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Landau second order to tricritical crossover behaviour for smectic A–smectic C* transitions

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The smectic A (S_A)–chiral smectic C (S_C^*) transition in binary mixtures of methylchloropentanoyloxy heptyloxybiphenyl (C7) and butyloxyphenyl decyloxybenzoate (10O.4) changes from first order to second order as a function of X, the mole per cent of 10O.4. High resolution heat capacity measurements show that the C_p behaviour is well-described by Landau mean field theory. Classical tricritical behaviour is observed near $X_{tc} \simeq 10{\cdot}6$ and the coefficient b of the quadratic term in the free energy varies like $(X - X_{tc})$ in good agreement with results from polarization data.

1. Introduction

For chiral liquid crystal molecules with a polar group perpendicular to the long axis and non-polar end groups, the tilted smectic C phase formed from smectic A (S_A) is denoted S_C^*. The order parameter for the S_A–S_C^* transition is $\psi = \theta e^{i\phi}$, where θ is the tilt angle and ϕ is the azimuthal orientation. Chiral interactions lead to a helicoidal ϕ variation in the absence of an external field. Application of a very small electric field will unwind this helix, yielding a non-zero bulk spontaneous polarization P_s.

The S_A–S_C transitions in non-polar non-chiral molecules are all second order transitions well-described by the extended Landau model [1, 2]. Recently, it has been discovered that several chiral liquid crystal systems exhibit first order S_A–S_C^* transitions [3, 4] and in some cases this first order transition can crossover via a tricritical point to a second order transition [5–9]. In particular, Bahr and Heppke [4, 8] have studied the tilt angle and electric displacement in 4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxybiphenyl (C7). The S_A–S_C^* transition is first order at low values of the electric field E, exhibits mean field critical behaviour at $E_c = 50\,\mathrm{kV\,cm^{-1}}$, and becomes supercritical for $E > E_c$. Mixtures of C7 and 4-butyloxyphenol-4′-decyloxybenzoate (10O.4) have also been studied at zero field [9]. This system shows S_A–S_C^* crossover from first order in C7 to tricritical at $X_{tc} \cong 10{\cdot}5$ to second order at higher X, where X is the mole per cent 10O.4. A partial phase diagram is shown in figure 1.

The present calorimetric study is designed to test the reported mean field Landau character of this S_A–S_C^* system. Earlier C_p measurements near the tricritical S_A–S_C^* point in 2f+3f mixtures of chiral esters of 2,5-diphenyl pyrimidine [7] showed general agreement with the Landau model but substantial rounding of the C_p peak and some excess heat capacity above background in the S_A phase that might be due to thermal

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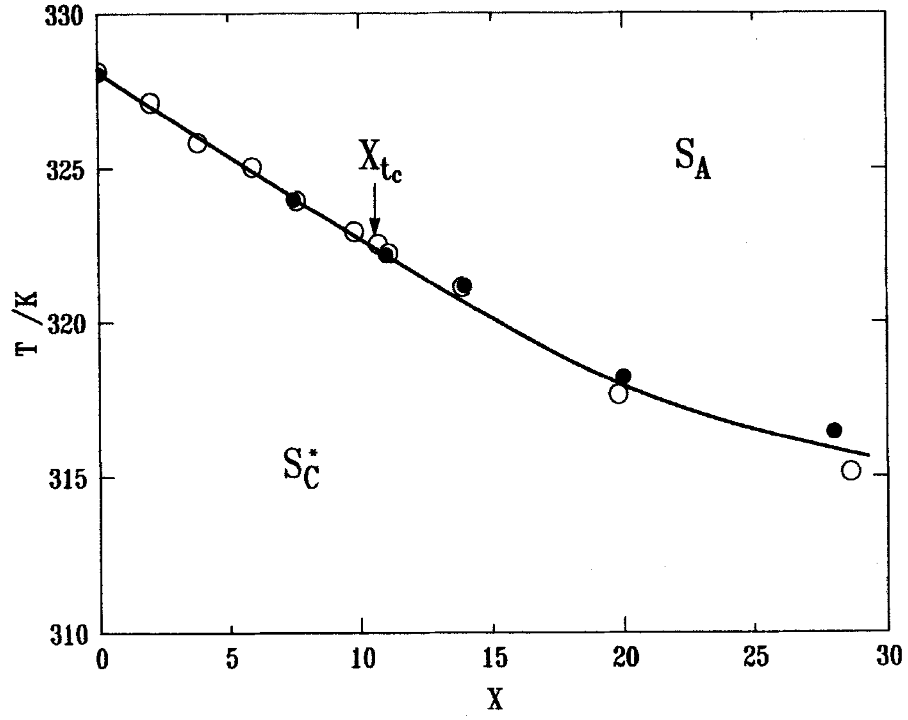


