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## Liquid Crystals

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### The writhing on the wall: first tentative steps toward a comprehensive theory of liquid crystal surfaces

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# The writhing on the wall: first tentative steps toward a comprehensive theory of liquid crystal surfaces

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A Commentary on the paper “Theory of the nematic-isotropic transition in a restricted geometry”, by A. Poniewierski and T.J. Sluckin. First published in *Liquid Crystals*, **2**, 281-311 (1987).

It is often the case that the most important contributions made by a researcher in a field are when they are still relatively new in that field. Best, it is said, for the researcher’s mind to be still untrammelled by knowledge overflow and have the advantage of fresh experience from other fields. This paper is one such. Both Poniewierski and myself were still young (in our mid-30s). Poniewierski had only relatively recently finished his Polish Ph.D., and I had switched fields from quantum fluids to liquid crystals.

The paper was written in the context of a research programme involving liquid crystal interfaces. The background to the programme is as follows. I finished my Ph.D. in quantum fluids at the University of Nottingham in 1975, and promptly set off for the United States, where I continued to work on liquid helium. At that time people were beginning to use ideas borrowed from classical fluids, in particular integral equation methods, to study structure in quantum fluids. The result was that I had to follow up the origins of these ideas and found myself becoming more interested in theories of classical fluids. By the mid 1970s it began to be possible to say, for the first time, that there existed viable theories of liquids, on a par with those of solids and gases. In 1978 I returned to the UK, having managed to arrange a postdoctoral position for myself working with Bob Evans in Bristol. At that time Evans, who is now a distinguished elder statesman in British statistical mechanics and was elected a Fellow of the Royal Society in 2005, was only 31 and had yet to obtain a permanent position.

One area of interest in Bristol at that time was the structure of liquid surfaces. The Bristol people were borrowing furiously the density-functional theory from electron physics and applying it to classical systems. The

idea was essentially to provide a microscopic input to a Ginzburg-Landau theory. Once one had studied uniform systems, the next obvious target was non-uniform systems. Surfaces (both free surfaces, and those provided by solid walls) provided ready-made examples, with both microscopic (e.g. surface thickness) and macroscopic quantities (e.g. surface tension or contact angle) to calculate and compare with experiment [1]. One particular focus at that time was the so-called wetting problem [2]. In this problem one was interested in determining how a film of liquid grew at a surface as the external pressure of the gas was increased towards the saturation vapour pressure. Sometimes the film grew continuously (*complete wetting*), sometimes to a finite thickness (*partial wetting*) and sometimes not at all (*non-wetting*). The basic feature governing this phenomenon was the competition between forces on molecules in the vapour from a surface and intermolecular forces.

My Bristol project concerned structure factors in various kinds of classical fluids. It did not go well, partly because I was unable to replicate the computational results of a previous postdoctoral worker [3]. A less tolerant postdoctoral supervisor would have become impatient and turned to a (no doubt overeager!) Human Resources Department for advice on how to ease out the inadequate and underskilled research assistant. Evans merely suggested another problem. He later completed the original project work more or less on his own in his spare time, and still generously included me on the resulting papers [4]. What is even more generous is that despite *including* me on his work on the structure factors, he *excluded* himself from authorship of the work which followed his suggestion.

The paper in question concerned molecular orientation at the free surface of molecular fluids, say nitrogen or oxygen [5]. This orientation could be expressed in terms of an orientational order parameter, which we

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now often call the *Saupe ordering tensor*, or simply the *Q-tensor*. I knew about these things because the Bristol School of Physics, having a powerful scientific pedigree, possessed a first class library, inside the building, with a ready supply of new books. I guess it must have been some time in early 1979 that I was attracted by two brightly coloured, large-sized, hard-backed new arrivals that were to govern my life for the next quarter century. The first was yellow and was entitled *The Physics of Liquid Crystals* [6] and was by Pierre-Gilles de Gennes, whose work in magnetism I was already familiar with. The second was light green, was wrapped in cellophane, and was an edited compendium of tutorial papers by two chemists with whose names I was not at all familiar – G.R. Luckhurst of the University of Southampton and G.W. Gray of the University of Hull [7].

It was originally the smell and feel of these two books that impelled me to open them. From them I learnt about the basics of liquid crystal physics. I also learned that the apparently slightly dodderly but nevertheless overwhelmingly forceful Charles Frank, who had an office just across the corridor to mine, was actually *Sir* Charles, and that he had written *the* fundamental paper in liquid crystals. Thus was born the idea to look for localised *liquid crystal* behaviour at the surface of apparently well-behaved and otherwise isotropic molecular fluids.

It was then with some excitement that when I came for interview in Southampton (albeit in the Department of Mathematics) in June 1981 I realised that sitting not so far away was a research group with interests that might overlap my own. And so I informed the interview panel who gingerly asked me whether there might be any other possible collaborators in Southampton. They must have been slightly encouraged (perhaps not by that remark), because they appointed me. Unfortunately it took several months after my arrival as a lecturer in Mathematics in Southampton in October 1981 before I was able to make contact with the famous Professor Luckhurst. After what seemed then to be an epoch, but in hindsight must have been little more than a year, we began to think how to collaborate.

The immediate impetus for collaboration turned out to be a visit – I think it was some time in spring 1982 – by Professor Jan Stecki, Head of the Physical Chemistry division of the Polish Academy of Sciences in Warsaw. Nowadays Warsaw is but a short plane hop from London and one can return the same day. But in 1982 the Iron Curtain still draped fiercely across central Europe. A visitor from Poland was a matter of some importance. Luckhurst invited me to lunch with the visitor. It turned out that the Polish group was one of

very few who had been using modern theoretical methods of liquid physics (and specifically the direct correlation function) in a liquid crystal context [8], so Stecki and I had an immediate common bond. And Stecki too had an agenda. He had a recent Ph.D. student with experience in just such methods, whom he was seeking to place in a sympathetic postdoctoral environment. This student was Andrzej Poniewierski.

Thus was born the idea of a joint project between myself and Geoffrey Luckhurst. A proposal, entitled “Theoretical investigation of surface structure involving liquid crystals” was submitted to the (United Kingdom) Science Research Council (SRC) in the summer of 1982. It requested the then magnificent sum of £49,825, for a project to begin on 1st January, 1983. The money was required partly to employ a postdoctoral worker (Poniewierski) and partly to support a research student who would work on computer simulation of liquid crystal surfaces. The Luckhurst group, we may recall, were pioneers in simulating liquid crystals [9], and by 1982 had already published a numbered series of papers on this subject. In truth, there was a good deal of what we might now call leverage in this project. I leveraged Luckhurst’s prestige in the field. And he leveraged my junior status, for first projects from new lecturers received privileged status in the reviewing process. Given the collaboration, we felt assured of success.

But the response from SRC was equivocal. Our models used molecular cylindrical symmetry as a starting point. A referee (probably the late Tom Faber from Cambridge, who generously gave of his time on numerous occasions to allow me to explore liquid crystal ideas) complained that, really, cylindrical symmetry was insufficient to explain liquid crystal behaviour. Luckhurst drafted an eloquent reply. I was too timid to argue. After some delay, (as always) too late for the original January starting date, a positive response to our proposal dribbled in. I employ the term “dribble” advisedly, because out of the magnificent £49,825 originally requested, only a sad £18,450 was forthcoming. This was only just enough for a post-doc and then only for two, and not, three years, with no graduate student.

Inadequate resource for a well-drafted project always causes problems. Luckhurst and I battled for control of the project. Eventually, after a well-placed call to the Funding Council, I was able to establish that the funds that had been granted were for the theoretical and not the computational part of the project. Poniewierski was unwilling to come if his work programme included simulation (with the benefit of hindsight, he was wrong; we *all* ought to have made sure we could simulate when we were still young!). Luckhurst made a generous

sacrifice, and in early October 1983 Poniewierski arrived in Southampton. Although he was primarily working with me, we arranged for his office to be in the Assembly Hall home to the Luckhurst group just outside the Chemistry Department. Thus my regular visits to Chemistry – visits which have continued over the ensuing quarter century – began.

The original aim of the project had been to repeat for liquid crystals the vigorous programme of the previous decade which had elucidated the connection between wetting, surface interactions and intermolecular interactions in liquids and mixtures. In fact it seems that much of this work merely replicated work of the Derjaguin school in the Soviet Union much earlier. One related aspect concerned the effect of finite geometries on the liquid-vapour phase diagram, an effect known as *capillary condensation* because usually the liquid onset occurred at higher temperatures and lower pressures than in small pores. The simplest case here involves two rather than a single, surface [9]. Clearly the liquid crystal analogy would involve replacing liquid densities by the liquid crystal orientational order parameter,  $\bar{P}_2$ . Generalised further, one would obviously need to use the full tensor order parameter  $Q_{ij}$ , but that seemed complicated and to begin with we resolved essentially to translate known results.

However, events can divert even the best-laid plans. It is the nightmare of all academics to have their work scooped. So when I chanced upon Ping Sheng's 1982 *Physical Review* paper entitled "Boundary-layer phase-transition in nematic liquid crystals" [10], I felt a peculiar mixture of elation and horror. This was *my* problem and Sheng had solved it! Worse still, it seemed that there had been a 1976 *Physical Review Letter* heralding this result (of which I was ignorant), and that Sheng had merely been overtardy in preparing a complete version. But 1976 predated the excitement in the wetting and surface physics community. Perhaps there was something that could still be done.

