PHYSICAL REVIEW A VOLUME 28, NUMBER 1 JULY 1983

Nematic—smectic-*A*—smectic-*C* end point: A volumetric study

J. Stecki, A. Żywociński, and S. A. Wieczorek
Laboratory No. III, Institute of Physical Chemistry, Polish Academy of Sciences,
01-224 Warsaw 42, Poland

(Received 16 October 1981; revised manuscript received 24 May 1982)

Sensitive volumetric measurements show a classical second-order *A*-*C* transition in mixtures of $\overline{8}S5$ with $\overline{7}S5$ in agreement with findings of Schantz and Johnson for pure $\overline{8}S5$, and apparently a first-order *A*-*N* transition (although an extremely weak one) for 30 and 37 mole % of $\overline{7}S5$; thus an earlier suggestion of a (critical) end point where a second-order *A*-*C* line meets the border of a first-order region, *N*-*A* and then *N*-*C*, is corroborated.

I. INTRODUCTION

Besides the indication of tricritical behavior[1] other interesting multicritical phenomena have been studied in liquid crystals and their mixtures.[2] An interesting case has been studied by Johnson *et al.*[3] In this binary mixture one pure compound, $\overline{8}S5$, displays the smectic-*C*, smectic-*A*, and nematic phases whereas the other, $\overline{7}S5$, shows no smectic-*A* phase. Thus the smectic-*A* phase gets squeezed out and hence on the temperature-mole fraction (T,x) phase diagram three lines of phase transitions, *A*-*C*, *N*-*A*, and *C*-*N*, meet at what was called the *NAC* point. In reality a first-order transition line in a mixture remains a line only in field variables, whereas it becomes a two-phase region, often narrow, bounded by two lines when *T*-*x* variables are used. The meeting of three first-order transitions results in a triple point just as is obtained in every pure substance when vapor, liquid, and crystal coexist. Such a case is depicted in Fig. 1(a). The meeting of three transitions, one second order and two of first order is shown in Fig. 1(b), whereas Fig. 1(c) shows a case where only one transition is first order.

Johnson *et al.*[3] have established that, as expected,[4,5] the transition *SC*-*N* is first order and also that the transition *SC*-*SA* is second order in pure $\overline{8}S5$. There was also strong conoscopic and orthoscopic evidence that the *SC*-*SA* transition was second order in mixtures. The entropy of the first-order *SC*-*N* transition decreased as the *NAC* point was approached although the graph of Johnson *et al.*,[3] we feel, is also compatible with the *SC*-*N* entropy decreasing to a small positive value at the *NAC* point, not necessarily to zero. This observation prompted us to hypothesize[6] that perhaps the case depicted in Fig. 1(b) was in fact that of the *NAC* point in this mixture. If it were so, the *NAC* point would in fact be a tie-line of finite length on the *T*-*x* plane and it would be adequately called a critical end point, or better, an end point.

Johnson *et al.* in their original paper,[3] Benguigui,[4] Imry,[4] and Chen and Lubensky,[5] as well as one of us,[6] have applied different versions of the Landau theory to this system. In one version[5] three

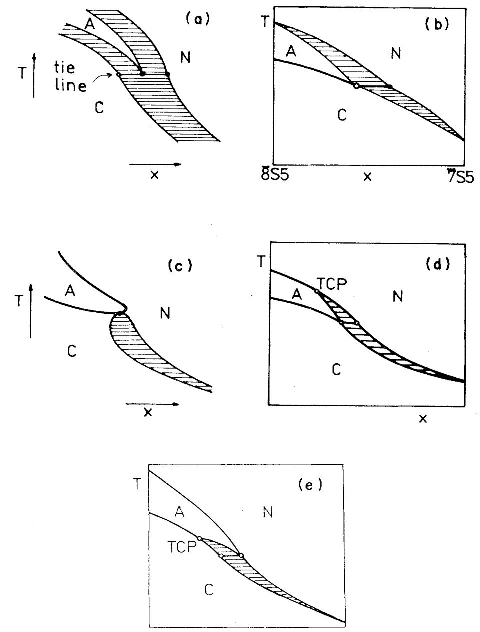

FIG. 1. (a) A triple point resulting from three lines of first-order transitions. (b) An end point if one line is second order, shown schematically, not to scale. (c) A case of two lines of second order. A meeting of three second-order lines as predicted by Ref. 5 is not shown. (d) A phase diagram with a tricritical point. (e) The case found in Ref. 4, with the *SC*-*N* transition first order (Ref. 4).