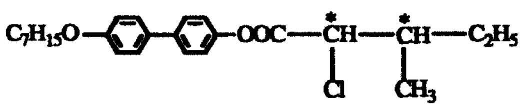
Figure 1. Partial phase diagram for C7+10O.4 mixtures with transition temperatures determined microscopically (○) and calorimetric transition temperatures (●). X is the mole per cent 10O.4. The tricritical point is indicated at $X_{tc} \simeq 10{\cdot}6$.

fluctuations. In contrast to this, the near tricritical behaviour in racemic methylchlorobutanoyloxy heptyloxybiphenyl (A7) is very well-described by classic Landau theory [5]. The present results are in excellent agreement with Landau theory, as shown in § 2. The previously observed peculiar behaviour in 2f+3f is, we now believe, due to concentration gradients within those samples due to incomplete mixing. Such gradients can distort and smear out the transition, as discussed in § 3.

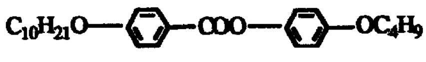
2. Results and analysis

The molecular formulae and molecular weights (MW) of the investigated compounds are

C7 (MW = 416·99)



10O.4 (MW = 426·59)



These compounds were synthesized and purified at the Technical University of Berlin [3], and the heat capacity measurements were made at MIT using a high resolution AC calorimeter described elsewhere [7, 10]. Pure C7 (the L enantiomer) and five C7+10O.4 mixtures with compositions $X = 7{\cdot}5$, $11{\cdot}1$, $14{\cdot}0$, $19{\cdot}7$, and $28{\cdot}0$ were investigated. The stability of these samples was good; the drift in transition temperatures observed during successive heating and cooling runs was in the range -10 to $-40\,\mathrm{mK\,day^{-1}}$. Furthermore, the calorimetric transition temperatures are in good agreement with those determined optically, as shown in figure 1. An example of the C_p data obtained with our calorimeter is given in figure 2. This figure shows the heat capacity variation in a mixture with $X = 11{\cdot}1$, which is near the tricritical point. It is necessary to stress that an AC calorimeter measures C_p values but not the enthalpy H. Thus any discontinuous jump ΔH (i.e. latent heat) at a first order transition is not measurable. However, there is a useful qualitative indication of two phase coexistence that occurs at a first order transition. Data taken in a two phase region exhibit anomalously high C_p values and an abrupt increase in the phase shift φ between the oscillating heat input $\dot{Q}(\omega)$ and the sample temperature $T(\omega)$ [10]. These characteristics