And so it turned out. We started slowly, like Sheng, with a single order parameter (so nothing specifically *liquid crystal* about it all, really), and replicated Sheng's results, but using the Maier-Saupe rather than the Landau-de Gennes theory to describe the bulk liquid crystal. With the benefit of hindsight it was but a practice problem. A follow-up piece of work allowed the surface to discourage rather than encourage surface order, a calculation not carried out by Sheng [11]. Now the surface layer of order material above  $T_{NI}$  was thinner, and sometimes there was no layer at all. Sheng's "boundary layer" had predicted that for a small range of intermediate surface order parameters there would be a transition of the surface order parameter at

a temperature *above* the bulk phase transition. We were able to identify this transition with the so-called *pre-wetting transition* and thus not peculiar to liquid crystals at all. Likewise Sheng had also found that the phase transition in a thin film was shifted (always upward according to Sheng). We were able to see that this shift could be down in temperature as well, and that moreover the shift could be identified with the (19<sup>th</sup> century) phenomenon of capillary condensation.

These results were presented at the 1984 York International Liquid Crystal Conference, my first outing at an international liquid crystal meeting. No-one seemed interested in our results, except for a polite young Japanese scientist who had the neighbouring poster. His name for Hiroshi Yokoyama and he had done some experiments on contact angles, a subject which, in principle, was accessible to us [12]. His papers had three names on them, and I asked him where his collaborators were. His rather un-Japanese answer was that these were not his collaborators, indeed they had not really contributed (I hope I recollect properly, because both he and they may well read this article!), but they were his boss and his boss's boss. It remains a mystery why the name of his boss<sup>3</sup> was omitted.

Some time in the spring of 1984 an invitation appeared in the post from Clive Croxton in Australia to contribute to his book on interfacial phenomena. He must have learned of our work by *samizdat*, for we had not yet published in this field. So in summer 1984 (a long hot summer, I recall) we wrote a review article summarizing our work so far entitled *Orientational wetting and related phenomena in liquid crystals* [13]. I cannot be sure, but I think this is the first time the now standard term *orientational wetting* was used. In this article we also began to formulate a phenomenological theory of *anchoring*, clearly of crucial interest to liquid crystal engineers. Despite appearing in a somewhat obscure edited book, the review article has attracted 234 citations over the years, even though it was superseded by an excellent review written in 1991 by Blandine Jérôme [14].

As we became more familiar with our subject we were able to play with the ideas and not merely transliterate from one field to another. A paper in *Molecular Physics* examined the structure of defects (which we regarded as an elaborate form of surface) [15]. A more interesting paper examined the possibility of orientational wetting by a planar-anchoring, rather than homeotropic anchoring surface. This paper, which was really the first in which we (or anyone else!) considered anything other than a scalar problem, was published in *Physical Review Letters* in the summer of 1985 and has attracted 73 citations [16].

The paper in *Liquid Crystals* under discussion here, in which we generalised our work from one to two surfaces, was the final piece of work carried out by Poniewierski during his two years in Southampton. The research itself was carried out partly in Southampton, partly in Grenoble during my sabbatical period, April–September 1985 and partly in Warsaw after Poniewierski's return to Poland in September, 1985. This explains why the manuscript was not submitted until September, 1986, and not published until May, 1987.

We were able to place Sheng's work in a thermodynamic context, understand which features in the theory led to an increase or decrease in the phase transition temperature in a pore, carry out asymptotic analyses of the solutions of the equations, and also make a connection between the theory and the well-known colloid science concept of *disjoining force*. The big disappointment, at least from my point of view, was that we were unable to develop computer programs to solve for a tensor order parameter. Nowadays, under the guise of Q-tensor theory, such analysis is standard, but at that stage it required more skill in numerical analysis than we possessed. Had we done so, we might also have investigated the disjoining torque so characteristic of liquid crystals in finite geometries.

A final piece of work in the context of this programme concerned computer simulation. Geoffrey Luckhurst's student Habtamu Zewdie simulated a lattice model of a liquid crystal [17]. The surface is a not really free, but one can calculate the "surface tension", and investigate its temperature dependence, and ask about the wetting properties of the surface. This paper was published, as no. 15 in Luckhurst's series on computer simulation of liquid crystals, in *Molecular Physics* in November, 1986.

After Poniewierski's return to Poland. I wrote some follow-up proposals, boasting of the great success of our previous proposal. But somehow the news had been muted in the post, for the proposals were unsuccessful; all that I received were doleful epistles from the Funding Council about how their funding had (yet again) been cut (implicitly, by the unsympathetic Thatcher government!).

We now look forward from 1987 and examine the impact of the paper on the field. One early citation in August, 1988, was particularly gratifying for theorists who always doubt whether their musings have any application to the real world. In this paper [18] in the *Faraday Transactions of the Journal of the Chemical Society*, Hiroshi Yokoyama quantitatively interpreted order parameter experiments on a liquid crystal sandwiched between a surface and a lens in terms of

what he called the "SPS theory" (i.e. a superposition of Sheng and Poniewierski-Sluckin).

The general topic of liquid crystals in finite systems has attracted considerable interest. This is partly because of the importance of liquid crystal displays, which have since that time been transformed from a niche to a mainstream market position. But there is also fundamental interest as well. The tensor nature of the liquid crystal order parameter changes the simple thermodynamic picture which we implicitly assumed in our paper and which governs all other isotropic phases. This topic has been investigated by Telo da Gama and coworkers [19], by Allender and coworkers [20], and Velasco and coworkers [21]. In addition, it is now clear that our model omitted important fluctuation effects, as discussed by Ajdari *et al.* [22], and in particular by Žumer and coworkers in Slovenia. The principal contribution of the Slovenia group has been to introduce the idea of the fluctuation-induced Casimir force into the disjoining pressure between two walls of a vessel filled with a nematic medium [23]. A contribution by Rey [24] in 2000 employed the full panoply of continuum mechanics in order to deepen understanding of the disjoining pressure in nematic systems.

Since the late 1990s there has been much interest in colloidal systems in a nematic matrix (the so-called filled liquid crystals). A good understanding of the finite geometry system is a necessary first step to understand the effective interparticle potential in the colloidal suspension. This topic has been studied by Stark and coworkers [25]. A physically related system occurs when the liquid crystal is confined inside a system of pores such as, for instance, an aerogel, and in this case too, the starting point for understanding the phase behaviour of the liquid-crystal-in-many-pores system is the simple liquid crystal in a slab system which we had discussed. A calculation along these lines has been made by Kralj and Popa-Nita [26]

The question of the microscopic calculation of anchoring forces at surfaces is relevant on both a fundamental and an applied level. The concept of anchoring (i.e. orientational forces on a nematic due to a surface) underlies most practical work on liquid crystal surfaces, and was always bubbling under our work in 1987. A calculation by Fournier and Galatola [27] finally enabled what might be termed microscopic (i.e. molecular forces) and mesoscopic (roughness and patterning) forces to be separated.

The 1987 *Liquid Crystals* paper has (as of late September, 2006) attracted 103 citations. This figure does not, of course, bestow block-buster status, but is a very respectable quantity nevertheless. A considerable fraction of these citations simply mark an indication

of continuing interest in a field in which we were fortunate enough to make early contributions. Our paper, although of course by now somewhat dated, has nevertheless attracted three citations in 2006, and 45 of its citations came after its 10<sup>th</sup> birthday. The current open questions tend to concern smectic rather than nematic liquid crystals, but the general area of liquid crystals in finite geometries continues to be active.

I am grateful to Andrzej Poniewierski for some recent correspondence which reminds me of the time that he so fruitfully spent in Southampton two decades ago. I thank also many coworkers with whom I have discussed liquid crystals in finite geometries. There are too many to mention individually; to pick some out at the expense of others would be invidious. Finally Geoffrey Luckhurst has been the most loyal and at the same time the most challenging of colleagues over the years. I am particularly grateful to him for reprinting our 1987 paper and allowing me the opportunity to share these thoughts and reminiscences with the readers of *Liquid Crystals*.

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# Theory of the nematic–isotropic transition in a restricted geometry

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We discuss, using a Landau–de Gennes formalism, the nematic–isotropic transition temperature for a system placed between two parallel plates, subject to identical homeotropic or homogeneous boundary conditions at each plate. The temperature at the phase transition may increase or decrease as the inverse sample thickness,  $D^{-1}$ , increases, depending on the nature of the boundary conditions. In all cases the transition terminates at a critical point for sufficiently large  $D^{-1}$ , beyond which the nematic and isotropic phases are no longer distinct. The phase transition temperature is well described by a liquid crystal analogy of the Kelvin equation which can be generalized to give an exact Clausius–Clapeyron relation. Under many circumstances the system behaves from a thermodynamic point of view as though it were in a bulk ordering field. The finite geometry restricts the growth of nematic or isotropic wetting films. We discuss the disjoining pressure experiment of Horn, Israelachvili and Perez [15]. Finally we place our work in the context of recent progress in the statistical mechanics of surfaces and systems in restricted geometries.

## 1. Introduction

The singularities in thermodynamic quantities which are associated with phase transitions in physical and chemical systems only occur in the so-called *thermodynamic limit*, that is, in the limit of infinitely large systems. If system size is restricted in any way, either as a result of the presence of surfaces, or because the system only has finite extent in one or more directions, these singularities are profoundly affected. Their position in the phase diagram may change, new singularities may occur, and the singularities themselves may cease to be. Particular cases of such systems are semi-infinite systems, with one wall, and systems which are infinite in two dimensions but of finite extent in a third; these systems have two walls. Such systems are sufficiently infinite that thermodynamic singularities do occur and sufficiently finite that qualitatively new phenomena also occur.

