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Alternative universality for a NAC multicritical point topology

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An alternative universal description of the topology of NAC (nematic–smectic A–smectic C) multicritical points is suggested. In this approach, the NA and AC transition lines have the same critical exponents $\phi_{NA} = \phi_{AC} = 0{\cdot}67 \pm 0{\cdot}03$, while the NC line critical exponent ϕ_{NC} is different. It appears that ϕ_{NC} is equal to $0{\cdot}87 \pm 0{\cdot}04$, which is close to the exponent for the dependence of the NC latent heat upon the proximity to the NAC point.

Recently, elaborate and comprehensive experimental studies of the transition latent heat and specific heat [1–4], X-ray scattering [5, 6] and phase diagram topology [6–8] in the vicinity of NAC (nematic–smectic A–smectic C) multicritical points have been carried out. These data demonstrate the fluctuational character of the critical behaviour near the NAC points, though the physical nature of this phenomenon is still obscure.

One of the remarkable peculiarities of NAC points is the universality of phase diagram topologies first discovered experimentally in binary liquid crystal mixtures (temperature–concentration plane) [7] and later in a one-component liquid crystal (temperature–pressure plane) [8]. Various phase diagrams were approximated by the equations [7]

$$\left.\begin{aligned} T_{NA} - T_{NAC} &= A_{NA}(x - x_{NAC})^{\eta} + B(x - x_{NAC}), \\ T_{NC} - T_{NAC} &= A_{NC}(x - x_{NAC})^{\eta} + B(x - x_{NAC}), \end{aligned}\right\} \qquad (1)$$

where T_{NA} and T_{NC} are the temperatures of NA and NC phase transitions, T_{NAC} and x_{NAC} are the temperature and concentration of an NAC point. The exponent $\eta = 0{\cdot}57 \pm 0{\cdot}02$ appears to be universal for all systems studied. The constants A_{NA}, A_{NC} and B are not universal. Incidentally AC transition lines are also approximated by a formula similar to equation (1) with universal exponent $\eta_{AC} = 1{\cdot}52 \pm 0{\cdot}03$. All the lines, converging in an NAC point, have a non-analytical character. Such behaviour is in evident contradiction with any mean field theory and illustrates the fluctuational nature of an NAC point.

We have studied the phase diagrams of two liquid crystal mixtures: 4-*n*-hexyloxyphenyl-4′-*n*-decyloxybenzoate in 4-*n*-hexyloxyphenyl-4′-*n*-octyloxybenzoate ($\bar{6}\mathrm{O}\bar{8}$-$\bar{6}\mathrm{O}\overline{10}$) and 4-*n*-hexyloxyphenyl-4′-*n*-butylphenyloxycarbonylphenylcarbonate in 4-*n*-hexyloxyphenyl-4′-*n*-decyloxybenzoate ($\bar{6}\mathrm{O}\overline{10}$-HOPBPOCPC) by adiabatic scanning calorimetry [1, 2, 4]. Our phase diagram description does not contradict the approximation in equation (1). In contrast to the mixtures studied in [7] both components of our mixtures have smectic C phases. Therefore the range for the fit of AC and NA lines is much wider in our case.

Though the universality of NAC point topology seems to be established there are two contradictions between such description and the behaviour of some thermodynamic properties in the vicinity of an NAC point. These contradictions are the following:

(1) The universality suggested in [6] is achieved with the NA and NC exponents being equal and less than one, i.e. the NA and NC lines are continuous at the NAC point, while the AC line comes in obliquely. The latter observation corresponds to the value of $\eta_{AC} > 1$. However, as the specific heat measurements show [1–4], an NAC point plays the role of a tricritical one for the transitions to a smectic C phase. This fact should correspond to the continuity of NC and AC lines: the AC line should be the natural prolongation of the NC one across the NAC point.

(2) If the NAC point is a tricritical one for transitions to a smectic C phase we can expect, according to Landau theory, that

$$\left.\begin{aligned}\frac{\Delta H}{RT_{NAC}} &\sim (T_{NAC} - T_{NC}),\\ &\sim (x_{NAC} - x)^{\eta_{NC}}.\end{aligned}\right\} \quad (2)$$

However the measurements of the NAC latent heat [2] show that

$$\frac{\Delta H}{RT_{NAC}} \sim (x_{NAC} - x)^{\psi}, \quad (3)$$

where $\psi = 0{\cdot}84 \pm 0{\cdot}02$ which differs from $\eta_{NC} = 0{\cdot}57$.