©1983 The American Physical Society

second-order lines meet. Benguigui postulated a tricritical point near the *NAC* tie-line. We used a simplified version with only two order parameters[6] and we were able to show that the hypothetical diagram of Fig. 1(b) can also be obtained from the Landau theory. Moreover, we pointed out that in a binary mixture it is not the equality of the total molar Gibbs potential that determines the phase equilibria but rather the equality of the chemical potentials in coexisting phases and for each component of the mixture. Then it becomes essential to specify the dependence of the phenomenological parameters of the Landau theory, on the composition, besides their dependence on temperature. Moreover, the concentration dependence of the Gibbs free energy in the reference disordered phase—nematic because there are only two order parameters—must also be specified. The simplest possibility is the ideal solution and it is not unreasonable since the chemical structure of the components is so similar. Perhaps one important consequence of these remarks is the appearance of another stability condition: Besides the usual stability of G with respect to small variation in order parameters, the thermodynamic stability condition

$$\left[\frac{d^2G}{dx^2}\right]_{p,T}>0$$

must also be fulfilled. Just to indicate the kind of results one obtains, we took the free energy of the same general form as used earlier[3–5] and supplemented by Benguigui[4] with a sixth-order term

$$G/NkT=G_0/NkT+\alpha S_1^2+0.5\beta S_1^4+\gamma S_1^6/3$$
$$+AS_2^2+BS_2^4/2+aS_1^2S_2^2\ .$$

Here G_0 is the free energy of the nematic phase, S_1 and S_2 associated with smectic-*A* and -*C* ordering are the order parameters; $A>0$ and $B>0$ eliminate the biaxial phase, β if large and positive makes the *SA-N* transition second order, $\gamma>0$ assures the stability of the smectic-*A* phase. For constant a,A,B,γ and for α and β linearly varying with composition, we obtained phase diagrams of the kind shown in Fig. 1(b). Insisting on a proximity of a tricritical point on the *SA-N* line, we can make this line a second order up to a tricritical point, as shown in Fig. 1(d). An opposite case shown in Fig. 1(e), with proper tie-lines, is probably what Benguigui really suggested if the firmly established first-order *SC-N* transition also resulting from calculation,[4] is taken into account and Fig. 2 of Ref. 4 is thus corrected.

There is no doubt that by varying the parameters in the Landau theory one can obtain very many different cases and different diagrams. To decide between these various possibilities one must have recourse to experiment and we investigated the volumetric behavior of the mixtures[7] of $\bar{8}S5+\bar{7}S5$. These are very sensitive measurements and, as we describe below, the *SA-SC* is second order in agreement with findings of Johnson *et al.* The diagram of Fig. 1(b) is verified by these experiments, at least under the tacit assumption that nothing unexpected happens between the fixed compositions of the mixture which were investigated.

II. EXPERIMENTAL

We use a circulating bath thermostat,[8] with two windows of float glass panes, stable to ±0.2 mK on the scale of minutes and stable to better than 1 mK on the scale of hours and days, in which a quartz dilatometer is placed.[8] It consists now of a 11-ml vessel topped with a capillary 1 mm in diameter, 30-cm long, and with a second wider tube connected with a glass tap. The dilatometer is filled under vacuum with a degassed substance, the tap closed and protected against contact with thermostat fluid, the top of the capillary connected to the atmosphere. All measurements are made with a meniscus rising in the capillary; the heights are measured with the aid of a Wild cathetometer offering readings to ±0.02 mm. The increments in the height of the fluid column in the capillary are directly proportional to increments of the volume of the given sample; on top of the corrections for the shape of the meniscus, minute corrections are introduced based on a calibration run with mercury. Each sample is weighed and the composition is known from weights—therefore each run of height versus temperature for a given composition of the mixture can be converted into molar volume versus temperature. Such conversion has also been made for the runs reported here and the tables of molar volume versus temperature as well as tables of (corrected and uncorrected) heights are available on request. The temperature was determined with a Tinsley Pt resistance thermometer and monitored to 0.1 mK with a HP quartz thermometer. One run took about 5–9 days and the sample was never allowed to cool, let alone crystallize or undergo any phase transition on cooling. The temperature was always rising or constant within tenths of mK during daytime measurements or within a few mK during overnight rest. The composition of the mixture was prepared by weighing solid pure compounds then melting them and degassing the liquid mixture under vacuum. During filling the mixture was flowing, from the vacuum container kept at some 60° under the force of gravity through the open tap warmed separately into the dilatometer already in the thermostat at the lowest recorded temperature about 45 °C. Never did the meniscus drop either during final stages of filling or during the measurements. Hence we are certain that we started each run with a homogenous one-phase mixture in the dilatometer. Anyway, starting with a two-phase sample would first affect the *SC-SA* transition which we found without a two-phase region (within the resolution of our experiments). The following compositions were studied: $x_{\bar{7}S5}=0.3000$, 0.3700, and 0.5000 in the temperature range 45–60 °C. One of them, $x=0.5000$, lies to the right of the *NAC* tie-line of Fig. 1(b) and the run shows the first-order *SC-N* transition. Another advantage of our experimental setup is the visual observation of the sample in the bulk and in the capillary. The appearance of the first drop of the new, less dense phase was noted and the less accurately known disappearing last drop of the low-temperature, denser phase could be also noticed. Some stirring with quartz balls inside the dilatometer was attempted but was inefficient in the smectic phases.

