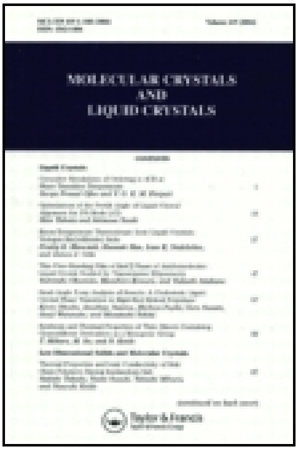

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A Landau-De Gennes Theory of the Nematic Liquid Crystal Surface

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A Landau–De Gennes Theory of the Nematic Liquid Crystal Surface†

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The Landau–de Gennes expression of the free energy density for a nematic liquid crystal system is extended to incorporate interfacial effects. It is found that qualitative descriptions of the pre- and post-transitional contributions to the orientational component of the surface tension are obtained which are in good agreement with experiment. In all cases it is found that the surface is characterized by a critical divergence of its interfacial thickness in the vicinity of the nematic-isotropic transition. This effect appears not to have been previously reported and would seem essential in any adequate description of the liquid crystal surface.

INTRODUCTION

The role and development of interfacial torque fields at the surface of strongly anisotropic molecular systems have received widespread attention both in terms of statistical mechanical description by Croxton and Osborn[1] and Haile,[2] and by computer simulation.[3]

The obvious relevance of these studies for liquid crystal systems has led to the proposal of a formal statistical theory of the smectic-nematic-isotropic liquid interface (Croxton and Chandrasekhar[4] and Croxton[5,6]) on the basis of which a variety of pre- and post-transitional effects were anticipated, a number of which have been reported experimentally. The principal surface excess thermodynamic functions exhibit an unusually complex range of behaviour depending upon a subtle interplay of bulk and local interfacial order parameters, thermal variation of density profile, and its local gradient.

The specification of a local order parameter $S(z)$ across the interfacial zone is central to the development, and although there have been treatments

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analogous to the Kirkwood-Buff analysis for simple liquids in which the bulk order parameter S_L is assumed to extend unmodified right up to a surface of density discontinuity,[7] it is felt that such a model forfeits many of the more subtle features which have been observed experimentally.

Despite the complexity of the integral equations specifying the local order parameter $S(z)$, a detailed statistical mechanical analysis (Croxton and Chandrasekhar[4] and Croxton[5] reveals that local modification of the order parameter arises as a response to ordering and disordering effects associated with the development of interfacial torque fields and the decrease of density across the surface, respectively. Numerical determination of $S(z)$ appears prohibitively difficult at present. However Croxton[5,6] has subsequently shown that the *orientational* contribution to the surface excess free energy unit area (orientational surface tension) may be written

$$\hat{\gamma} \propto \int_{-\infty}^{\infty} \rho(z)S(z)\,\mathrm{d}z - \int_{-\infty}^{0} \rho_L S_L\,\mathrm{d}z - \int_{0}^{\infty} \rho_V S_V\,\mathrm{d}z \tag{1}$$

which, presuming a knowledge of $S(z)$, enables an immediate qualitative comparison with experiment to be made since the primary features of the surface tension-temperature curve may be directly attributed to the molecular anisotropy of the system. $\rho(z)$ is the local number density of particles across the liquid-vapour transition zone; ρ_L, ρ_V are the bulk liquid and vapour densities, respectively.

In this paper we introduce a further aspect of the interfacial structure which appears to have been entirely overlooked, and that is a critical divergence in interfacial thickness as the critical temperature T_c^* is approached. A critical divergence of the isothermal compressibility χ_T at T_c^* is well-established (Kapustin and Bykova,[8] and Pople and Karasz[9]) as is the relation $L \propto \gamma\chi_T$, where L is the interfacial thickness.[10] Clearly, the interfacial thickness will diverge roughly as χ_T—a feature entirely neglected in all treatments so far and one which invalidates all analyses based upon an interfacial surface of density discontinuity. In this paper we shall adopt a variety of qualitative forms for the critical broadening of the profile in the vicinity of T_c^*, and investigate the consequent response of $S(z)$ upon which $\hat{\gamma}$ is sensitively dependent.

THE LANDAU–DE GENNES EXPRESSION OF INTERFACIAL FREE ENERGY DENSITY

The bulk free energy of a nematic liquid crystal system is phenomenologically described by the well-known Landau–de Gennes expression in terms of the order parameter S.[11] A variational minimization of the free energy with respect to S yields the temperature dependence of S which shows a first-order phase transition at a transition temperature T^* when S distontinuously jumps to zero indicating the onset of the isotropic phase. More recently, Mada and Kobayashi,[12] in their study of nematic systems against a rigid boundary, introduced a linear term into the Landau–de Gennes expression for the free energy;

$$\bar{F} = \bar{F}_0 - \tfrac{1}{3}\Delta\beta\bar{S} + \tfrac{1}{3}\bar{A}\bar{S}^2 - \tfrac{2}{27}\bar{B}\bar{S}^3 + \tfrac{1}{9}\bar{C}\bar{S}^4 \tag{2}$$

The quantity $\Delta\beta$ represents an anisotropy of anchoring strength at the boundary: the bulk system is characterized by $\Delta\beta = 0$. $\bar{S}$ represents the *average* order parameter in the vicinity of the boundary and to that extent gives a non-local specification of the order. The coefficient $\bar{A} = \bar{a}(T - T^*)$ as in the bulk, whilst $\bar{a}$, $\bar{B}$ and $\bar{C}$ are positive constants. Mada and Kobayashi[12] find that even for temperatures $\bar{A} > 0$ a residuum of orientational order remains in the vicinity of the boundary.

Here we adopt a result of an earlier analysis by Croxton and Chandrasekhar[4] and set the local orienting field strength to be

$$\Delta\beta(z) = \left\{ m[\rho_{(1)}(z) - \rho^*] + n\left(\frac{\mathrm{d}\rho_{(1)}(z)}{\mathrm{d}z}\right)^2 \right\} \tag{3}$$

where m and n are positive constants and $\rho^* = \rho_L(\rho_V)$ according as $z < (>)0$. Of course, $\rho(z, A)$ remains to be specified and this we do in terms of the qualitatively uncontroversial tanh profile.

$$\rho_{(1)}(z, A) = \rho_L + \frac{\rho_V - \rho_L}{\exp(-tz) + 1}, \qquad t = t(A) \tag{4}$$

from which it may be readily shown that the interfacial thickness $L \propto t^{-1}$. For example, liquids in the vicinity of the triple point $t \sim 0.3$ yield an interfacial thickness of three or four atomic diameters, in reasonable agreement with machine simulations. For simplicity we also take $\rho_L = 1.0$, $\rho_V = 0$ throughout. $t(A)$ remains to be specified, and we consider two families of characteristics, the first in which the surface shows an infinite critical divergence (Figure 1(a)) and a second which shows a restricted divergence (Figure 1(b). For completeness we also consider a linear variation of $t(A)$. As we shall see, the consequences of this critical divergence for the principal interfacial thermodynamic functions of the system prove to be of central importance.