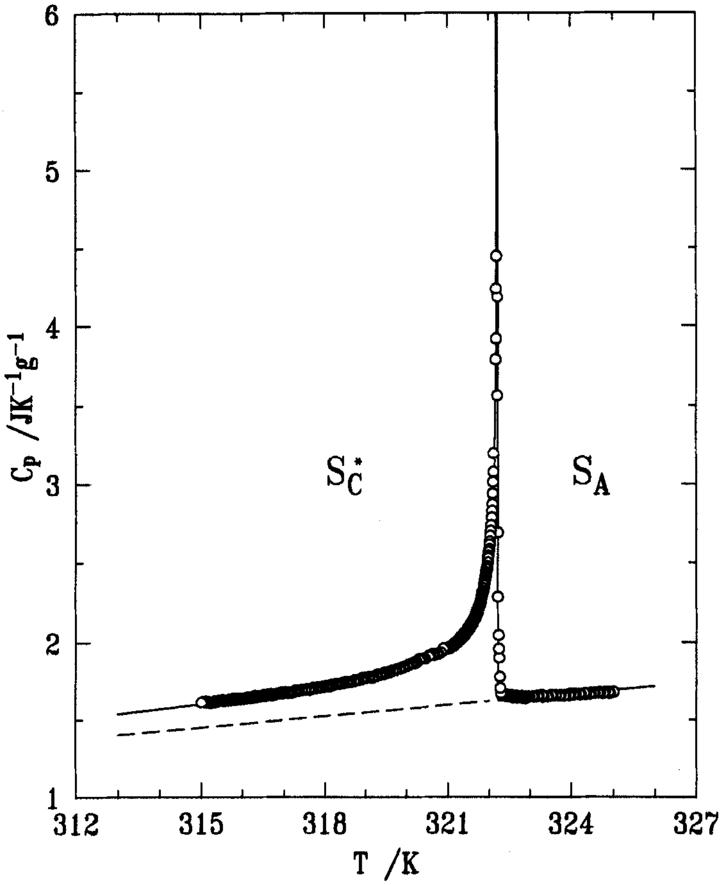


Figure 2. Specific heat capacity C_p in a near tricritical C7+10O.4 mixture with $X = 11{\cdot}1$. The solid curve represents a Landau fit with equation (6), and the dashed line represents the background heat capacity $C_p^0(T)$.

of first order phase coexistence were clearly observed for $X=0$ and $X=7{\cdot}5$, and the widths of the coexistence ranges were 150 mK for $X=0$ and 120 mK for $X=7{\cdot}5$.

In the extended Landau model, the Gibbs free energy has the form.

$$G=G_0+at\psi^2+b\psi^4+c\psi^6, \tag{1}$$

where G_0 is the free energy of the disordered (S_A) phase, ψ is the order parameter and $t\equiv(T-T_0)/T_0$ is the reduced temperature. The Landau coefficients a and c are positive, while b can be positive (second order), zero (tricritical), or negative (first order). As in all mean field models, there is no critical contribution above the transition temperature and the disordered phase heat capacity can be represented by a linear expression $C_p^0(T)=B+E(T-T_0)$, which is the background value coming from G_0. Below the transition, the critical excess heat capacity $\Delta C_p=C_p-C_p^0$ is given by [11]

$$\Delta C_p=A\frac{T}{T_0}\left(\frac{T_k-T_0}{T_k-T}\right)^{1/2}, \quad T<T_0 \quad \text{for} \quad b>0, \tag{2}$$

or

$$\Delta C_p=2A\frac{T}{T_0}\left(\frac{T_k-T_1}{T_k-T}\right)^{1/2}, \quad T<T_1 \quad \text{for} \quad b<0, \tag{3}$$

where $A=|a^2/2bT_0|$ is the mean field jump in C_p at T_0 for a second order transition and $2A$ is the jump at T_1 for a first order transition. The metastability limit T_k is given by

$$T_k\equiv T_0+(b^2T_0/3ac). \tag{4}$$

When $b>0$, a second order transition occurs at T_0. When $b<0$, a first order transition occurs at T_1, where

$$T_1=T_0+(b^2T_0/4ac)=T_k-(b^2T_0/12ac). \tag{5}$$

When $b=0$, a Landau tricritical point occurs at $T_k=T_0$. Since (T/T_0) ranges from 0·97 to 1·0 for the present data sets, we can neglect this trivial temperature dependence in equations (2) and (3) and rewrite these equations in the convenient form

$$\Delta C_p=A^*(T_k-T)^{-1/2}, \tag{6}$$

where $A^*=(a^3/12cT_0)^{1/2}$. It should be noted that this form is also valid at the tricritical point, where ΔC_p diverges. It is usual to quote the value of a quantity $t_0\equiv b^2/ac$, which equals $3(T_k-T_0)/T_0$ for a second order transition and $12(T_k-T_1)/T_0\simeq12(T_k-T_1)T_1$ for a first order transition. In the case of second order transitions, t_0 has a special meaning—the reduced temperature width of the C_p peak at half maximum (i.e. $\Delta C_p=A/2$ at $t=-t_0$).

The fit with equation (6) to the C_p data for $X=11{\cdot}1\simeq X_{tc}$ is shown in figure 2 over a 10 K temperature range. In this sample, it is not possible to distinguish whether the transition occurs at T_k or just below T_k, but in any case the system is very close to tricritical. No anomalous increase in the phase shift φ, the usual indication of two phase coexistence at a first order transition, was observed for $X=11{\cdot}1$.