We have ourselves recently made a theoretical study of nematic liquid crystals in a semi-infinite system [1, 2], and in this paper we extend our study to deal with the two-wall problem. In the liquid crystal context the pioneer of such investigations was Sheng [3]. He studied a semi-infinite sample of nematic liquid crystal in contact with a wall which exerts an ordering potential on the nematic. Under some circumstances a separate

first-order phase transition occurs at the wall, at a temperature slightly above the bulk nematic–isotropic phase transition  $T_{NI}$ , and at which orientational ordering occurs close to the wall. In fact, as observed by ourselves [1, 2] and others [4] this so-called boundary layer phase transition is none other than the prewetting transition, a rather general phenomenon occurring when two critical phases are influenced by a third non-critical phase [5]. Sheng also studied a finite size nematic sample between two parallel ordering walls. The phase transition between the disordered isotropic phase and the ordered nematic phase is shifted slightly to higher temperatures. The coexistence curve has its own critical point for some critical value of the thickness. In addition, features of the semi-infinite system phase diagram are preserved. The boundary layer phase transition can occur, although it is rather insensitive to sample thickness  $D$ .

There has also been recent experimental work. Kuzma and Labes [6] studied the thermodynamics of a liquid crystal in a cylindrical pore and found, that the transition temperature dropped slightly as the pore size was reduced. Yokoyama *et al.* [7] used the birefringence method to study thin nematic films bounded by solid substrates, and their results are consistent to some extent with Sheng's picture. They observed a shift in the transition temperature and there is evidence that the transition becomes continuous at a critical point when the nematic film is still as thick as a few thousand Ångströms. However, in contradiction with Sheng's

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study the transition temperature shifted either upward or downward, depending both on the type of nematic and on the type of substrate.

In this paper we study the consequences of the Landau-de Gennes theory of the nematic confined between two walls. We extend somewhat the model of Sheng in order to discuss disordering as well as ordering walls. In the Landau form the theory is in fact applicable to any first-order phase transition in a restricted geometry, in particular magnetic systems and the liquid-gas transition. Such problems have been studied for many years and there has recently been a resurgence of interest associated with the progress made in understanding wetting and spreading phenomena. Kelvin, in the last century, used a thermodynamic argument to derive the shift in the saturated vapour pressure of a vapour in a pore [8]. We shall make the analogous thermodynamic argument, but also be interested in the limits to such arguments. More recently Nakanishi and Fisher [9] were interested in the effect of plate geometry on the liquid-vapour critical point. Their arguments demonstrate that a critical point is expected for a sufficiently thin sample for a system undergoing a first-order phase transition. Lipowsky and Gompper [10] and Sornette [11] have looked at a Landau model between purely disordering plates, and have in particular concentrated on the asymptotic regime of large sample thicknesses. In our work we present calculations over the whole range of  $D$ , and for the more generic case of walls which have both ordering and disordering terms. We also discuss the asymptotic regime, which is extremely useful in checking approximate formulae for critical parameters. In addition a number of authors have recently studied the phenomenon of capillary condensation [12], which is essentially the same phenomenon as that which we discuss.

A related phenomenon which can be examined theoretically using the Landau-de Gennes formalism is that of the so-called structural force between two solid walls, the region between which is filled with fluid. This force, sometimes also known as the disjoining force or pressure, exists because each wall independently affects the fluid structure close to it; the presence of the other wall changes this effect slightly, and hence changing the separation affects the free energy. Interest in this phenomenon goes back many years [13]. More recently, Perez *et al.* [14] have made a thermodynamical study of a liquid crystal system placed between two walls, emphasizing the structural force, and Horn *et al.* [15] have carried out an experimental study of such a system.

The paper is arranged as follows, In §2 we set the scene by deriving various thermodynamic relations

which are useful in the development of the theory. In §3 we describe the model. In §4 we explain in principle how the model is solved, and describe how some crucial quantities which crop up in the solution of the model are related to the thermodynamics. In §5, which is of more theoretical interest, we examine asymptotic properties of the model in the large slab thickness limit. In §6 we give the results of the calculation of the nematic-isotropic phase diagram as a function of temperature and slab thickness. We also compare the predictions of the theory for the critical parameters with a simpler heuristic theory, and thus relate this finite size transition to the nematic-isotropic transition in an ordering field. We also make some comments about the relation of the theory to experimental work. In §7 we concentrate on the predictions of the theory for the structural forces between the two walls. Finally in §8 we make some concluding remarks. Although the model is very simple, the calculations are rather long-winded and most of the technical detail of the calculations has been relegated to the two Appendices.

## 2. Thermodynamics

In this section we discuss various elementary thermodynamical considerations which it will be useful to bear in mind during our discussions of the microscopic model studied in subsequent sections. Although in principle the microscopic model can allow for the presence of a finite magnetic field which has an ordering effect on a nematogen, we shall confine our discussion in this section to the zero magnetic field case.

We first discuss the shift in transition temperature in a system of thickness  $D$ . The grand thermodynamic potential  $\Omega$  is a suitable free energy for this system (the chemical potential  $\mu$  is supposed fixed). Per unit area, in the simplest approximation, this is given by

$$\frac{\Omega}{A} = -pD + 2\gamma, \quad (1)$$

where  $\gamma$  is the surface free energy  $p$  is the bulk pressure and  $A$  is the area. We denote the surface free energies of the nematic and isotropic phases by  $\gamma_N$ ,  $\gamma_I$ , respectively, and the Young-Laplace surface tension formula yields

$$\gamma_I = \gamma_N + \gamma_{NI} \cos \theta, \quad (2)$$

where  $\theta$  is the contact angle at a nematic-isotropic-wall line of contact, and  $\gamma_{NI}$  is the surface tension at the nematic-isotropic interface. We denote the pressures in the isotropic and nematic phases at temperature  $T$  by  $p_I(T)$  and  $p_N(T)$ , respectively. The bulk coexistence



temperature  $T_{\text{NI}}$  is defined by

$$p_{\text{I}}(T_{\text{NI}}) = p_{\text{N}}(T_{\text{NI}}). \quad (3)$$

In the finite thickness sample the phase transition occurs at  $T_{\text{NI}}(D) = T_{\text{NI}} + \Delta T_{\text{NI}}(D)$ . At this temperature  $\Omega_{\text{N}} = \Omega_{\text{I}}$ , or

$$-p_{\text{N}}(T_{\text{NI}}(D)) + \frac{2\gamma_{\text{N}}}{D} = -p_{\text{I}}(T_{\text{NI}}(D)) + \frac{2\gamma_{\text{I}}}{D}. \quad (4)$$

The shift is small, so

$$\begin{aligned} p_{\text{N}}(T_{\text{NI}}(D)) &= p_{\text{N}}(T_{\text{NI}}) + \frac{\partial p_{\text{N}}}{\partial T}(T_{\text{NI}})\Delta T_{\text{NI}}(D), \\ &= p_{\text{N}}(T_{\text{NI}}) + S_{\text{N}}(T_{\text{NI}})\Delta T_{\text{NI}}(D), \end{aligned} \quad (5)$$

where  $S_{\text{N}}$  is the entropy per unit volume of the nematic phase at  $T_{\text{NI}}$ , and a similar equation obtains for  $p_{\text{I}}$ . Substituting equation (5) into equation (4), we obtain

$$-S_{\text{N}}\Delta T_{\text{NI}} + \frac{2\gamma_{\text{N}}}{D} = -S_{\text{I}}\Delta T_{\text{NI}} + \frac{2\gamma_{\text{I}}}{D}, \quad (6)$$

or

$$\Delta T_{\text{NI}} = \frac{2(\gamma_{\text{I}} - \gamma_{\text{N}})T_{\text{NI}}}{LD}, \quad (7)$$

where

$$L = T_{\text{NI}}(S_{\text{I}} - S_{\text{N}})$$

is the latent heat per unit volume at the bulk nematic–isotropic transition. Variations of this equation date back to Kelvin [8] and we call this the Kelvin approximation [16]. A trivial consequence of equation (7), using equation (2), is that

$$\Delta T_{\text{NI}} = \frac{2\gamma_{\text{NI}} \cos \theta T_{\text{NI}}}{LD}, \quad (8)$$

and thus if  $\cos \theta > 0$  then  $T_{\text{NI}}$  is increased, whereas if  $\cos \theta < 0$  then  $T_{\text{NI}}$  is decreased, as might be expected intuitively.

However, the formulae (7) and (8) are only approximate. They ignore the interaction between the walls. Equation (1) must be supplemented in order to take this into account. We then obtain

$$\frac{\Omega}{A} = -pD + 2\gamma + \Xi(D), \quad (9)$$

where all wall interaction effects are taken account of by the interaction potential  $\Xi(D)$ , which must be calculated microscopically. However,

$$-\frac{1}{A} \left( \frac{\partial \Omega}{\partial D} \right)_{T, \mu} = p - \frac{\partial \Xi}{\partial D} = p + \pi_D \quad (10)$$

defines the *disjoining pressure* or *disjoining force* [13],  $\pi_D$ . The quantity  $\pi_D$  is the force required, per unit area, to keep two walls a distance  $D$  away from each other when the whole system is immersed in an infinite bath of the same fluid as is between the walls. The infinite bath provides the pressure  $p$ , but the extra pressure  $\pi_D$  must be supplied mechanically.