On the basis of Eqs. (3) and (4), we may solve for the order parameter

$$\begin{aligned}\frac{\partial F(z)}{\partial S(z)} &= -\frac{1}{3}\Delta\beta(z, A) + \frac{2}{3}AS(z) - \frac{2}{9}BS^2(z) + \frac{4}{9}CS^3(z)\\ &= 0.\end{aligned} \tag{5}$$

where B and C are positive constants.

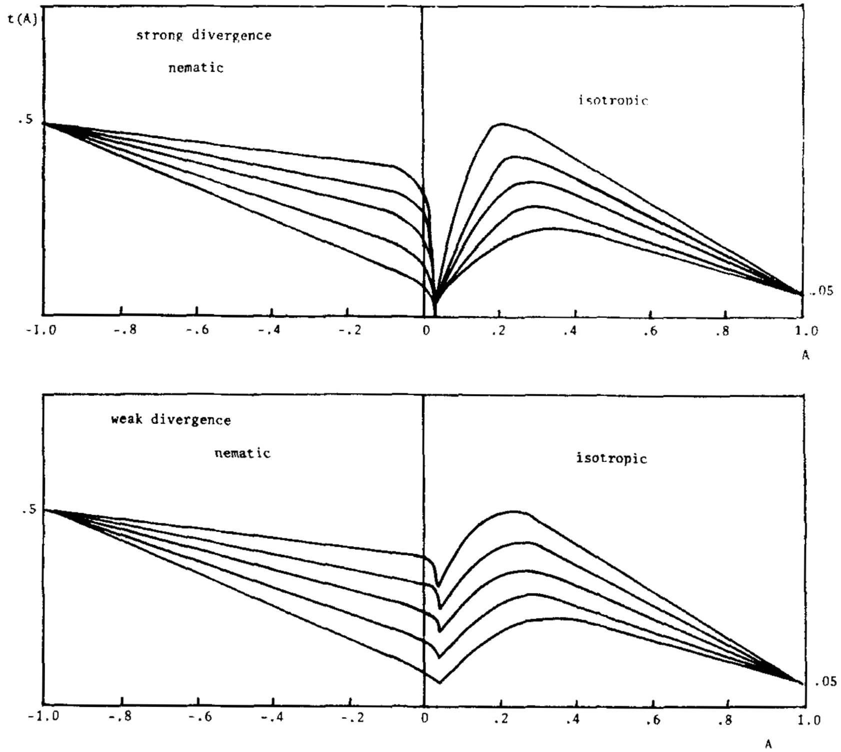


FIGURE 1 Families of inverse interfacial thickness curves as a function of temperature showing (a) strong divergence, (b) weak divergence at the critical temperature. The first-order nematic-isotropic phase transition occurs at $A = 0$. Any combination of the branches $A < 0$, $A > 0$ may be taken.

Clearly, for regions of non-zero $\Delta\beta$—at the surface for example—there can be no solution $S = 0$ even in the isotropic phase, although $S \to 0$ as A increases. The general solutions of (5) for given A are:[12]

$$\begin{aligned} S(z, A) &= \frac{B}{6C} + \alpha_1^{1/3} + \alpha_2^{1/3} \\ &\quad \frac{B}{6C} - \frac{1}{2}(\alpha_1^{1/3} + \alpha_2^{1/3}) \pm \frac{\sqrt{3}}{2}(\alpha_1^{1/3} - \alpha_2^{1/3})\sqrt{-1} \end{aligned}$$

where

$$\left.\begin{matrix}\alpha_1\\ \alpha_2\end{matrix}\right\} = \frac{1}{6^3C^3}\left[B^3 + 81C^2\Delta\beta(z) - 27ABC \pm 9C\sqrt{D}\right]$$

D is the discriminant $72A^3C - 3A^2B^2 + 81C^2(\Delta\beta(z))^2 - 54ABC\Delta\beta(z) + 2B^2\Delta\beta(z)$. Of course, the equilibrium states must be real solutions. If $D = 0$, then $\alpha_1 = \alpha_2$ and we have

$$S(z) = \frac{B}{6C} + 2\gamma(z)^{1/3} \quad \text{and} \quad \frac{B}{6C} - \gamma(z)^{1/3}$$

where

$$\gamma(z) = \frac{B}{6^3C^3}(B^3 + 81C^2\Delta\beta(z) - 27ABC)$$

If $D > 0$ there is only one solution

$$S(z) = \frac{B}{6C} + \alpha_1^{1/3} + \alpha_2^{1/3}$$

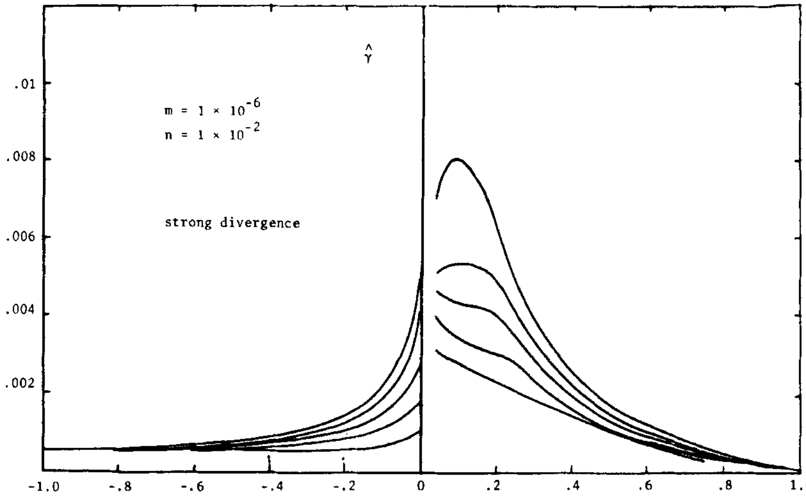
It is found that, in the vicinity of T_c^* multiple roots of (5) exist, reflecting the instability of the system in this region; experimental investigations are similarly characterized by instabilities of this type.