In fitting ΔC_p for each sample with equations (2) or (3), we omitted any anomalous points taken in the coexistence region for the two samples with $X=0$ and 7·5 and points in the near vertical ramp at T_0 for other samples. The values of the fitting parameters A, B, E, T_k and T_0 (or T_1) are listed in the table, together with t_0 values and A^* values given by $A^*=A(T_k-T_0)^{1/2}$ for second order and $A^*=2A(T_k-T_1)^{1/2}$ for first order. A scaling

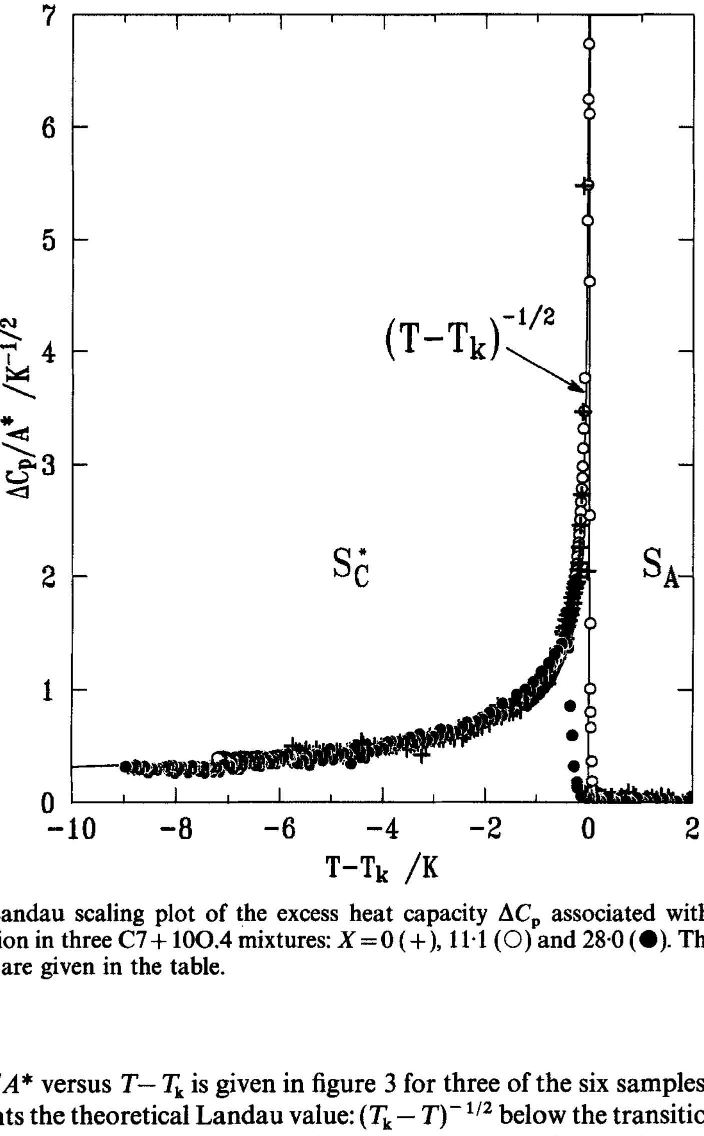


Figure 3. Landau scaling plot of the excess heat capacity ΔC_p associated with the S_A–S_C^* transition in three C7+10O.4 mixtures: $X=0$ (+), 11·1 (○) and 28·0 (●). The A^* and T_k values are given in the table.

plot of $\Delta C_p/A^*$ versus $T-T_k$ is given in figure 3 for three of the six samples. The solid line represents the theoretical Landau value: $(T_k-T)^{-1/2}$ below the transition and zero above. The data for the other three samples also agree very well with the Landau curve but are omitted in the interests of clarity. A detailed view of the scaled ΔC_p behaviour near T_k for all six samples is shown in figure 4. The positions are marked corresponding to T_0 and T_1 values for samples with $X>X_{tc}$ and $X<X_{tc}$, respectively. As expected these values shift systematically with respect to T_k as X varies. It must be stressed that the fitting curve is insensitive to these T_0 or T_1 values, as indicated by equation (6). The role of T_0 and T_1 is to determine the transition temperature where ΔC_p drops from $A^*(T_k-T)^{-1/2}$ to zero. The T_0 values in the table and indicated in figure 4 are set at the mid-point of the rapid near linear rise in C_p between C_p^0 and C_p(max), as is usually done [2]. The T_1 values were taken at the mid-point of the coexistence range.