The thermodynamical potential appropriate at constant disjoining pressure is  $\Psi$ , where

$$\begin{aligned} \frac{\Psi}{A} &= \frac{1}{A} \left[ \Omega - D \frac{\partial \Omega}{\partial D} \right] = 2\gamma + D\pi_D + \Xi, \\ &= 2\tilde{\gamma}(D). \end{aligned} \quad (11)$$

This obeys the equation

$$\left( \frac{\partial \tilde{\gamma}}{\partial D} \right)_{\pi_D} = 0. \quad (12)$$

Then  $\tilde{\gamma}(D)$  is the surface tension per wall on the two-wall system, and in some sense is the finite  $D$  analogue of  $\gamma$ .

A more exact analogue of equation (7) can now be calculated. This equation will be the Clausius–Clapeyron equation for the nematic–isotropic coexistence curve with changing  $D$ . If  $T_{\text{NI}}(D)$  and  $T_{\text{NI}} + dT_{\text{NI}}(D + dD)$  are neighbouring points on the coexistence curve, we have, following the usual Clausius–Clapeyron-type arguments,

$$\Delta \Omega = \Omega_{\text{N}} - \Omega_{\text{I}} = 0 \quad (13)$$

and

$$\frac{1}{A} \frac{\partial \Delta \Omega}{\partial D} dD + \frac{1}{A} \frac{\partial \Delta \Omega}{\partial T} dT_{\text{NI}} = 0. \quad (14)$$

Following the argument of equation (6) and (7),

$$\frac{1}{A} \frac{\partial \Delta \Omega}{\partial T} = D \frac{\tilde{L}(D)}{T_{\text{NI}}(D)}, \quad (15)$$

where  $\tilde{L}(D)$  is the latent heat per unit volume in the finite system. Also from equation (11), and using equation (13),

$$\frac{1}{A} \frac{\partial \Delta \Omega}{\partial D} = \frac{2}{D} (\tilde{\gamma}_{\text{I}} - \tilde{\gamma}_{\text{N}}). \quad (16)$$

Combining the results in equations (14)–(16) we obtain

$$\begin{aligned} \frac{\Delta T_{\text{NI}}}{\Delta D} &= \frac{dT_{\text{NI}}(D)}{dD} \text{ coexistence curve}, \\ &= \frac{2}{D^2} \frac{(\tilde{\gamma}_{\text{N}} - \tilde{\gamma}_{\text{I}})}{\tilde{L}(D)} T_{\text{NI}}(D), \end{aligned} \quad (17)$$

as the equation of the coexistence curve. This is the natural generalization of the Kelvin equation (7) but is

now in its exact differential form. We make use of this equation to calculate coexistence curves in our model calculations. Taking the limit  $D = \infty$ ,  $\tilde{\gamma} = \gamma$ ,  $\tilde{L} = L$  reproduces equation (7). The formula applies so long as a true phase transition does occur.

Finally, in this section, we discuss the phenomenon of capillary condensation. If there were merely one wall, the potential at the wall might favour either phase. When the contact angle  $\theta = 0$  the nematic phase is favoured, when  $\theta = \pi$  the isotropic phase is favoured, and intermediate values of  $\theta$  apply to intermediate situations. As has been much discussed recently [4],  $\theta = 0$  and  $\theta = \pi$  are special situations in that *complete* wetting occurs. We discuss, for definiteness, the  $\theta = 0$  case. The nematic phase is then so favoured that as the thermodynamic conditions for nematic–isotropic coexistence are approached a layer of nematic phase forms at the wall, and the thickness of this layer *diverges* as the bulk phase transition is approached. How does this phenomenon generalize to the two-wall situation, where the surface layer is precluded from divergence by the finite thickness of the sample?

The answer to this question depends on the thickness of the sample. Recall, from equation (8), that the phase transition occurs at a higher temperature than in the bulk. The shift in phase transition temperature is  $T_{NI} \sim D^{-1}$ . Now, for short-ranged surface forces, the thickness of the nematic layer at the wall is given by [5]  $H \sim \ln |T_{NI}|$ . For a sufficiently thick sample,  $T$  will be small,  $D \gg H$ , and the phase transition will occur *before* the nematic layer has had a chance to grow thick. Indeed, at each wall the maximum thickness of the nematic layer, before the bulk transition takes place, will be  $H \sim \ln D$ . This is the phenomenon of capillary condensation. On the other hand for a thin sample, the Kelvin equation (8) suggests a phase transition at a temperature at which the nematic layer thickness at the walls is already larger than the sample thickness. Then we expect no sharp transition. Somewhere in between there will be a critical point. We expect our model calculations to conform to these general observations, and we shall be interested in features of the transition under these circumstances.

### 3. Model

We consider a nematic sample between two parallel walls placed at  $z = 0$  and  $z = D$  respectively, and unbounded in the  $xy$  plane. The nematic is assumed to be subject to homeotropic boundary conditions (i.e. with its director perpendicular to the walls), although our results may be partly applicable to the case when the nematic is subject to identical homogeneous boundary conditions at each wall (i.e. each plane has an identical easy axis in the  $xy$  plane), in which case the system is dominated by the

behaviour of the order parameter along this direction. This restriction enables us to assume that the nematic director is uniform throughout the sample. We also ignore nematic density variations in the sample. Thus the only variable depending on  $z$  is the nematic order parameter  $Q(z) = Q_{zz}(z)$ . Following Sheng [3] we take the free energy density in the Landau–de Gennes form

$$\mathcal{F} + L \left( \frac{dQ}{dz} \right)^2 = \mathcal{F}_0 + \frac{3}{4} A Q^2 - \frac{1}{4} B Q^3 + \frac{9}{16} C Q^4 - \frac{1}{2} \chi_a H^2 Q + L \left( \frac{dQ}{dz} \right)^2, \tag{18}$$

where  $A = A'(T - T^*)$ ,  $B$  and  $C$  are temperature-independent parameters,  $\chi_a > 0$  is the anisotropic part of the magnetic susceptibility, and  $H$  is a uniform magnetic field along the  $z$  axis. It is convenient to deal in dimensionless quantities, and in order to do this we introduce a dimensionless order parameter  $\eta = (C/B)Q$ , and divide  $\mathcal{F}$  by  $B^4/C^3$ , to obtain [17]

$$F(\eta) = (\mathcal{F} - \mathcal{F}_0) / B^4 / C^3 = \frac{3}{4} t \eta^2 - \frac{1}{4} \eta^3 + \frac{9}{16} \eta^4 - h \eta, \tag{19}$$

where  $F$ ,  $t = AC/B^2$  and  $h = \frac{1}{2} \chi_a H^2 C^2 / B^3 > 0$  are the dimensionless free energy density, temperature and ordering field respectively. The bulk phase diagram resulting from this free energy has been much studied [17, 18]; however it is useful to recapitulate its basic features.

At temperatures  $t > t_c = \frac{1}{18}$  there is just one phase. At temperatures lower than this there are two phases: a low field paranematic phase (at zero field this becomes the isotropic phase) and a high field nematic phase. The coexistence line terminates at a critical point at  $t_c$ ,  $h_c = \frac{1}{324}$ ,  $\eta_c = \frac{1}{4}$ . It is linear in the  $(t, h)$  plane:

$$h - h_c = (t - t_c) / 6, \tag{20}$$

and

$$\eta_p - \eta_c = -2(h_c - h)^{1/2}, \tag{21}$$

$$\eta_N - \eta_c = 2(h_c - h)^{1/2}. \tag{22}$$

Thus at zero magnetic field we have the usual isotropic–nematic transition at  $t_{NI} = \frac{1}{27}$ ,  $\eta_P = 0$ ,  $\eta_N = \frac{2}{9}$ . Below  $t_{NI}$  only the nematic phase exists.

The total dimensionless free energy functional per unit area has the form

$$\phi(\eta) = \xi^{-1} \int_0^D \left[ F(\eta) + \xi^2 \left( \frac{d\eta}{dz} \right)^2 \right] dz + \int_0^D V_s(\eta) [\delta(z) + \delta(z - D)] dz, \tag{23}$$

where  $\xi=(LC/B)^{1/2}$  is the nematic correlation length, and the second integral gives the surface contribution to the free energy. We assume, as in our previous work [1, 2], the surface potential due to the walls is a contact potential, of zero range, and that it consists of two terms

$$V_s(\eta) = -h_1\eta + \frac{1}{2}g\eta^2. \quad (24)$$

The first term is responsible for surface-induced order ( $h_1>0$ ), and the second term for surface-induced disorder ( $g>0$ ). From a microscopic point of view, the second term is a result of the fact that molecules close to an interface have fewer nearest neighbours than in the bulk. Sheng [1] considered only the first term, although other workers have studied surface-induced disorder [10, 11, 19]. To understand the full range of possible behaviours it is necessary to consider both terms. The equilibrium profile  $\eta(z)$  results from the minimization of  $\phi\{\eta(z)\}$ . This yields the Euler–Lagrange equation

$$2\xi^2 \left( \frac{d^2\eta}{dz^2} \right) = F'(\eta), \quad (25)$$

together with boundary conditions

$$2\xi \left( \frac{d\eta}{dz} \right)_{z=0} = V'_s(\eta)|_{z=0}, \quad (26a)$$

$$2\xi \left( \frac{d\eta}{dz} \right)_{z=D} = -V'_s(\eta)|_{z=D}. \quad (26b)$$

Although this model is very simple, it contains an extremely rich set of behaviours, and the procedure required to solve the model is rather detailed. We discuss the method of solution and the results in the following sections.

#### 4. Solution of model: general considerations

In this section we give a general outline of the procedure required to solve the model introduced in the last section, and make contact between properties of the model and the thermodynamics discussed in §2.