RESULTS

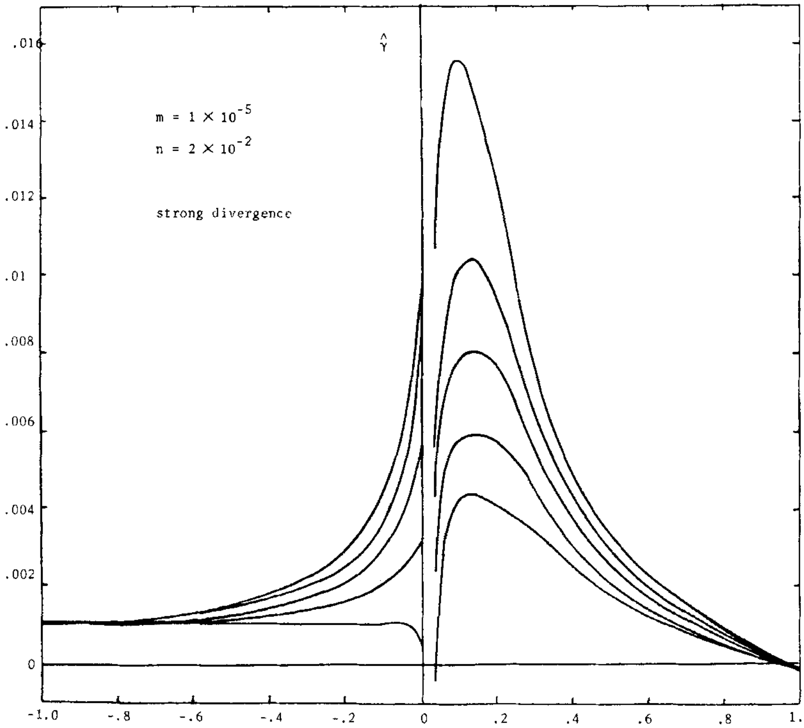
Our primary intention in this paper is to present a phenomenological description of the processes responsible for the principal features of the surface tension-temperature characteristics which are undoubtedly attributable to the pronounced molecular anisotropy of the system. On the basis of Eq. (1) we have determined the orientational contribution $\hat{\gamma}$ to the surface tension of the system for a variety of parametric forms of interfacial density profile both with and without critical divergence of the correlation length or interfacial thickness.

In Figures 2(a)–2(d) we present the $\hat{\gamma}$ curves arising from the family of $t(A)$ characteristics shown in Figure 1(a), characterized by an infinite critical divergence at T_c^*. It is seen that throughout the temperature range $A < 0$ orientational effects make a small positive contribution to the total surface tension, whilst immediately below the transition, the $\hat{\gamma}$ curves turn upwards in agreement with recent experimental determinations (Figure 3; Krishnaswamy and Shashidhar.[13,14] This pre-transitional effect may be directly attributed to the rapid decline in the *bulk* order parameter as $A \to 0$ (see Eq. (1)), with S discontinuously vanishing at $A = 0$ and $\hat{\gamma}$ showing a corresponding discontinuity.

Beyond a small thermal range $A = 0+$ characterized analytically by a multiplicity of roots to Eq. (5) and experimentally by thermodynamic instability, we see that in virtually every case the $\hat{\gamma}$ curve exhibits a pronounced


$\hat{Y}$
$m = 1 \times 10^{-6}$
$n = 1 \times 10^{-2}$
strong divergence
.01
.008
.006
.004
.002
-1.0
-.8
-.6
-.4
-.2
0
.2
.4
.6
.8
1.0

(a)


$\hat{Y}$
$m = 1 \times 10^{-5}$
$n = 2 \times 10^{-2}$
strong divergence
.016
.014
.012
.01
.008
.006
.004
.002
0
-1.0
-.8
-.6
-.4
-.2
0
.2
.4
.6
.8
1.0

(c)

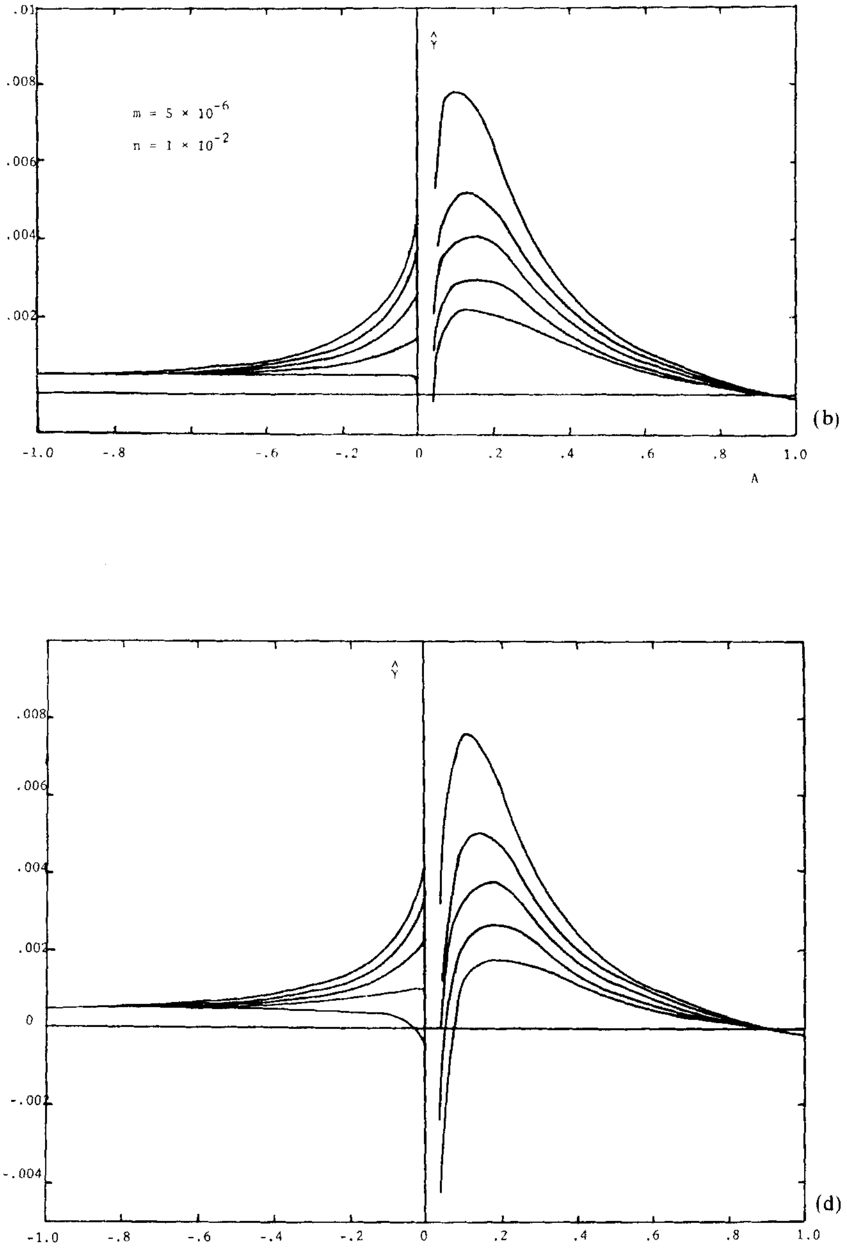


Figure 2 Orientational contributions to the surface tension $\hat{\gamma}$ as a function of temperature shown under conditions of 'strong' critical divergence of the interfacial thickness for a range of the parameters m, n. Any combination of the branches $A < 0$, $A > 0$ may be taken.