3. Discussion

For a Landau system that exhibits crossover, we expect the fourth order coefficient b to change from negative in the first order regime to positive in the second order

Least-squares values of the Landau parameters in equations (2)–(6) obtained on fitting S_A–S_C^* heat capacity data. The background quantity $C_p^0(T)$ is given by $B+E(T-T_0)$. The units are $J\,K^{-1}\,g^{-1}$ for A and B, $J\,K^{-2}\,g^{-1}$ for E, $J\,K^{-0\cdot5}\,g^{-1}$ for A^*, and K for T_k and T_0 (or T_1). The quantity $t_0=b^2/ac$ is dimensionless. For first order transitions when $X\leqslant 10$, T_1 values are given in place of T_0.

X	$T_0(T_1)$	T_k	A	A^*	B	10^3E	χ_ν^2	10^4t_0
0	(328·064)	328·141	0·94	0·52	1·26	16·0	1·19	28·2
7·5	(323·986)	323·991	3·37	0·48	1·20	17·7	1·24	1·9
11·1	322·198	322·200	9·37	0·42	1·62	24·1	0·93	0·2
14·0	321·185	321·213	2·21	0·37	1·51	12·0	1·04	2·6
19·7	318·221	318·400	0·60	0·25	1·56	1·8	0·88	16·9
28·0	316·439	316·787	0·30	0·18	1·45	7·5	0·91	33·0

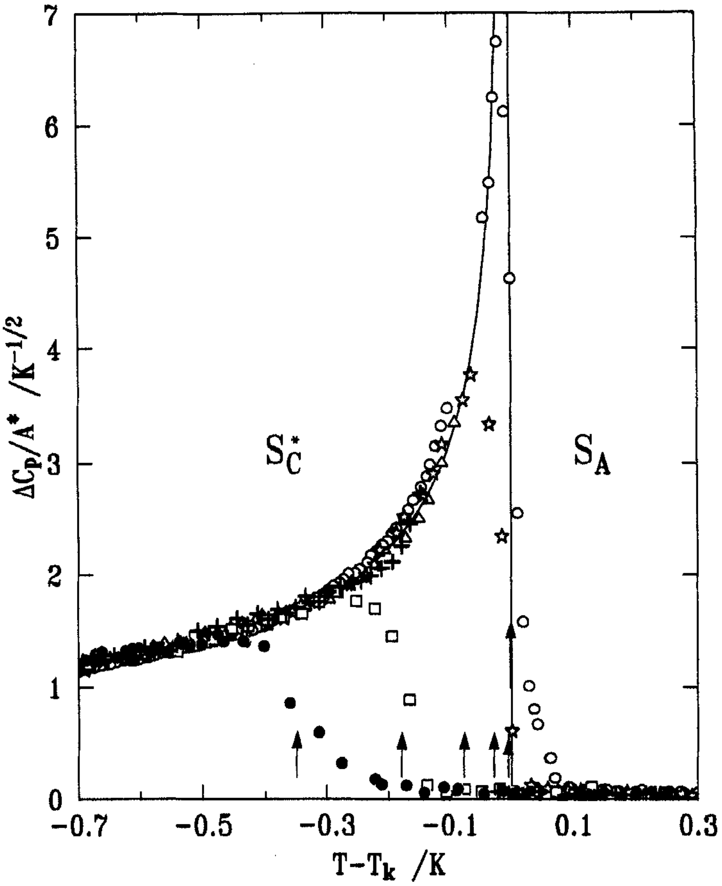


Figure 4. Detailed view of the Landau scaling plot for all six samples. The locations of T_0 for samples with $X>X_{tc}$ and T_1 for samples with $X<X_{tc}$ are indicated by arrows at the bottom of the figure. The data points corresponding to anomalous values in a two phase coexistence region have been omitted. $X=0$ (+), 7·5 (△), 11·1 (○) 14·0 (☆), 19·7 (□), 28·0 (●).