We start with the basic equations of the model, equations (25) and (26). A crucial physical point to note is that the system is symmetric about  $z=D/2$ , from which it follows that  $(d\eta/dz)_{D/2}=0$ . Thus integration of equation (25) yields

$$\xi^2 \left( \frac{d\eta}{dz} \right)^2 = F(\eta) - F(\eta_m), \quad (27)$$

where  $\eta_m=\eta(z=D/2)$  is the order parameter at the

middle of the sample. The quantities  $\eta_m$  and  $F(\eta_m)$  have considerable importance in the theory.

Equations (27) and (23) can be combined to yield an explicit expression for the free energy per unit area

$$\phi = 2\sigma + \left( \frac{D}{\xi} \right) F(\eta_m), \quad (28)$$

where

$$\sigma = \pm 2 \int_{\eta_0}^{\eta_m} \sqrt{[F(\eta) - F(\eta_m)]} d\eta + V_s(\eta_0); \quad (29)$$

here the signs +, – correspond, respectively, to a profile increasing or decreasing at  $z=0$ , and  $\eta_0=\eta(z=0)$ . Now we can treat  $\phi$  as a function of  $\eta_0$  and  $\eta_m$ , which should be minimized with respect to these variables. The minimization with respect to  $\eta_0$  gives

$$\pm 2\sqrt{[F(\eta_0) - F(\eta_m)]} = V'_s(\eta_0), \quad (30)$$

which is consistent with the result we would obtain by combining equations (27) and (26). The minimization with respect to  $\eta_m$  leads to a relation between  $\eta_0$ ,  $\eta_m$ , and  $D$ , namely

$$D/\xi = \pm 2 \int_{\eta_0}^{\eta_m} \frac{d\eta}{\sqrt{[F(\eta) - F(\eta_m)]}}. \quad (31)$$

If  $D \rightarrow \infty$  then  $\eta_m$  tends to the bulk order parameter of the infinite system  $\eta_b$  and we recover the semi-infinite sample problem with  $\sigma$  being the wall–nematic or wall–paranematic surface tension. For finite  $D$ , on the other hand, the parameters  $\eta_0$  and  $\eta_m$  are coupled and we have to solve equations (30) and (31) to find them as a function of  $D$ ,  $t$  and  $h$ .

From a physical point of view  $D$  is the independent variable, and we wish to solve for  $\eta_0(D)$  and  $\eta_m(D)$ . However, in the context of equations (30) and (31) it is clear that if  $\eta_0$  and  $\eta_m$  are chosen as the independent variables then equation (31) provides an explicit expression for  $D(\eta_0, \eta_m)$ . The quantities  $\eta_0$  and  $\eta_m$  are connected by equation (30), which can be recast as

$$F_m(\eta_0) = F(\eta_m) = F(\eta_0) - \frac{1}{4} [V'_s(\eta_0)]^2. \quad (32)$$

In this equation it is clear that if  $\eta_m$  is treated as the independent variable,  $\eta_0$  is an ambiguous function of  $\eta_m$ . On the other hand if  $\eta_0$  is regarded as the independent variable, then  $F_m(\eta_0)=F(\eta_m)$  is well defined. The solution of this equation for  $\eta_m(\eta_0)$  is not in fact unique; indeed there may be up to four solutions. The physical solution, however, must obey two further conditions, and this does impose uniqueness. We are thus able to establish a functional relationship  $D(\eta_0)$ .

The conditions are

$$(\eta_m - \eta_0) V'_s(\eta_0) \geq 0, \quad (33)$$

and

$$F(\eta) - F(\eta_m) \geq 0 \quad \text{for} \quad \min(\eta_0, \eta_m) \leq \eta \leq \max(\eta_0, \eta_m). \quad (34)$$

Equation (33) follows directly from equations (26);  $(\eta_m - \eta_0)$  has the same sign as  $(d\eta/dz)_{z=0}$ , and hence the same sign as  $V'_s(\eta_0)$ . Equation (34) is merely the condition that equation (27) is satisfied for all physical  $\eta$ , i.e. all those  $\eta$  lying between  $\eta_0$  and  $\eta_m$ .

Having shown that  $\eta_m$  is a single-valued function of  $\eta_0$ , we proceed in the following way.

- (i) We determine the physical regions of  $\eta_0$ , using the inequality

$$F_m = F(\eta_0) - \frac{1}{4} [V'_s(\eta_0)]^2 > \min F(\eta). \quad (35)$$

No solutions for  $\eta_m$  exist if equation (30) is not satisfied.

- (ii) We calculate

$$D(\eta_0) = D(\eta_0, \eta_m(\eta_0)) \quad (36)$$

using equation (31).

- (iii) We seek solutions to the equation

$$D = D(\eta_0). \quad (37)$$

- (iv) We isolate the stable solutions of equation (37). The stability conditions are most conveniently written as

$$F'_m(\eta_0) / V'_s(\eta_0) < 0, \quad (38)$$

$$D'(\eta_0) / F'_m(\eta_0) < 0. \quad (39)$$

We postpone the derivation of these inequalities to Appendix 1.

- (v) Finally we find the equilibrium values of  $\eta_0$  and  $\eta_m$ , corresponding to the absolute minimum of  $\phi(\eta_0, \eta_m)$ .

#### 4.1. Thermodynamic properties of the model

At this stage it will be useful, even before we solve the model by carrying out the set of procedures just outlined, to make contact between the quantities occurring in the model and the general thermodynamic considerations described in §2.

The relevant normalized surface free energy in our model system can be rewritten from equation (28) as

$$\phi = 2\sigma + (D/\xi)F(\eta_b) + (D/\xi)(F(\eta_m) - F(\eta_b)). \quad (40)$$

We can compare this to the thermodynamic expression for the grand thermodynamic potential,  $\Omega$ , obtained by combining equations (9) and (11) to give

$$\Omega = 2\tilde{\gamma} - Dp - D\pi_D. \quad (41)$$

We identify  $F(\eta_b)$  with  $-p$ , the free energy per unit area of a system of thickness  $D$  immersed in the bulk system. The disjoining pressure  $\pi_D$  can now be identified with  $-(F(\eta_m) - F(\eta_b))$ , and the surface free energy  $\sigma$  can be identified with the thermo-dynamic quantity  $\tilde{\gamma}$ . We also note that  $\pi_D$  is the force per unit area required to hold the plates at a distance  $D$  apart. The work required to expand the system from a thickness  $D$  to a thickness  $D+dD$  is

$$\begin{aligned} dW &= \pi_D dD \\ &= - \left( \frac{\partial \Omega}{\partial D} \right)_p dD. \end{aligned} \quad (42)$$

Mechanical stability demands that [15]

$$\pi_D(dD + dD) < \pi_D(D), \quad (43)$$

or equivalently

$$\frac{d\pi_D}{dD} < 0. \quad (44)$$

This is a condition on the *physical accessibility* of the system of thickness  $D$ , which is produced by supplying physically the force  $\pi_D$ . At a given  $\pi_D$  the system will *slip* through a region where  $(d\pi_D/dD) < 0$ .

#### 5. Asymptotic behaviour

In this section, before investigating in detail the function  $D(\eta_0)$ , we find it useful to extract as much information as possible about the large  $D$  behaviour of the finite thickness system by carrying out an analysis of its asymptotic behaviour in this regime. We shall first discuss the behaviour, at fixed  $t$ , of the quantities  $\eta_m(D)$  and  $\eta_0(D)$ . This analysis gives some further insight into the Kelvin equation for the temperature shift of the phase transition, discussed in §2. We then discuss some aspects of the ordering phase transition at finite  $D$ .

At large  $D$  we may suppose that  $\eta_m$  is close to  $\eta_b = \eta_m(D = \infty)$ , and that  $\eta_0$  is also only slightly perturbed.  $D$ ,  $\eta_0$  and  $\eta_m$  are related through equation (31). The principal contribution to this integral comes in the region of  $\eta$  close to  $\eta_m$ . In this regime  $F(\eta)$

can be expanded in the following way.

$$F(\eta) - F(\eta_m) \cong \frac{1}{2} \left( \frac{\partial^2 F}{\partial \eta^2} \right)_{\eta_b} [(\eta - \eta_b) - (\eta_m - \eta_b)]^2. \quad (45)$$

Substituting equation (45) into equation (31) yields the asymptotic expression

$$\eta_b - \eta_m \sim \pm \exp \left\{ -\frac{1}{2} \left[ \frac{1}{2} F''(\eta_b) \right]^{1/2} D / \xi \right\}. \quad (46)$$

For  $h=0$  and  $t=t_{NI}$ ,  $\eta_b=0$  or  $\eta_b=\eta_N=\frac{2}{9}$  and  $[\frac{1}{2} F''(\eta_b)]^{1/2} = \frac{1}{6}$ . We may show in a straightforward way, using equations (29) and (32), that  $\eta_0(D)$  and  $\sigma(D)$  also differ from their values at  $D=\infty$  by terms which are exponentially small as a function of  $D$ .