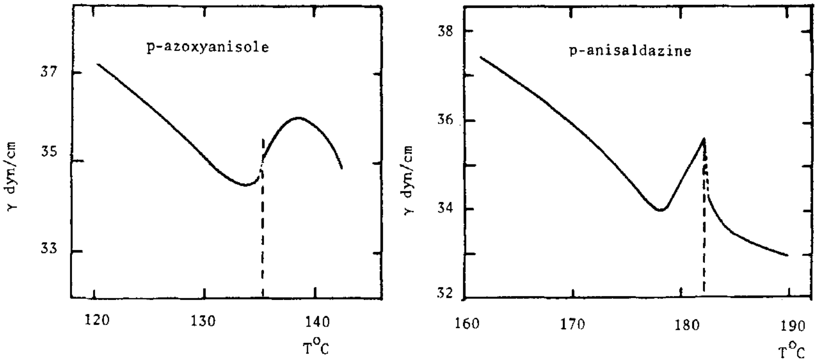


FIGURE 3 The *total* surface tension of (a) *p*-azoxyanisole (PAA) and (b) *p*-anisaldazine as a function of temperature (Krishnaswamy and Shashidhar[13]). Particular attention is drawn to the pronounced pre- and post-transitional effects which are directly attributed to the orientational contribution$\hat{\gamma}$.

maximum followed by a monotonic decay to zero at high temperatures when orientational contributions have largely vanished. Throughout this region there exists a weak residuum of orientational order associated with the interfacial torque field (Figure 4). The development of strong interfacial torque fields associated with the dramatic post-transitional recovery of the interfacial structure appears sufficient to offset the effects of increasing temperature, with the result that $\hat{\gamma}$ shows a pronounced maximum before exhibiting a monotonic relaxation at higher temperatures. As we shall see, a weaker critical divergence of interfacial thickness appears incapable of off-setting the temperature effect and no inversion in $\hat{\gamma}$ develops.

The $A < 0$ and $A > 0$ branches of the $t(A)$ curves shown in Figure 1(a) may be associated to form a variety of combinations depending upon the differing behaviours of the nematic and isotropic phases. The orientational contributions to the surface tension of *p*-oxyanisole (PAA) (Figure 3(a)) may now be readily understood in terms of the relative local order with respect to the bulk order at a surface showing a strong critical divergence. The density-order product $\rho(z)S(z)$ at various temperatures is shown in Figure 4, and we see quite clearly how at $A > 0$ a residuum of interfacial order is stabilized by the existence of torque fields proportional to $[\nabla\rho_{(1)}(z)]^2$.

A "weak" critical divergence of the interfacial thickness (Figure 1(b)) results in a family of $\hat{\gamma}$ curves showing the same pre-transitional effects as the "strong" system (Figure 5(a), (b)), but with a distinct post-transitional form. For such systems $\hat{\gamma}(A > 0)$ shows a monotonic decrease, actually becoming negative for systems strongly dependent upon the density term (large m). Again, any combination of branches $A < 0$, $A > 0$ is envisaged for the total description of the nematic-isotropic system. We see immediately that the surface tension of PAA is readily explicable in these terms with the residuum of order $A > 0$ accounting for the large positive post-transitional contribution (Figure 3(a)). The development or otherwise of a distinct *peak* in $\hat{\gamma}$ may evidently be attributed to the strength of the divergence in the region $A = 0+$. For comparison, the effects of zero critical divergence (linear $t(A)$) are shown in Figure 6: we see that for this system of "limiting weakness" the usual pre-transitional upturn is obtained, followed by a large positive discontinuity which subsequently monotonically decays to zero. The $\rho(z)S(z)$ profiles at various temperatures are shown in Figure 7, and for a linear $t(A)$ in Figure 8.

THE COEFFICIENTS *m, n*

Thus far we have made only passing reference to the rôle of the coefficients m and n in Eq. (3) which control the local specification of the ordering field energy $\Delta\beta(z)$. Clearly, the relative magnitudes of m and n control the density (disorienting) and density gradient or torque field (orienting) contributions to the local value of $\Delta\beta(z)$. First of all we point out that $[\rho'(z)]^2$ is several orders of magnitude smaller than $\rho(z)$ itself, and consequently $m \ll n$ throughout the entire range. Moreover, the spatial range of $(\rho')^2$ is much more localized than that of the density term and accordingly *negative* $\Delta\beta(z)$ will arise in the wings of the density profile. For temperatures $A < 0$ this will merely result in a depression of the order parameter below its bulk value leading to a slightly diminished estimate of $\hat{\gamma}$ for a given $t(A)$ curve. In the isotropic phase, however, where the bulk order parameter is zero, we conclude that there is a weak tendency for *orthogonal* alignment to that induced by the interfacial torque field (Figure 7(b)). It is interesting to note that there may have been a number of reports of just this phenomenon on the basis of analytical[2] and machine simulation[3] studies of diatomic interfacial structures.

CONCLUSIONS

The local order parameter $S(z)$ is related to interfacial structure and the orientational contributions $\hat{\gamma}$ to the surface tension on the basis of a modified Landau–de Gennes theory coupled with the results of an earlier analysis by Croxton and Chandrasekhar,[4] and Croxton.[5,6] In the present treatment it is found that the existence of a critical divergence in the interfacial thickness at T_c^* yields orientational contributions to the surface tension $\hat{\gamma}$ in good qualitative agreement with experiment. The "strength" of the divergence appears to control sensitively the nature of the pre- and post-transitional effects upon