Any plot of the volume versus temperature or height versus temperature would reveal nothing; we represent in the figures the deviations from a linear or quadratic background. The thermal expansion of the nematic phase turns out to be linear with excellent accuracy, far away of course from the transition to the isotropic phase which we have not studied. The thermal expansion of the smectic *C*, on the contrary, is strongly nonlinear and could be well represented by a second-order polynomial against which a pretransitional increase near the *SC-SA* transition point could be seen. The *SC-SA second-order* phase transition is thus shown in Fig. 2 for one composition $x=0.3700$. Thus the later findings of Johnson[3] who measured heat capacity of pure $\bar{8}S5$ are confirmed also for mixtures. An additional experimental test is provided by the plot of the numerical first and second derivative of height versus temperature, computed in a simpleminded fashion from neighboring data points, shown in Fig. 3 for one composition $x=0.3700$. Any doubts as to the correctness of the interpretation of these data are dispelled by these figures: There is no volume change at the transition, it is a sharp transition occurring at one temperature, where there is a jump in the first derivative, and the course of this curve is quite similar to the course of the heat capacity C_p vs *T*, studied by Johnson[3] whereas any jump in the second derivative is too small to be seen; most importantly, there is no systematic variation in the second derivative near the transition point and this enables one to exclude with the resolution of our experiments the possibility of a weak first-order transition.

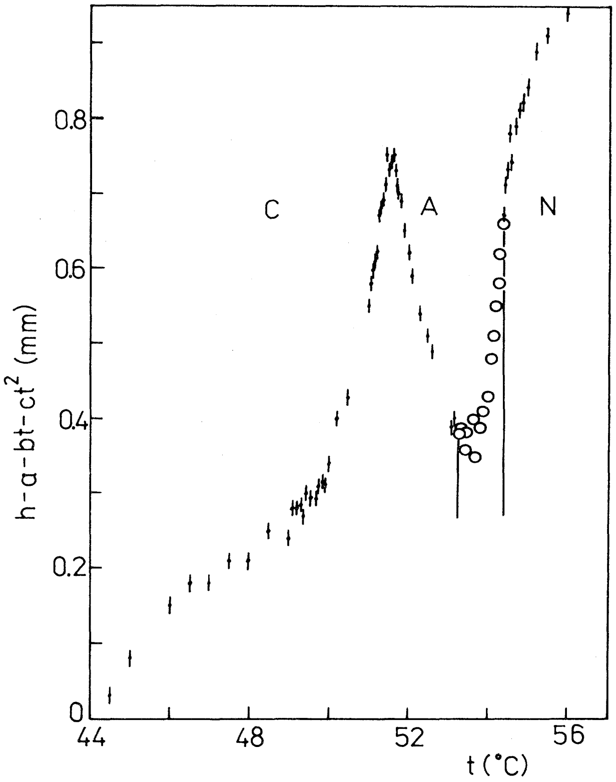

FIG. 2. Volume changes near *SC-SA* transition of $\bar{8}S5$ containing 37 mole % of $\bar{7}S5$, with quadratic background subtracted: $a=-274.50$ mm, $b=3.04$ mmK^{-1}, $c=0.0898$ mmK^{-2}, $t=T-273.15$. Arbitrary scale. Temperature scale compressed for clarity.