The thermodynamic argument of §2 derives the Kelvin equation (7) for the shift in the transition temperature by balancing bulk and surface free energy terms. In the context of the present model this can be derived from the free energy expression of equation (40),

$$\begin{aligned} \phi = 2\sigma(D=\infty) + D/\xi F(\eta_b) + 2[\sigma(D) - \sigma(\infty)] \\ + D/\xi [F(\eta_m) - F(\eta_b)]. \end{aligned} \quad (47)$$

The asymptotic behaviour of  $\Delta t_{NI}$  as a function of  $D$  results from the first two terms in this expression; the last two terms are exponentially small and can be neglected. Thus in the asymptotic regime the normalized shift in the phase transition temperature  $\Delta t_{NP}$  is given by

$$\Delta t_{NP} = 2t_{NP}[\sigma_P(\infty) - \sigma_N(\infty)]\xi/Dl, \quad (48)$$

where  $\sigma_P, \sigma_N$  are the paranematic-wall and nematic-wall surface free energies respectively,  $l=t_{NP}(S_P-S_N)$  is the (normalized) latent heat at the phase transition, and

$$s = -\frac{\partial F}{\partial t} \quad (49)$$

is the bulk entropy density, with the subscripts p and N applying to the paranematic and nematic phases respectively. Expression (48) is expected to be exact in the limit  $D \rightarrow \infty$ , but, as we shall see, this approximation can also be rather good for quite small  $D$  so long as the wall potential is not too strong. These observations have been made before in discussing phase transitions in finite systems [10, 11]; Evans *et al.* [12] drew attention to their connection with the thermodynamic results.

We have already emphasised in §2 the dependence of  $t_{NP}$  on the nematic-wall contact angle  $\theta$ , and the particular significance of the cases  $\theta=0$  and  $\theta=\pi$  when complete wetting by the nematic and paranematic phases occurs, respectively. We recall that in the one-wall case

for  $\theta=0$  there can, under some circumstances, be a boundary layer transition at which  $\eta_0$  (but not  $\eta_b$ ) jumps. For finite  $D$  this transition persists, although now the large jump in  $\eta_0$  is accompanied by an exponentially small jump in  $\eta_m$  with a functional form given by equation (46). Sheng [3] found that this line of boundary layer transitions is parallel to the  $D$  axis, essentially because of the exponentially small corrections to  $\eta_0$  and  $\eta_m \approx \eta_b$ . For smaller  $D$  the boundary layer transition temperature would no longer be independent of  $D$ , but apparently the transition disappears at rather large thicknesses ( $D/\xi \approx 100$ ) where the asymptotic relations still hold.

For paranematic wetting ( $\theta=\pi$ ) the situation is analogous, although  $\Delta t_{NP} < 0$ . However, in the case of zero bulk magnetic field ( $h=0$ ) the conditions for complete wetting by the isotropic phase are rather restrictive; in particular  $h_1=0$ . The nature of the wetting phase diagram now prohibits a boundary layer transition [1].

The distinguishing feature of complete wetting in the semi-infinite system is that the surface structure shows no discontinuity at the phase transition. In particular, in the context of the present model, even though  $\eta_b$  jumps discontinuously at the phase transition,  $\eta_0$  only undergoes a continuous transition at  $t_{NI}$ . This is no longer the case for a sample of finite thickness. A question of some theoretical interest is the functional form and magnitude of the jump  $\eta_0(D)$  at the transition temperature  $t_{NP}(D)$ . To investigate this we first note that

$$F(\eta_m(D), t_{NP}(D)) \cong F(\eta_b, t_{NI}) - s_b \Delta t_{NP}, \quad (50)$$

$$F(\eta_0(D), t_{NP}(D)) \cong F(\eta_0, t_{NI}) - s_0 \Delta t_{NP}, \quad (51)$$

where  $s_b(\eta_b)$  is the bulk entropy density,  $\eta_b$  corresponds to either the nematic or isotropic phases, and  $s_0 = -\frac{\partial F}{\partial t}|_{\eta_0, t_{NI}}$ . Terms exponentially small in  $D$  have been neglected; they are small compared to  $\Delta t_{NP} \sim D^{-1}$ . We now combine equation (50) and (51) with the relation (32) to obtain

$$\begin{aligned} F_m(\eta_0^+, t_{NI}) - F_m(\eta_0^-, t_{NI}) = \\ [(s_0^+ - s_0^-) + (s_N - s_I)] \Delta t_{NP}, \sim D^{-1} \end{aligned} \quad (52)$$

where

$$\eta_0^\pm = \eta_0(t_{NP}^\pm(D)).$$

In general we expect  $\eta_0^+ \approx \eta_0^- \approx \eta_0(D=\infty)$ ; then from equation (32)

$$F_m(\eta_0^+) - F_m(\eta_0^-) \approx \left( \frac{\partial F_m}{\partial \eta_0} \right)_{\eta_0} \Delta \eta_0, \quad (53)$$

where  $\Delta \eta_0 = \eta_0^+ - \eta_0^-$  and hence combining

equations (52) and (53)

$$\Delta\eta_0 \sim D^{-1}. \tag{54}$$

This behaviour applies if the nematic phase wets the wall. However, if the isotropic phase wets the wall this reasoning does not apply. Now  $\eta_0(D=\infty)=0$ , and as we have observed previously this only obtains when

$$V_s(\eta_0) = \frac{1}{2}g\eta_0^2. \tag{55}$$

We must still have  $\eta_0^+ = 0$ , although  $\eta_0^- \neq 0$ . In this case, using equation (32),

$$\frac{\partial F_m}{\partial \eta_0} = \frac{\partial F}{\partial \eta_0} - \frac{1}{2}V_s'(\eta_0)V_s''(\eta_0). \tag{56}$$

Now  $\eta_0=0$  is itself a local solution of the bulk statistical mechanics, so  $F|_0=0$ , and hence by combining equations (55) and (56), we have  $F_m|_0=0$ . Thus in this case

$$F_m(\eta_0^+) - F_m(\eta_0^-) \simeq \frac{1}{2} \frac{\partial^2 F_m}{\partial \eta_0^2} \Delta\eta_0^2, \tag{57}$$

and combining equations (52) and (57) yields the asymptotic behaviour

$$\Delta\eta_0 \sim D^{-1/2}. \tag{58}$$

Finally in this section we discuss the behaviour of the average order parameter

$$\tilde{\eta} = \frac{1}{D} \int_0^D \eta(z) dz = \pm \frac{2}{D} \int_{\eta_0}^{\eta_m} \frac{[\eta - \eta_m] d\eta}{\sqrt{[F(\eta) - F(\eta_m)]}} + \eta_m \tag{59}$$

close to the paranematic–nematic phase transition. This quantity is experimentally accessible in, for example, a birefringence experiment. Whereas in the bulk system  $\eta_b$  jumps from zero to  $\eta_N$  at  $t_{NI}$  (for  $h=0$ ), in general in the finite  $D$  case  $\tilde{\eta}$  shows some pretransitional behaviour, and is non-zero (although relatively small) even above  $t_{NI}$ . The only exception to this is the case when the surface field  $h_1$  is identically zero; as we have discussed, then and only then  $\eta_0 = \eta_m = \tilde{\eta} = 0$  everywhere above  $t_{NI}$ . We shall, for definiteness, study the behaviour of  $\tilde{\eta}(t_{NP}^+(D))$ , the value of the average order parameter in the paranematic (‘isotropic’) phase just above the phase transition. We must deal with the two cases, complete wetting by the nematic phase, and partial wetting, separately. In both cases, however, because the corrections to  $\eta_0$  and  $\eta_m$  are exponentially small, the leading behaviour for large  $D$  is given by

$$\tilde{\eta} \simeq \frac{2\Gamma}{D}, \tag{60}$$

where

$$\Gamma = \int_0^\infty (\eta(z) - \eta_b) dz$$

is the adsorption on a single wall in the semi-infinite system.

As discussed in §2, for complete wetting,

$$\Gamma(t) \sim \ln(t - t_{NI}), \tag{61}$$

from which  $\Gamma(t_{NP}^+(D)) \sim \ln \Delta t_{NP} \sim \ln D$ , and hence

$$\tilde{\eta}(t_{NP}^+(D)) \sim \ln D / D. \tag{62}$$

On the other hand for partial wetting  $\gamma$  remains finite at  $t_{NI}$ , and is an analytic function of  $t$  in this region. Thus

$$\Gamma(t_{NP}) \approx \Gamma(t_{NI}) + \Delta t_{NP} \left( \frac{\partial \Gamma}{\partial t} \right)_{t_{NI}} + \dots, \tag{63}$$

and substituting from equation (63) into equation (60) we obtain

$$\tilde{\eta}(t_{NP}^+(D)) \sim \frac{1}{D} + 0 \left( \frac{1}{D} \right)^2. \tag{64}$$

There are analogous effects below the phase transition; the relevant quantity to study is  $\tilde{\eta}(t_{NP}^-(D)) - \eta_N(t_{NI})$ . However these effects are much more difficult to measure.

### 6. The nematic–paranematic phase diagram

We first present the method for the calculation of the nematic–paranematic phase diagram. for  $h=0$ , and the results of the calculations. The calculations themselves are by no means trivial, and we postpone a more complete description to Appendix 2, in which we also give some general arguments about the shape of  $\eta(z)$  under various circumstances.