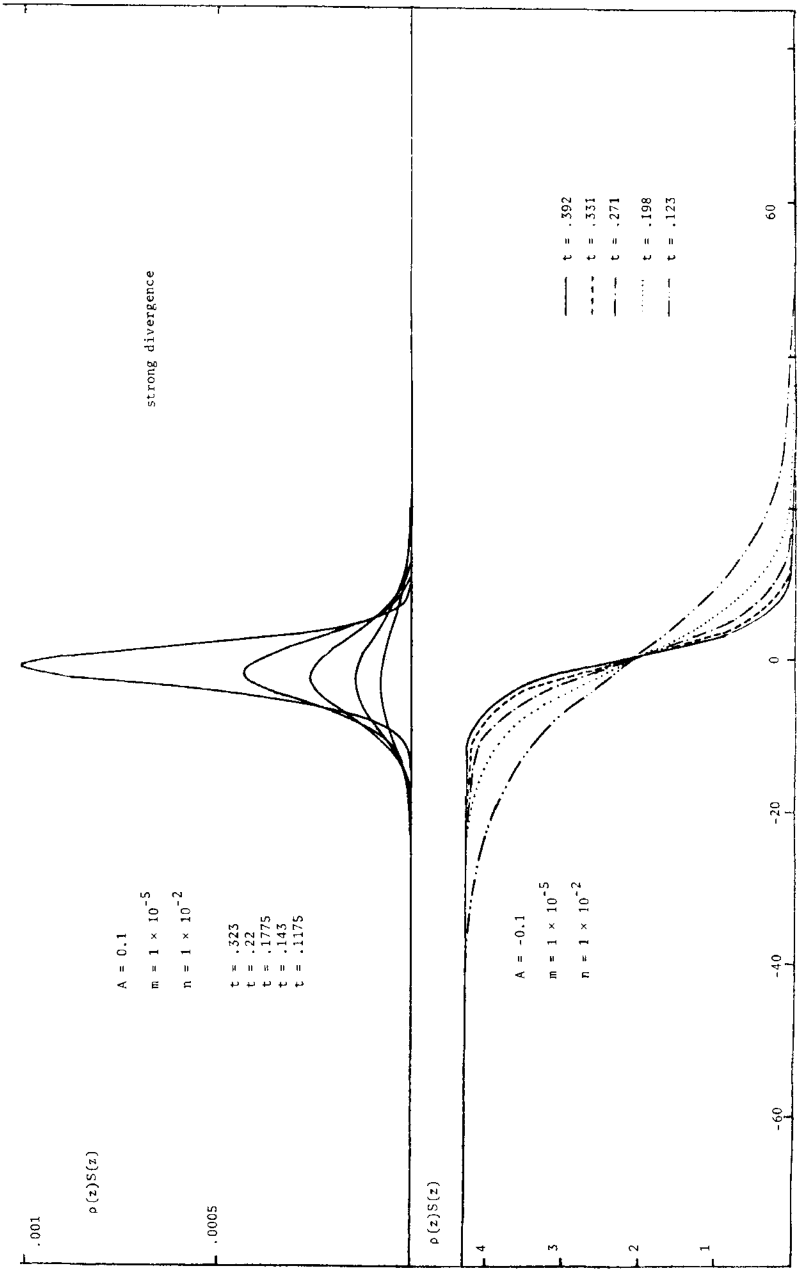
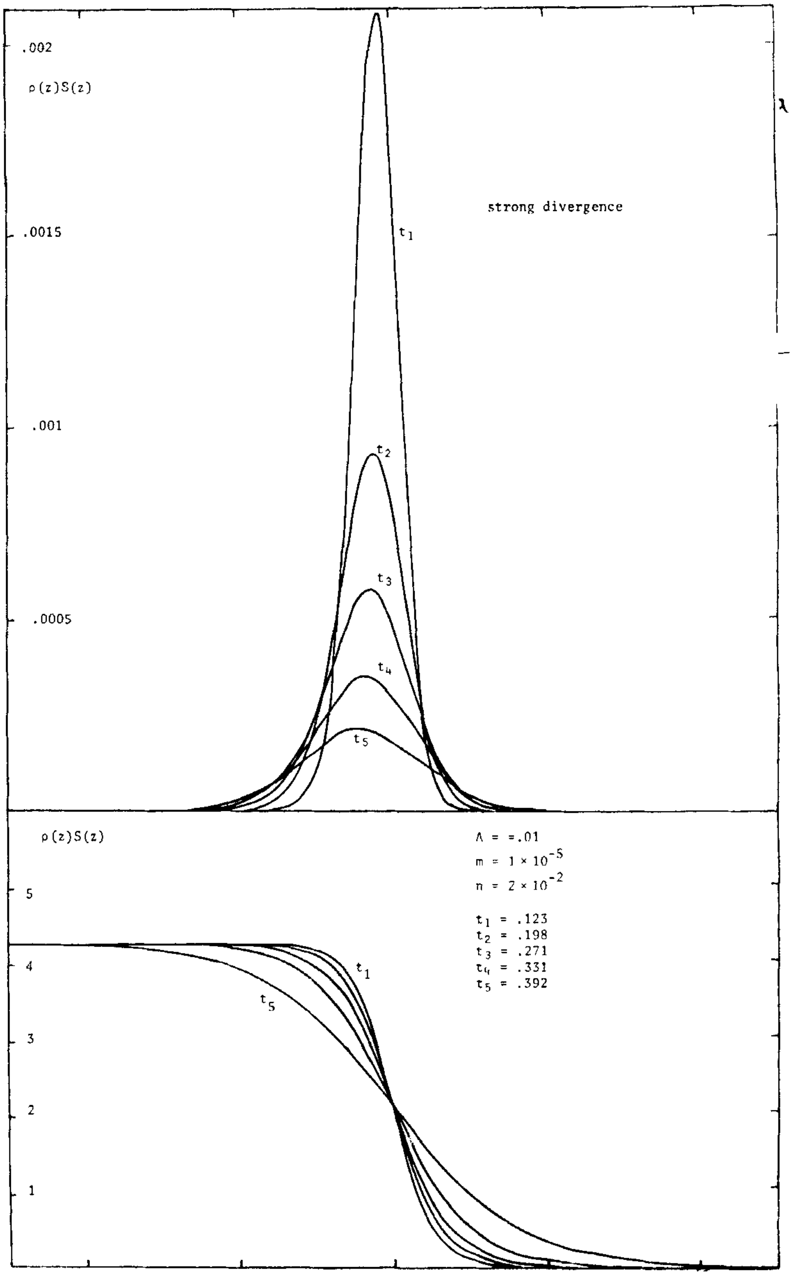


FIGURE 4 Spatial variation of the density-order product $\rho(z)S(z)$ for inverse interfacial thicknesses showing 'strong' critical divergence (See Figure 1(a). The product is shown for both



the nematic ($A = 0.1$) and isotropic ($A = +0.1$) phases) In the latter case a residuum of interfacial orientation survives the nematic-isotropic transition.

$\hat{\gamma}$. This aspect of interfacial structure of liquid crystal systems appears not to have been reported before. Clearly, experimental determinations of the isothermal compressibility, to which the interfacial thickness is closely related, and/or direct optical measurements of interfacial thickness appear warranted. Certainly transitional divergence of the interfacial thickness appears to be an essential aspect of any adequate theoretical description of the liquid crystal surface and would seem to invalidate any earlier analyses based upon a discontinuously sharp surface. Almost certainly the smectic-nematic transition is similarly characterized, and a more complete specification of the critical divergence of the interfacial correlation length would seem essential for any general description of the liquid crystal surface.