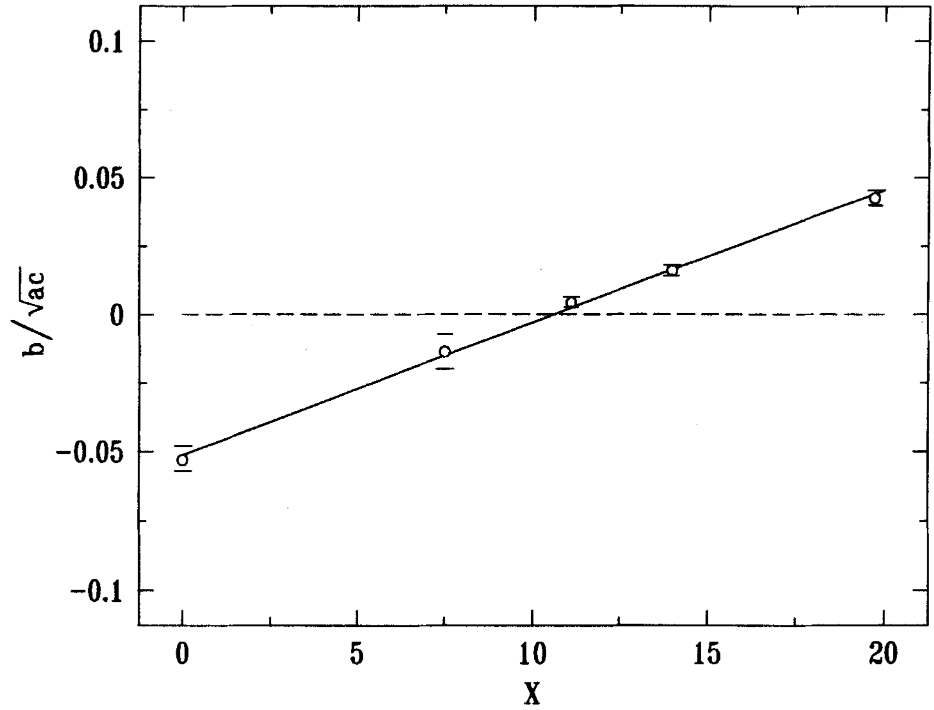


Figure 5. Variation with composition near X_{tc} of the Landau coefficient ratio $b/\sqrt{(ac)}$ derived from C_p fits. The error bars are 95 per cent confidence limits based on the least-squares uncertainty in T_k and our estimated uncertainty in choosing T_0 or T_1. The assumed linear dependence of $b/\sqrt{(ac)}$ on X yields $X_{tc} = 10{\cdot}6 \pm 0{\cdot}4$.

regime. The spontaneous polarization measurements on C7 + 10O.4 mixtures show that P_s data are consistent with $b \sim (X - X_{tc})$ and $X_{tc} \simeq 10{\cdot}5$ [9]. Our heat capacity analysis yields values of $(T_k - T_0)$ and $(T_k - T_1)$ that determine $t_0 = b^2/ac$ together with a knowledge of the sign of b. The resulting $b/\sqrt{(ac)}$ values are plotted against X in figure 5. Assuming that ac is slowly varying (which is consistent with P_s data [9]), we see that C_p data also yield $b \sim (X - X_{tc})$. The linear fit line in figure 5 gives $X_{tc} = 10{\cdot}6 \pm 0{\cdot}4$. This value is in excellent agreement with that determined from the X dependence of the jump ΔP_s at first order transitions when $X < X_{tc}$. Thus the present results provide a classic example of Landau mean field crossover from first to second order behaviour [12].

An earlier study [7] of such crossover in a different chiral mixture seemed to indicate the possibility of fluctuation effects, which are clearly absent in C7 + 10O.4. We now feel that the earlier results do not represent fluctuation effects but can be understood as the consequence of sample heterogeneities. In this case, equation (6) can be replaced by

$$\Delta C_p \cong A^* \int_T^{\infty} (T_k - T)^{-1/2} g(T_0)\, dT_0, \tag{7}$$

where

$$g(T_0) = \frac{1}{\sqrt{(2\pi)}\sigma} \exp\left[-(T_0 - \bar{T}_0)^2/2\sigma^2\right], \tag{8}$$