To avoid this contradiction we have tried to find an alternative universal description of phase diagrams in the vicinity of NAC points. We assume that there should be equal critical exponents for the NA and AC lines, i.e.

$$\left.\begin{aligned}T_{NA} - T_{NAC} &= A_{NA}(x - x_{NAC})^{\phi} + B(x - x_{NAC}),\\ T_{AC} - T_{NAC} &= A_{AC}(x - x_{NAC})^{\phi} + B(x - x_{NAC}).\end{aligned}\right\} \quad (4)$$

The NC line exponent ϕ_{NC} appears to be independent of ϕ

$$T_{NC} - T_{NAC} = A_{NC}(x_{NAC} - x)^{\phi_{NC}} + B(x - x_{NAC}). \quad (5)$$

To verify this assumption we should fit the experimental data with the formula following directly from equation (4)

$$T_{NA} - T_{AC} = A(x - x_{NAC})^{\phi}, \quad (6)$$

where $A = A_{NA} - A_{AC}$.

The results of such fits for various NAC phase diagrams are represented in figure 1. The non-universality of amplitudes A for different systems is eliminated by an appropriate normalization procedure. The slope in figure 1 corresponds to the universal exponent $\phi = 0{\cdot}67 \pm 0{\cdot}03$. The given value of the exponent ϕ allows us to deduce the base line $B(x - x_{NAC})$ from equation (4) and consequently obtain the value of ϕ_{NC} from equation (5). The fit of the NC transition lines with the formula

$$\left.\begin{aligned}\Delta &= \frac{1}{A_{NC}}[(T_{NC} - T_{NAC}) - B(x - x_{NAC})],\\ &= (x - x_{NAC})^{\phi_{NC}}\end{aligned}\right\} \quad (7)$$

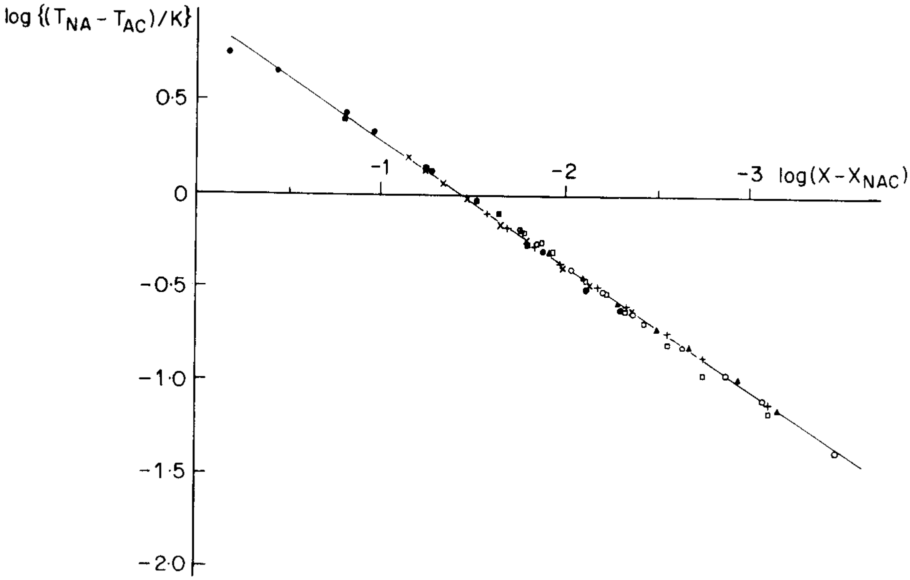

Figure 1. Fit to NAC transition temperatures with equation (6). ● ($\bar{6}$O$\bar{8}$-$\bar{6}$O$\overline{10}$) and ■ ($\bar{6}$O$\overline{10}$-HOPBPOCPC) are our data; + ($\bar{7}$S5-9S5), ▲ ($\bar{8}$O$\bar{8}$-XC), ○ ($\bar{7}$S5-XC) and □ (7ONE-8OCB) are data of [7]; x (7APCBB) are data of [8] (in this case the deviation of pressure from its value at the NAC point was used instead of $x - x_{NAC}$).