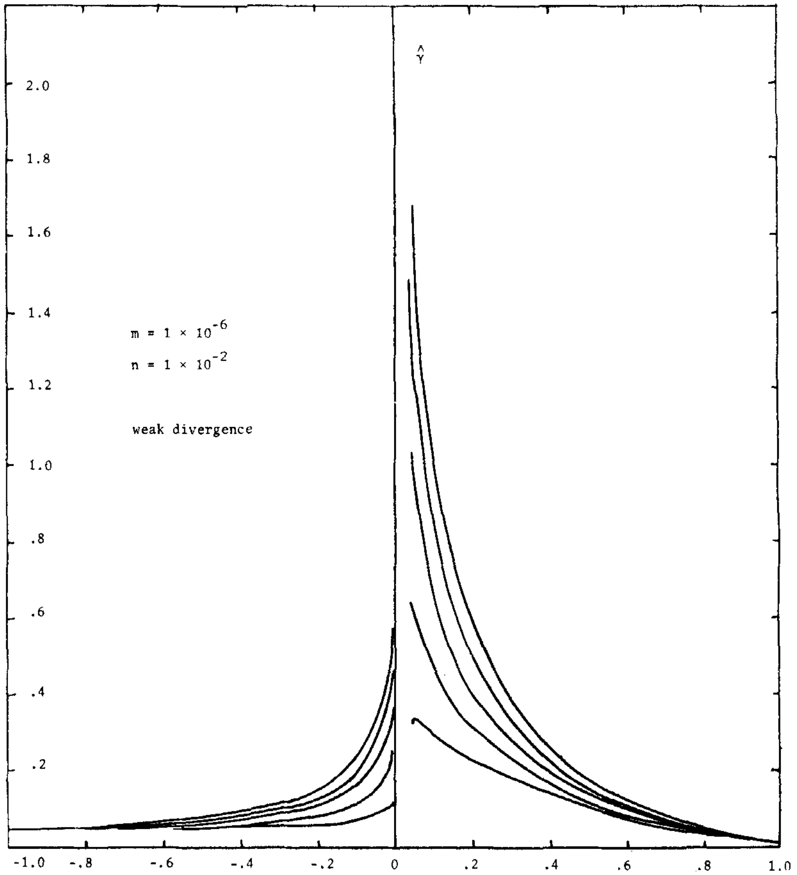
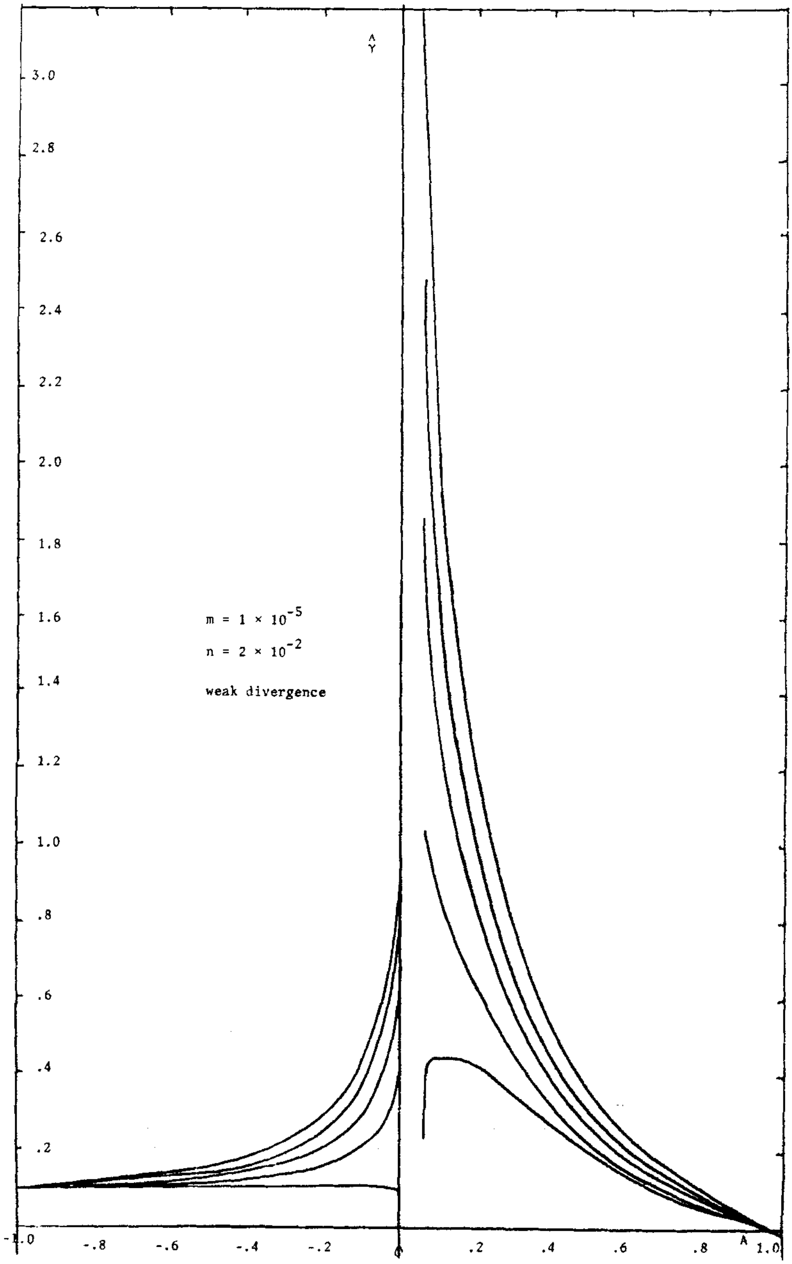


FIGURE 5 Orientational contributions to the surface tension $\hat{\gamma}$ as a function of temperature shown under conditions of 'weak' critical divergence of the interfacial thickness for a range of the parameters m, m. Any combination of the branches $A < 0$, $A > 0$ may be taken.