In general, the strategy used to determine the phase diagram is to plot  $D(\eta_0)$  for a given temperature  $t$ . This graph, in general, has a number of branches, one of which is the thermodynamic branch. At the phase boundary the free energy corresponding to two different branches is the same. The phase boundary at  $D=\infty$  is known. For very small  $D^{-1}$  the phase boundary can be plotted using the Kelvin equation (48). For higher  $D^{-1}$ , the Clausius–Clapeyron relation (17) must be used. In the context of the present model this equation becomes

$$\left( \frac{dt}{dD} \right)_{\Delta\phi=0} = - \frac{\left( \frac{\partial \Delta\phi}{\partial D} \right)_t}{\left( \frac{\partial \Delta\phi}{\partial t} \right)_D} = \frac{\Delta F_m}{D \Delta \bar{s}} = - \frac{2\xi \Delta \sigma}{D^2 \Delta \bar{s}}, \tag{65}$$

where

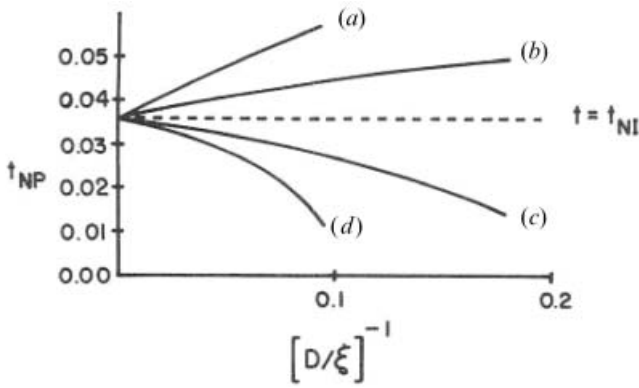


Figure 1. Phase boundaries in the  $(D^{-1}, t)$  plane. (a)  $h_1=0.02, g=0$ ; (b)  $h_1=0.01, g=0$ ; (c)  $h_1=0.01, g=0.15$ ; (d)  $h_1=0.02, g=0.4$ .

$$\left(\frac{\partial\phi}{\partial t}\right)_D = \left(\frac{\partial\phi}{\partial t}\right)_{D+\eta_0+\eta_m} = -\bar{s}D/\zeta = -\int_0^D s(z)\frac{dz}{\zeta}, \quad (66)$$

and  $s(z)$  is the local entropy density. Using  $D^{-1}$  as the independent variable we obtain

$$\frac{dt_{NP}}{dD^{-1}} = 2\zeta \frac{(\sigma_P - \sigma_N)}{(\bar{s}_P - \bar{s}_N)}. \quad (67)$$

The average entropy  $\bar{s}$  can be expressed in terms of  $\eta_0$ ,  $\eta_m$  and  $D$  as

$$\bar{s} = s(\eta_m) - \frac{3}{2} \left(\frac{\xi}{D}\right) \left| \int_{\eta_0}^{\eta_m} \frac{\eta^2 - \eta_m^2}{F(\eta) - F(\eta_m)} d\eta \right|. \quad (68)$$

Inprinciple the relation (67) is exact. In practice this relation is used to provide a guess for  $t_{NP}(D)$ , and knowledge of the functions  $D(\eta_0)$  and  $\phi(D, \eta_0)$  is then used to improve this guess.

We show in figure 1 the phase diagram in  $(t, D^{-1})$  space for a number of different values of  $h_1$  and  $g$ . Certain generic features of the phase diagram (the shift in coexistence curve and the existence of a critical point) are universal. Only when the wall is completely disordering ( $h_1=0$ ), do we not find the existence of a critical point. Depending on the value of the contact angle  $\cos\theta$ , the phase transition temperature  $t_{NP}(D)$  increases or decreases as a function of  $D^{-1}$ . The other dramatic feature which accompanies the shift in  $t_{NI}$  is a change in the behaviour of the mean order parameter  $\bar{\eta}(t)$ . We show in figure 2 schematic representations of the behaviour of  $\bar{\eta}(t)$  as  $D^{-1}$  is increased, for a number of different cases. In figure 2(a) we show the behaviour of  $\bar{\eta}(T)$  for different  $D$  for strongly ordering walls. Roughly speaking this corresponds to the phase diagram of figure 1(a) or (b). In figure 2(b) we show the behaviour of  $\bar{\eta}(T)$  for weakly ordering walls, for which

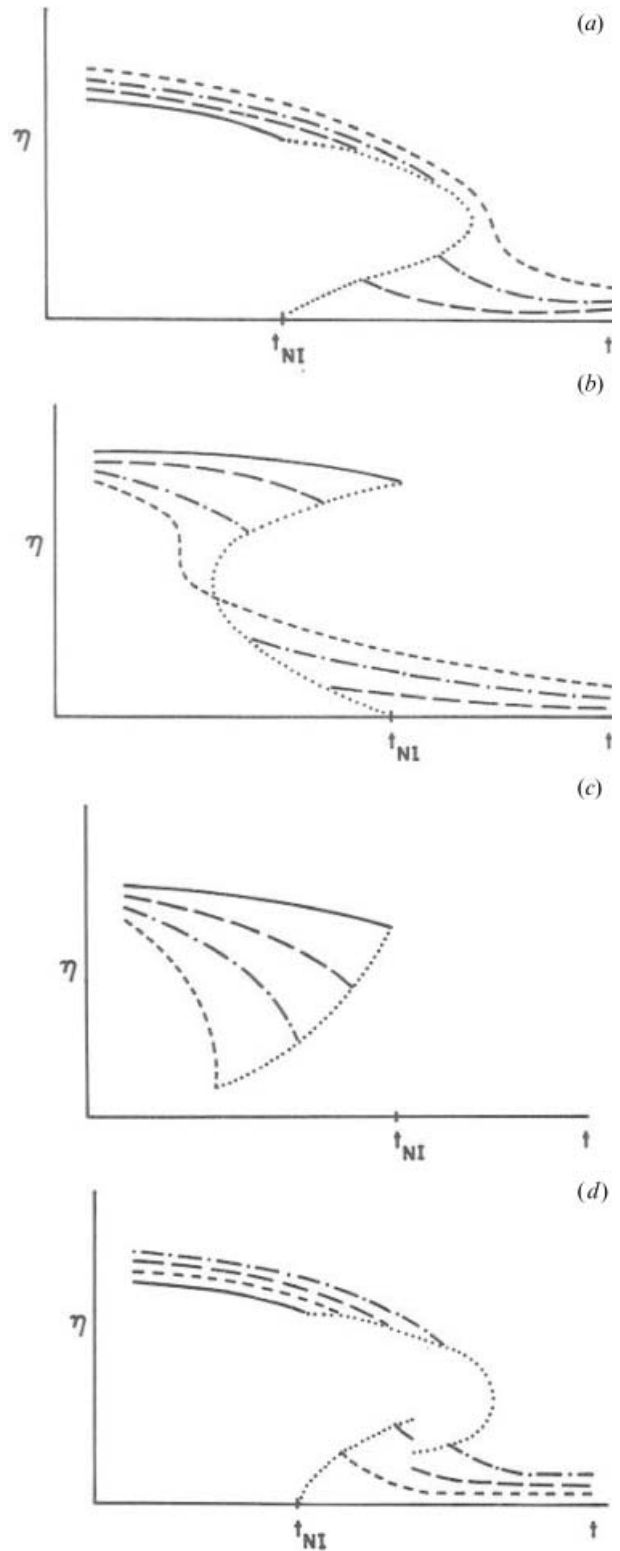


Figure 2. Schematic plots of the mean order parameter  $\bar{\eta}$  against temperature  $t$ . (a)  $\cos\theta > 0$ ; (b)  $\cos\theta < 0$ ; (c)  $g=0$ ; purely disordering boundary. Curves 1 (—), 2(— —) , 3(- · - ·) and 4(- - - -) are in order of decreasing thickness. Curve 1 is  $D = \infty$ . (d) includes the boundary transition.

$\cos \theta < 0$ . This corresponds to the phase diagram 1 (c) or (d). In figure 2(c) we show  $\bar{\eta}(T)$  for disordering walls. In the first two cases there is a small amount of ordering above  $t_{\text{NI}}$ . In the last case there is no critical point.

In figure 1 the dependence  $t_{\text{NI}}(D)$  is described by the Kelvin approximation  $\Delta t_{\text{NI}} \sim D^{-1}$  in the asymptotic regime  $D^{-1} \rightarrow 0$ . For small values of  $h_1$  and  $g$  this approximation is good in practice up to the critical point. We find that the Kelvin equation can only be satisfied for smaller separations if partial wetting conditions obtain. Figure 1(a) with  $h_1 = 0.02$ ,  $g = 0$  appears to give linear  $D^{-1}$  dependence for  $t_{\text{NI}}$ . However, its slope for larger  $D^{-1}$  differs from that predicted by the Kelvin equation. This phenomenon is connected to the boundary phase transition, which occurs ( $g = 0$ ) for  $0.014 < h_1 < 0.024$ . For smaller values of  $D$  the modified transition temperature is sufficiently high that it pre-empts the boundary phase transition. The behaviour of  $t_{\text{NI}}(D)$  is still governed by the asymptotic rule, but now the appropriate surface free energy to take is the metastable low  $\eta_0$  value, rather than the stable high  $\eta_0$  value. The low  $\eta_0$  value is stabilized by the increase in  $t_{\text{NI}}$ . It corresponds to a higher value of  $\sigma_I$  than the stable value (which is just  $\sigma_N + \sigma_{\text{NI}}$ ), or equivalently, a value of  $\cos \theta > 1$ . Thus in figure 1(a) we have the apparently anomalous example of a surface phenomenon governed by a value of  $\cos \theta = (\sigma_I - \sigma_N) / \sigma_{\text{NI}} > 1$ .

At this point we remark on the strong analogy between the nematic phase diagram in a bulk system in a bulk magnetic field  $h$ , and the nematic phase diagram in a confined system as a function of the inverse wall spacing  $D^{-1}$ . This analogy was noticed by Sheng [3], and is implicit in the use of the term *paranematic* for the less ordered phase in both cases. However, unrealistically large bulk magnetic fields are required to observe the bulk nematic–paranematic critical point. We therefore pose the question: is the analogy between these two phenomena more than just a formal analogy, so that by observing the finite geometry phenomena we may think of ourselves as observing the bulk nematic–paranematic phase diagram in another guise? We examine this question further in the next subsection.

