi}{RT_{NA}} = \frac{1}{2} a_1 t \psi^2 + \frac{1}{6} C \psi^6 + \gamma x \psi^2 + F(x). \quad (2)$$

Allowance for the terms that depend on the nematic order parameter Q has led to vanishing of the coefficient in front of ψ^4 ($B=0$), as well as to a shift in T_{NA} and renormalization of the regular function $F(x)$. Using the condition $\partial(\Delta \Phi)/\partial x = 0$ and representing $F(x)$ in the form

$$F(x) = F(x_0) + \frac{1}{2} \left(\frac{\partial^2 F}{\partial x^2} \right)_{x=x_0} (x-x_0),$$

we obtain

$$\frac{\Delta \Phi^*}{RT_{NA}} = \frac{1}{2} a_1 t^* \psi^2 + \frac{1}{6} C \psi^6 - \frac{1}{4} B^* \psi^4, \quad (3)$$

where $t^* = t + 2\gamma x/a_1$, $B^* = 2\gamma^2/(\partial^2 F/\partial x^2)$, $\gamma = -(a_1/2T_{NA})(dT_{NA}/dx)$. For dilute solutions, $(\partial^2 F/\partial x^2) \sim x^{-1}$. It is evident from (3) that the presence of an impurity always leads to a first-order transition if the tricritical point is sufficiently close.

4. Finally, we shall estimate the effect of the width of the nematic zone on the heat of the $N-I$ transition. We shall assume that in the isotropic phase the smectic short-range order is much weaker than in the nematic phase. Then the entropy of the A phase will be lower than the entropy of the I phase by an amount $\delta S/$

$R = \int_{\Delta}^{t_0} (\delta c_p / R) dt$, where $\delta c_p / R = A(t^{-\alpha} - 1)$ is the fluctuation part of the heat capacity near the N - A transition. Thus the "cutoff" of smectic fluctuations by the N - I transition leads to an additional contribution to the entropy of the N - I transition, which increases with decreasing width of the nematic zone Δ . For $\Delta \approx 2 \times 10^{-2}$ and $\alpha \approx 0.3$, taking a reasonable value $t_0 = 0.1$, we obtain for 8CB ($A \approx 2$) and HOPDOB ($A \approx 10$) $\delta S \approx 0.1R$, and $\delta S \approx 0.5R$, respectively, while for $\Delta \approx 3.5 \times 10^{-3}$ and $\alpha \approx 0.5$ for OOHCS ($A \approx 3$) $\delta S / R \approx 0.9$, consistent with experiment.^{8,10} The analysis presented above indicates the possibility of a universal description (at least qualitatively) of the thermodynamic properties near N - A transition based on "classical" ideas,² although systematic inclusion of fluctuations (smectic and nematic) will undoubtedly change the quantitative estimates (for example, the effect of impurities).

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