Ŷ
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
$m = 1 \times 10^{-5}$
$n = 2 \times 10^{-2}$
weak divergence
-1.0
-.8
-.6
-.4
-.2
0
.2
.4
.6
.8
Â
1.0

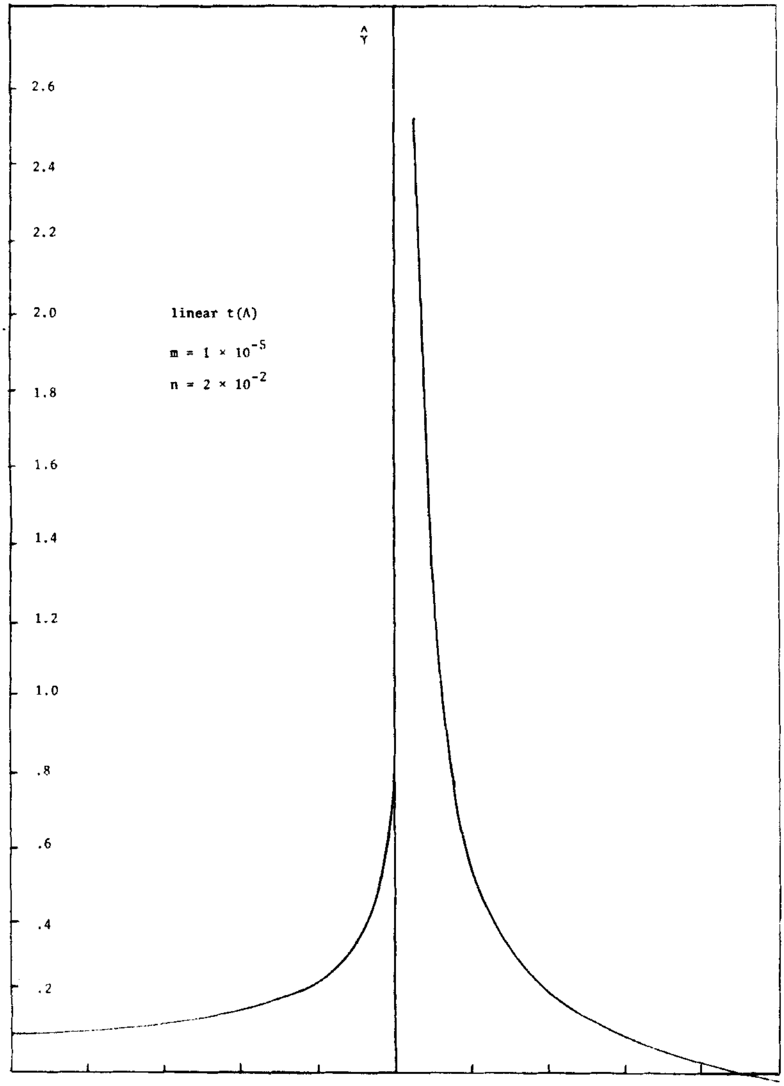


FIGURE 6 Orientational contribution to the surface tension $\hat{\gamma}$ as a function of temperature for a linear variation of the inverse interfacial thickness $t(A)$. Such a system shows zero critical divergence.

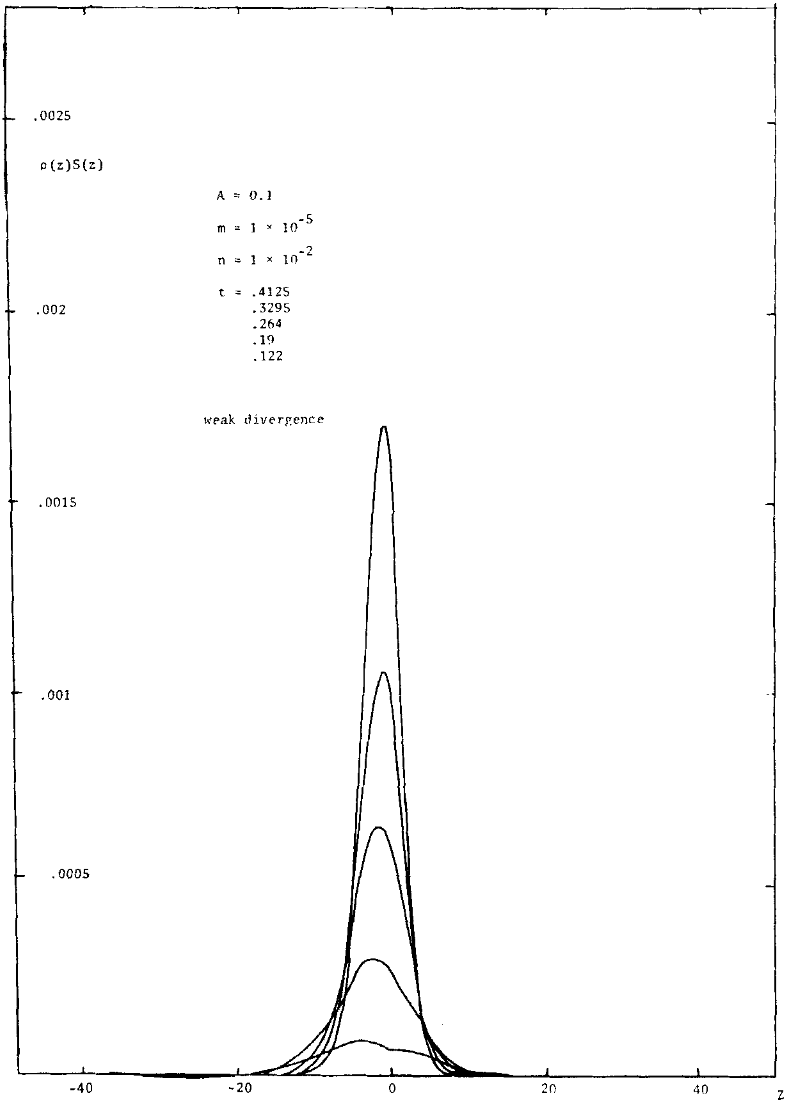


FIGURE 7 Spatial variation of the density-order product $\rho(z)S(z)$ for inverse interfacial thicknesses showing 'weak' critical divergence (See Figure 1(b)). The product is shown for both the nematic ($A = -0.1$) and isotropic ($A = +0.1$) phases. In the latter case a residuum of interfacial orientation survives the nematic-isotropic transition.