Since the thermal expansion of the smectic *C* was so visibly nonlinear not only in the immediate neighborhood of the transition, we tried to represent the volume by $V=V_0\exp(-B/T)$. This was only a partial success since the $\log_{10} V$ vs $1/T$ plot was slightly deviating from a straight line so that there was no immediate advantage over using the second-order polynomial in *T* as the subtracted background. To compare the volumes of different phases, *SC*, *SA*, and *N*, of the same mixture, we subtracted a linear background term. The result is shown in Fig. 4 for all three compositions studied so far, with the same linear background subtracted. The disadvantage of this representation is the decrease of the difference (height-background) in the

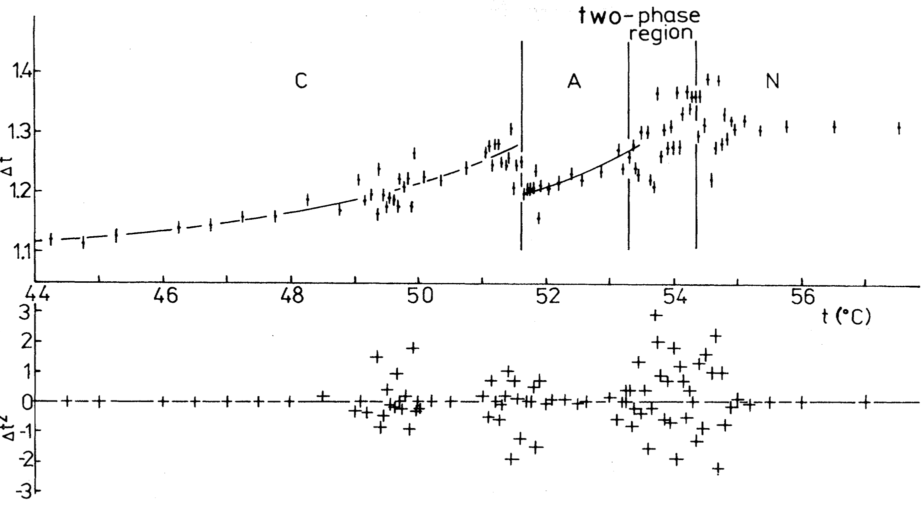

FIG. 3. Numerical (first and second) derivatives computed for all pairs and triplets of neighboring unsmoothed data points. Several marks stand for two data points indistinguishable on the scale of the plot. The estimated thermal expansion dV/dT at the SC side is 0.343 cm^3 mol^{-1} K^{-1} and at the SA side, 0.319 cm^{3}mol^{-1}K^{-1}, at 37% and 324.74 K.

smectic-*C* phase which might be misleading at first—it does not correspond to any decrease in height or volume. The marked changes in slope correspond well with visual observations indicated by arrows (0% *N* and 100% *N*) which correspond to the first drop of nematic and to the last drop of the smectic, respectively. We find in this mixture a smectic-*A* —nematic transition of first order, occupying a finite width in the *T-x* plane.

ΔV for this transition would be 0.366 ± 0.017 cm^3/mol at $x=0.3700$ if the thermal expansion over the two-phase region were not subtracted. If subtraction is attempted we find (in cm^3/mol)

$$\Delta V=0.007\pm0.005$$

for $x=0.3700$ and

$$\Delta V=0.012\pm0.008$$

for $x=0.3000$.

III. DISCUSSION

The shape of the phase diagram as shown in Fig. 1(b) corresponds to a case of the *NAC* point being an end point at which a second-order line meets a first-order line and ends there; the nematic phase represented by the rightmost point of this *tie-line* is in equilibrium with the *SC* phase at lower, and with the *SA* phase at higher, temperature. Hence all that happens is the *SC-SA* transition *in the presence* of the *N* phase. Incidentally the calculations of Benguigui[4] also in fact predict *a NAC tie-line,* as shown in Fig. 1(e), but with *SA-N* second-order transition occurring in the presence of the *SC* phase. All experiments[9] favor a second-order *SC-SA* transition and we also find such behavior in the mixtures when studying the volume. The pretransitional increase on the *SC* side follows the mean-field behavior according to $V_{\text{pretr}} \sim |T_{AC}-T|^{+1}$. The order parameter is known[9] to go to zero as $|T_{AC}-T|^{+1/2}$. The data in the region of the straight portion visible in Fig. 2 are for $T_{AC}/T-1>0.001$ and, according to Litster,[9] still smaller values are needed if deviations from mean-field behavior are to be detected. A closer examination of Fig. 4, also on an enlarged scale, suggests that we can expect then slight rounding (see Fig. 5) of the sharp intersection of the two curves of $V(T)$ for *SA* and *CS* phases. In fact, in Fig. 2, there are two or three last points which are consistently low if different backgrounds are subtracted. Also, on the *SA* side in Fig. 4 this slight rounding may be detected. It is confirmed to some extent by the numerical first derivative (see Fig. 3); fits of some 10—15 point closest to the transition on the *SC* side show maxima which disappear when more data points are included or if four points closest to the transition are deleted and the same (second- or third-degree) polynomial is fitted. A firm and quantitative conclusion can be reached if the region $t<10^{-3}$ is studied.