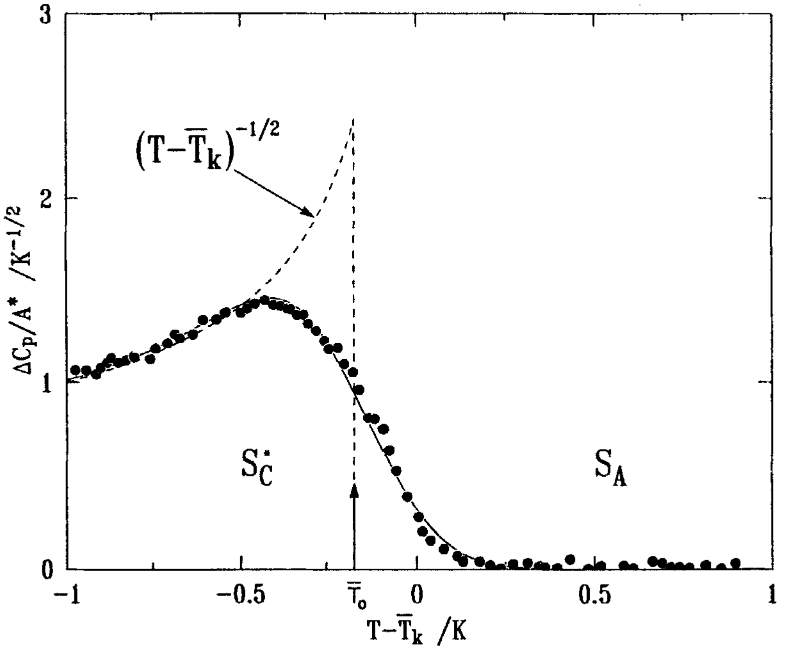


Figure 6. Smearing effect of sample inhomogeneities in a 2f+3f mixture with $X_{2f}=38{\cdot}72$ (see [7]). The dashed lines represent the behaviour in a homogeneous sample

is the distribution function, which has been taken to be gaussian, for T_0 around an average value $\bar{T}_0$.

Now let us rewrite (T_k-T) in the form

$$T_k-T\cong[T_0+(b^2/3ac)_0T_0+(b^2/3ac)_1(T_0-\bar{T}_0)T_0-T]. \tag{9}$$

where equation (4) has been used and the quantity $(b^2/3ac)$ has been expanded about $\bar{T}_0$. Since $(b^2/3ac)$ is not varying rapidly with composition, it is numerically justified to ignore $(b^2/3ac)_1$ and retain only $(b^2/3ac)_0\equiv(\bar{T}_k-\bar{T}_0)/\bar{T}_0$. We have carried out the integration in equation (7) using equation (8) and $(T_k-T)\simeq T_0+(\bar{T}_k-\bar{T}_0)T_0/\bar{T}_0-T$. The values of the parameter A^* are given in [7], and we have used $\bar{T}_k-\bar{T}_0$ and σ as adjustable parameters. The results of fitting three 2,5-diphenyl-pyrimidine mixtures 2f+3f are $\bar{T}_k=393{\cdot}96\,\mathrm{K}$, $A^*=0{\cdot}1226$, $\bar{T}_k-\bar{T}_0=0{\cdot}17\,\mathrm{K}$ and $\sigma=0{\cdot}17\,\mathrm{K}$ for $X=38{\cdot}72$; $T_k=396{\cdot}50\,\mathrm{K}$, $A^*=0{\cdot}1372$, $\bar{T}_k-\bar{T}_0=0{\cdot}10\,\mathrm{K}$ and $\sigma=0{\cdot}10\,\mathrm{K}$ for $X=44{\cdot}87$; and $\bar{T}_k=403{\cdot}89\,\mathrm{K}$, $A^*=0{\cdot}1777$, $\bar{T}_k-T_0=0{\cdot}005\,\mathrm{K}$ and $\sigma=0{\cdot}075\,\mathrm{K}$ for $X=54{\cdot}90$. The result for $X=38{\cdot}72$ is shown in figure 6 as an example; comparable quality fits were obtained for the other two compositions. Except for this heterogeneity broadening, the earlier 2f +3f results are fully compatible with the present conclusions about the mean field nature of this S_A–S_C^* crossover.

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[12] It should be noted that no attempt has been made to generalize the Landau theory by taking into account an explicit composition dependence for G. For a first order transition in a binary mixture, we expect in general a finite coexistence temperature range with coexisting phases of slightly different composition, in contrast to the sharp first order transition in a pure single compound. See, for example, Alben, R., 1973, *Solid St. Commun.*, **13**, 1783. However, the compositions of such coexisting phases are unknown here and the associated temperature width is uncertain. Note that pure C7 (i.e. $X=0$) exhibits S_A–S_C^* coexistence over 150 mK, which is wider than the 120 mK coexistence range for the first order mixture with $X=7{\cdot}5$. Since these two coexistence ranges are narrow and not well correlated with ideal expectations, we have simplified the analysis by choosing a value for T_1 that lies at the middle of the coexistence range.