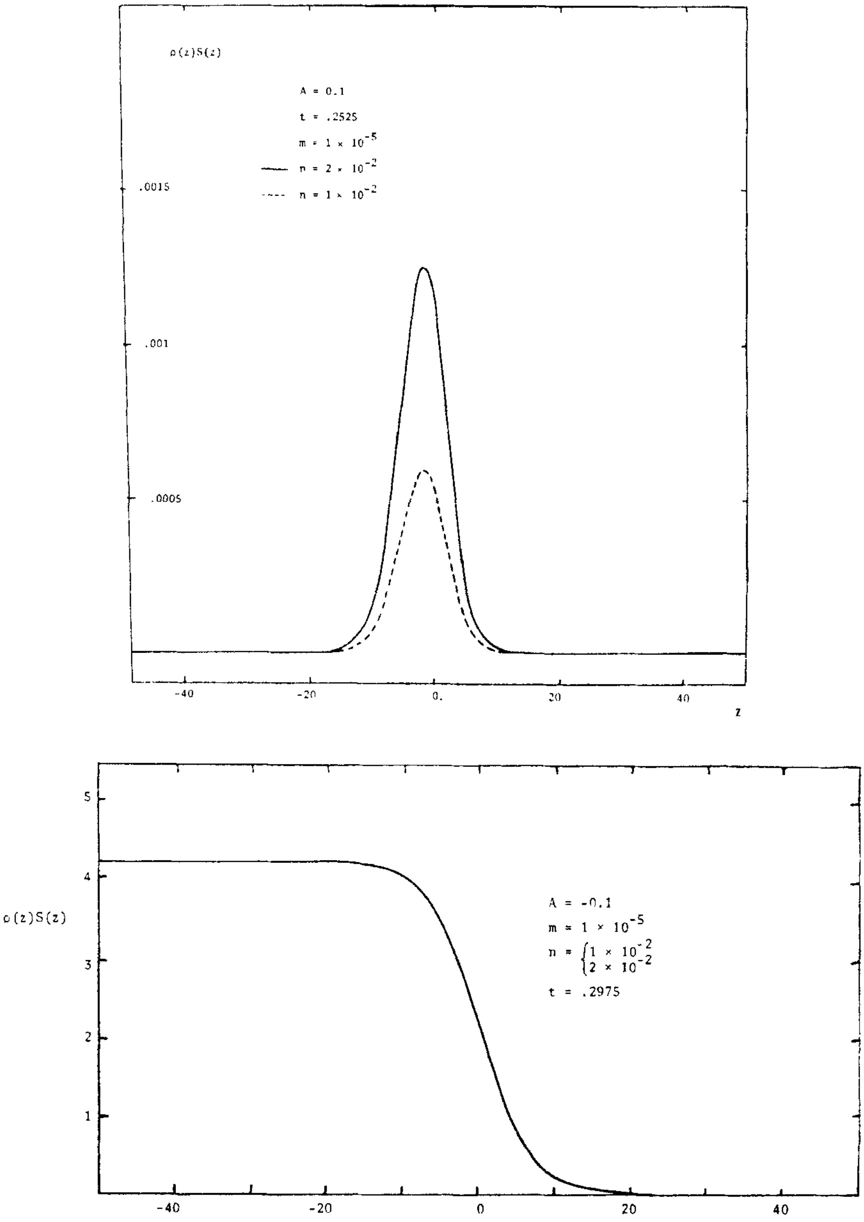
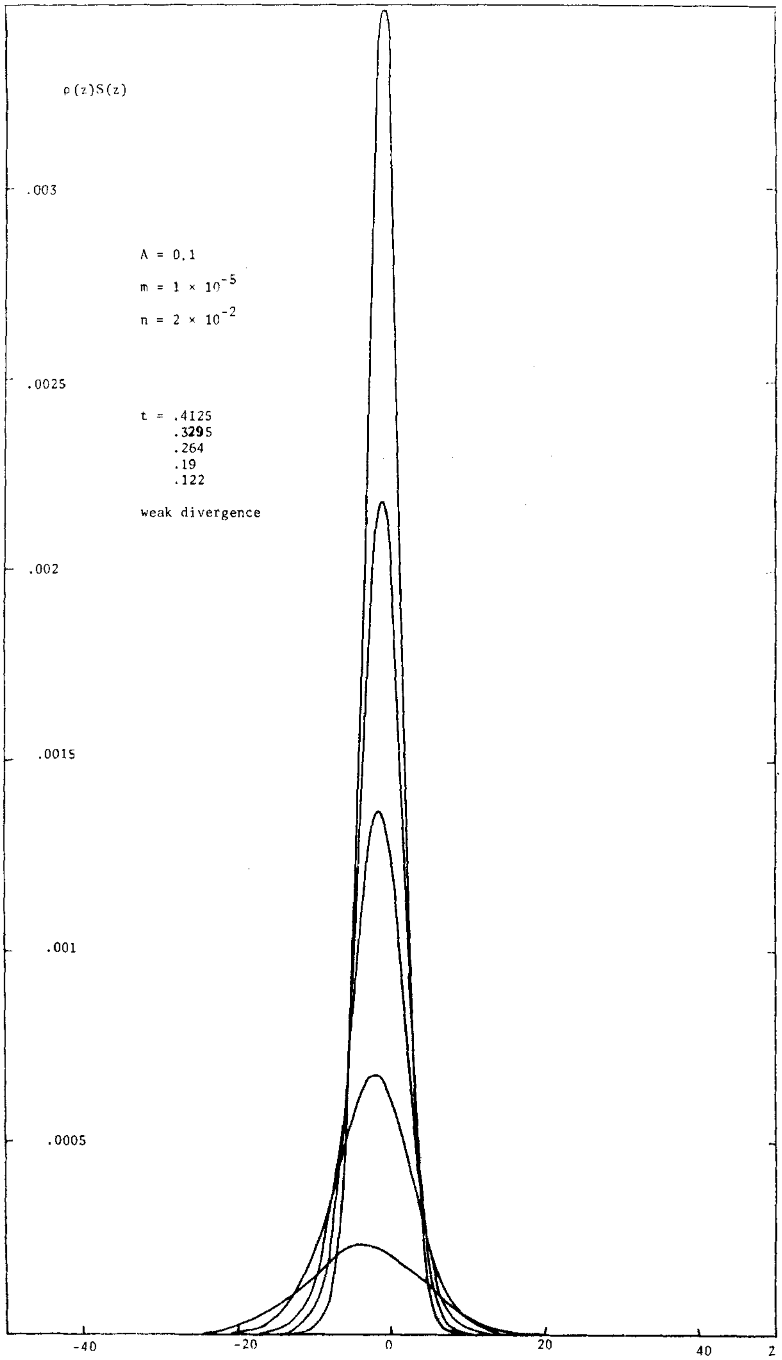


FIGURE 8 Spatial variation of the density-order product $\rho(z)S(z)$ for an inverse interfacial thickness showing a linear variation with temperature. The product is shown for both the nematic ($A = -0.1$) and isotropic ($A = +0.1$) phases. In the latter case a residuum of interfacial orientation survives the nematic-isotropic transition. The $\rho(z)S(z)$ product at $A = -0.1$ is graphically indistinguishable for the two values of n shown.


ρ(z)S(z)
.003
.0025
.002
.0015
.001
.0005
A = 0.1
m = 1 × 10^-5
n = 2 × 10^-2
t = .4125
.3295
.264
.19
.122
weak divergence
-40
-20
0
20
40
z

Acknowledgements

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