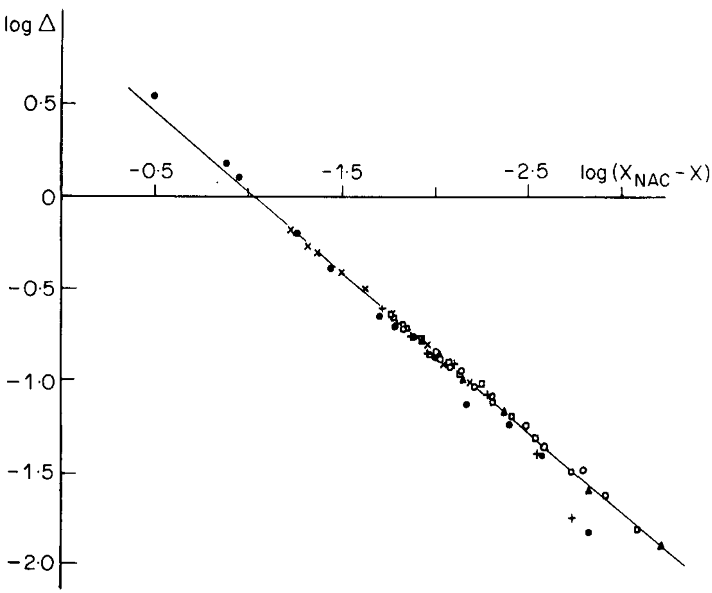

Figure 2. Fit to $T_{NC}(x)$ with equation (7) (for the symbols see figure 1).

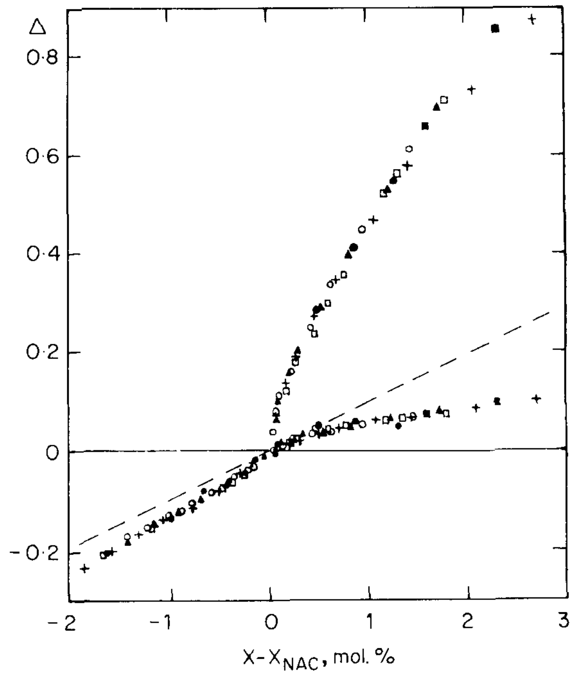

Figure 3. Universal NAC phase diagram (for the symbols see figure 1). Every transition line was fitted with a formula which was similar to equation (7).

is represented in figure 2. We can see that the exponent $\phi_{NC} = 0{\cdot}87 \pm 0{\cdot}04$ is also universal for all the phase diagrams studied.

Thus the fit of NAC phase diagrams proves a possible alternative universality of NAC points. This universality allows us to avoid the contradictions mentioned previously:

(1) All transition lines are 'continuous' at the NAC point since $\phi < 1$ and $\phi_{NC} < 1$.
(2) The value of the universal exponent $\phi_{NC} = 0{\cdot}87 \pm 0{\cdot}04$ coincides within the limits of experimental error with the exponent of the NC latent heat dependence $\psi = 0{\cdot}84 \pm 0{\cdot}02$.

The universal phase diagram for various mixtures is presented in figure 3. The axis $\Delta = 0$ is the base line of our universality while the base line of the universality suggested in [7] is the dashed line. Scaling analysis of the NAC multicritical point, which is in progress now [9], justifies the suggested universality.

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