When including all data points we also used third-degree polynomials with excellent results; no improvement was obtained when nonintegral E was used in $V=a+bt+ct^2+dt^E$; $t=(T_{AC}-T)/T_{AC}$,

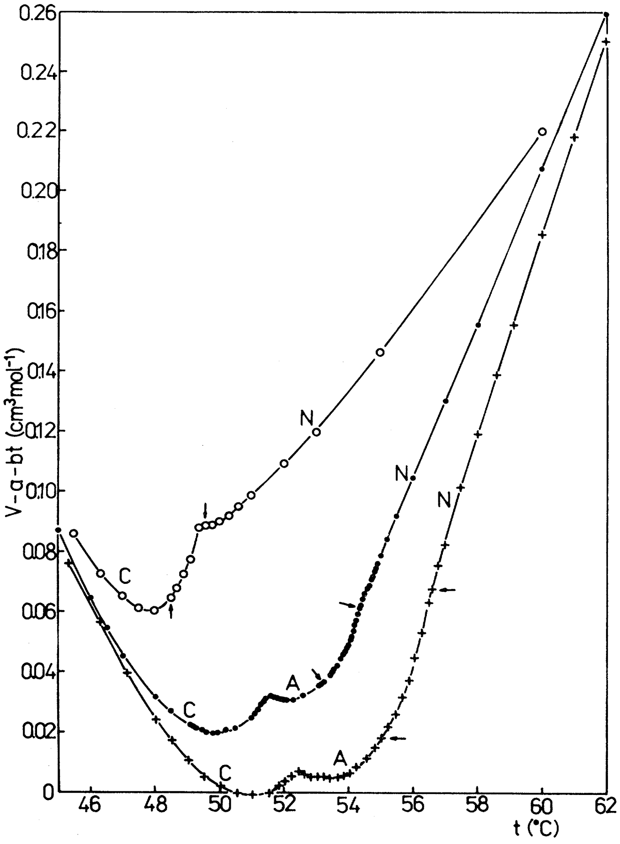

FIG. 4. Molar *V-a-bt* volumes of three mixtures containing 30, 37, and 50 mole% of $\bar{7}S5$ in $\bar{8}S5$, with a linear background subtracted, plotted against temperature: (+) $x_{\bar{7}S5}=0.3000$, $a=383.469$ cm^{3}mol^{-1}; (●) $x_{\bar{7}S5}=0.3700$, $a=382.714$ cm^{3}mol^{-1}; (○) $x_{\bar{7}S5}=0.5000$, $a=380.177$ cm^{3}mol^{-1}, $t=T-273.15$, $b=0.32515$ cm^{3}mol^{-1}K^{-1}. Arrows point out to the beginning or to the end of apparently two-phase regions (which must be excluded from any fitting procedures or treated separately).

with positive E. In particular, the derivative dV/dT did not show the square-root divergence suggested for C_p by Schantz and Johnson[3] but, on the contrary, at least on the *SC* side, the weak but rather convincibly visible rounding mentioned above, possibly produced by impurities.

The first-order transition *N-SA* may seem at first surprising since in some of the previous work second-order transitions were found. Most *N-SA* transitions are first order but the Landau mean-field theory predicts a possibility of a second-order transition and, physically, one expects[9] a second-order transition when the nematic order parameter $\mathscr{S}$ is saturated since then the layered structure can be created with greatest ease. It has not yet been found conclusively whether one should expect a second-order transition only in the limit of *full* saturation of the nematic order parameter $\mathscr{S}=1$ or a tricritical point is to be found at $\mathscr{S}<1$. There are theoretical arguments summarized in Ref. 9 suggesting that the director fluctuations will make this transition always first order. What we find is a transition so extremely weak that an estimate of the volume jump ΔV is very uncertain because it is washed out by the thermal expansion of the sample. Were it not for the visual observation and for subtraction of various backgrounds in the analysis of the data of first-order character of the transition would not have been revealed because its quantitative consequences are so minimal. The general character of the *N-SA* transition seems to be common to many different systems: very strong posttransitional and pretransitional effects, e.g., in volume or heat capacity, weak or immeasurably weak first-order jumps quite overshadowed by temperature variations of the property in question—quite different from a traditional picture of first-order transitions such as crystallization.

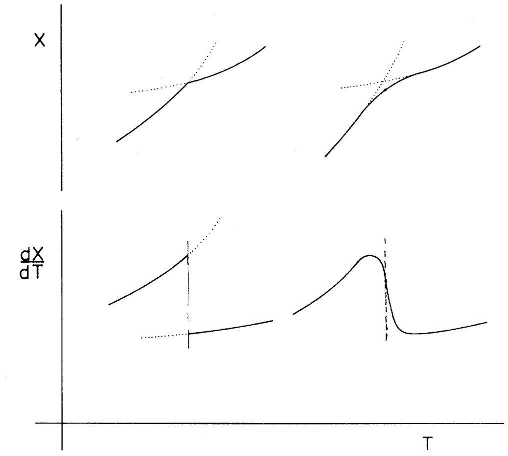

FIG. 5. Conjectured "rounding" or "deadening" of a sharp transition.

Note added in proof. The referee pointed out to us that the appearance of droplets (streaks) may not be as conclusive a proof of a two-phase region since our sample has not been homogenized in a magnetic field. We fully agree and point out that the phase diagram shown in Fig. 1(d), but not 1(e), appears a distinct possibility. In either case the *NAC* point is a tie-line of nonzero length.

ACKNOWLEDGMENTS

This work was supported by the Polish Academy of Sciences Research Program No. 03.10.1.

[1] P. H. Keyes and J. R. Shane, Phys. Rev. Lett. 42, 722 (1979).

[2] F. Hardouin, G. Sigaud, M. F. Achard, and H. Gasparoux, Ann. Phys. (Paris) 3, 381 (1978); see P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[3] D. Johnson, D. Allender, R. De Hoff, C. Maze, E. Oppenheim, and R. Reynolds, Phys. Rev. B 16, 470 (1977); see also C. A. Schanz and D. L. Johnson, Phys. Rev. A 17, 1504 (1978); P. E. Cladis, D. Guillon, J. Stamatoff, D. Aadsen, W. B. Daniels, M. E. Neubert, and R. F. Griffith, Mol. Cryst. Liq. Cryst. Lett. 49, 279 (1979); R. De Hoff, R. Biggers, D. Brisbin, R. Mahmood, C. Gooden, and D. L. Johnson, Phys. Rev. Lett. 47, 664 (1981).

[4] J. Imry, J. Phys. C 8, 567 (1975); L. Benguigui, J. Phys. (Paris) Colloq. 3, 419 (1979).

[5] J. Chen and T. C. Lubensky, Phys. Rev. A 14, 1202 (1976).

[6] J. Stecki, in Proceedings of the Third Liquid Crystal Conference, Budapest, August, 1979 (unpublished).

[7] The compounds are 4-*n*-pentylphenylthiol-4′-*n*-octyloxybenzoate ($\bar{8}S5$) and 4-*n*-pentylphenylthiol-4′-*n*-heptyloxybenzoate ($\bar{7}S5$). The *N*-*I* transition points were 85.4 – 85.6 °C and 82.1 – 82.6 °C, respectively.

[8] G. Van Hecke and J. Stecki, Phys. Rev. A 25, 1123 (1982); E. Molga and J. Stecki, J. Chem. Thermodyn. 9, 79 (1977); S. A. Wieczorek and J. Stecki, *ibid.* 10, 177 (1978).

[9] J. D. Litster, R. J. Birgeneau, M. Kaplan, C. R. Safinya, and J. Als-Nielsen, in *Proceedings of the NATO Advanced Study Institute,* on Strongly Fluctuating Condensed Matter Systems, Geilo, Norway, April, 1979 (Plenum, New York, 1979), pp. 357 – 382.