### 6.1. The critical point

We make the simplest approximation, which is to suppress spatial variations of the order parameter, and suppose that surface fields can be averaged over the bulk. The liquid crystal is now treated as if it were in an effective external uniform ordering field

$$h_{\text{eff}}(\bar{\eta}) = 2V_s(\bar{\eta}) / (D/\xi), \quad (69)$$

where  $\bar{\eta}$  is a (suitably defined) average order parameter,

and the free energy density is now given by equation (19)

$$F(\bar{\eta}) = \frac{3}{4}t\bar{\eta}^2 - \frac{1}{4}\bar{\eta}^3 + \frac{9}{16}\bar{\eta}^4 + h_{\text{eff}}(\bar{\eta}), \quad (70)$$

$$= \frac{3}{4} \left( t + \frac{4}{3}g\xi/D \right) \bar{\eta}^2 - \frac{1}{4}\bar{\eta}^3 + \frac{9}{16}\bar{\eta}^4 - 2h_1(\xi/D)\bar{\eta}.$$

The net effect is not only to introduce an effective ordering field but also to shift the temperature scale downwards. The reduced number of surface nearest neighbours means that the temperature required for the onset of nematic behaviour is lowered.

The critical parameters can now be found by comparing the parameters in the free energy of equation (70) to those in equation (19). We obtain for the critical thickness,

$$2h_1(\xi/D_{\text{cr}}) = h_c, \quad (71)$$

and hence

$$D_{\text{cr}}/\xi = .2h_1/h_c; \quad (72)$$

for the critical temperature

$$t_{\text{cr}} + \frac{4}{3}g\xi/D_{\text{cr}} = t_c, \quad (73)$$

whence, combining equations (72) and (73) we obtain

$$t_{\text{cr}} = t_c - \frac{2}{3}g(h_c/h_1). \quad (74)$$

In figures 3, 4 and 5 we compare the predictions of equation (72) and (74) with those of the full non-uniform theory. In figure 3 a plot of  $D_{\text{cr}}$  against  $h_1$  is shown for a number of different values of  $g/h_1$ . The predictions of equation (72) are remarkably well satisfied, especially for low  $h_1$ . Discrepancies occur for higher  $h_1$ , in particular for large values of  $g/h_1$ . Equation (74) predicts that  $t_{\text{cr}} = t_{\text{cr}}(g/h_1)$ , and for  $h_1 \sim 0.02$  this is very well satisfied. Equation (74) also predicts that if  $h_1 = 0$ ,  $t_{\text{cr}} \rightarrow -\infty$ , or equivalently that no critical point exists, and this also is consistent with the predictions of the full theory. On the other hand if  $g = 0$ , equation (74) predicts that  $t_{\text{cr}}$  should be independent of  $h_1$ . In figure 4 we compare this approximation to the full theory. For low  $h_1$  this is well-satisfied, although we find numerically a slight decrease in  $t_{\text{cr}}$ . Above  $h_1 \sim 0.02$  there is a more marked decrease in  $t_{\text{cr}}$ , which then stabilizes at a lower value of  $t_{\text{cr}}$  around  $h_1 \sim 0.03$  [20]. In figure 5 we check the prediction of equation (72) for the functional dependence of  $D_{\text{cr}}$  on  $h_1$ , for the case  $g = 0$ . Once again we notice that the prediction is well satisfied for  $h_1 \sim 0.02$ , but there are significant deviations for higher  $h_1$ .



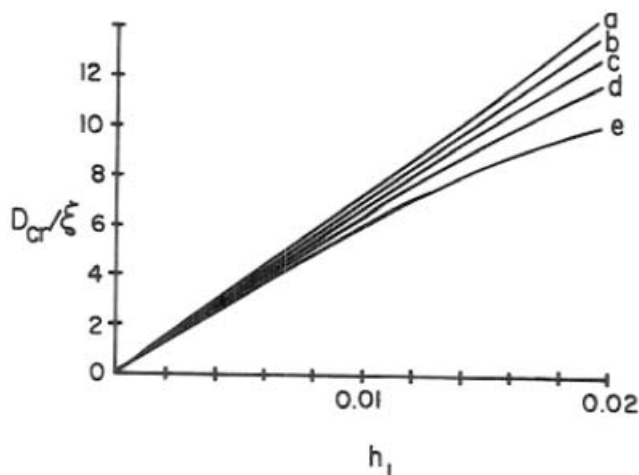


Figure 3. Comparison of the predictions for  $D_{cr}$  as a function of  $h_1$  using the full non-uniform theory and a simple averaged field approximation. Line (a) corresponds to  $g=0$ ; line (c),  $g/h_1=5$ ; line (d),  $g/h_1=10$ ; line (e),  $g/h_1=30$ . Line (b) is the prediction of the averaged field approximation.

We now make some brief comments on these results. The simple theory approximates the full theory well, from the point of view of predicting the critical parameters, for  $h_1 < 0.02$ . By comparison we remark that complete wetting by the nematic phase occurs at  $h_1 = 0.014$ , and the last vestige of non-wetting behaviour, the surface critical point, occurs at  $h_1 = 0.024$ . It seems likely, therefore, that the approximate theory loses its validity at the onset of complete wetting. Why this should be is not clear. We speculate that this might be because the finite thickness system has two nematic-isotropic interfaces which in some sense screen the effect of the surface field from the centre of the sample, thus lowering the critical temperature. We observe that at

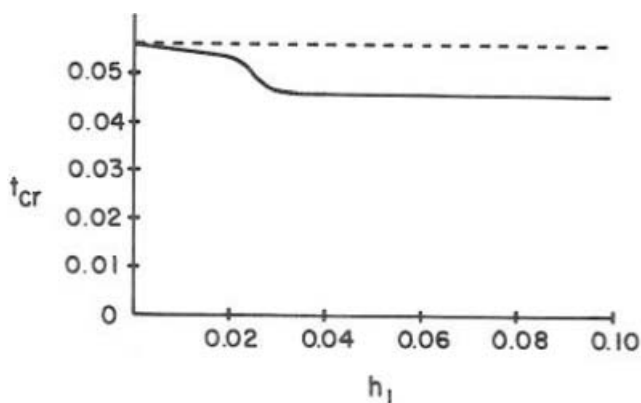


Figure 4. Prediction for  $t_{cr}$  as a function of  $h_1$  for  $g=0$ . The dotted line  $t=t_c$  is the average field prediction.

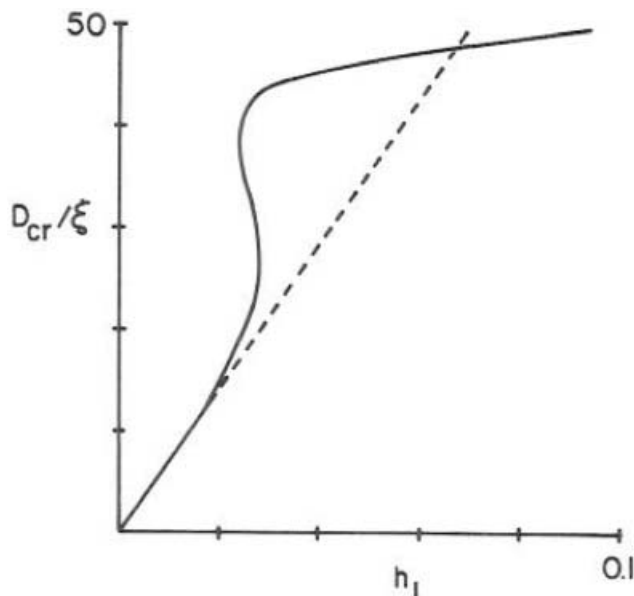


Figure 5. Prediction for  $D_{cr}$  as a function of  $h_1$  for  $g=0$  in the large  $h_1$  regime.

very high fields the critical temperature seems to stabilize, but at a lower temperature from that predicted by the simple theory. We do not understand this phenomenon, although it seems likely that there is a simple qualitative explanation. This is, however, precisely the regime in which the Kelvin equation also needs corrections as a result of the growth of nematic layers close to the wall.

## 6.2. Comparison with experiment

Yokoyama *et al.* [7] carried out experiments on liquid crystal 4-*n*-pentyl-4'-cyanobiphenyl (5CB) between SiO and PVA substrates. Essentially the experiment measures  $\bar{\eta}(T)$ . A quantitative comparison between experiment and theory is rather difficult at this stage mainly because the experimental data do not provide a precise determination of the critical thickness and temperature. Nevertheless we have been able to estimate values for the surface parameters  $h_1$  and  $g$  using the approximate formulae (72) and (74). If for the SiO surfaces we estimate  $D_{cr} \approx 1100 \text{ \AA}$  and  $T_{cr} - T_{NI} = -0.1 \text{ K}$ , then we find  $h_1 = 0.129$  and  $g = 1.38$ . In physical units this leads to  $h_1 \sim 0.53 \times 10^{-3} \text{ J m}^{-2}$  and  $g = 0.57 \times 10^{-2} \text{ J m}^{-2}$ . For the PVA surfaces if we estimate  $D_{cr} \approx 1600 \text{ \AA}$  and  $T_{cr} - T_{NI} = 0.03 \text{ K}$ , this leads to  $h_1 = 0.187$  and  $g = 1.6$ , corresponding to physical values of  $h_1 \sim 0.77 \times 10^{-3} \text{ J m}^{-2}$  and  $g \sim 0.66 \times 10^{-2} \text{ J m}^{-2}$ . In both cases we have used for  $A$ ,  $B$ ,  $C$  and  $L$  values given by Sheng [21], and the matching between model and physical parameters is as

described in equation (18) and (19). We notice, however, that the energy scale seems rather large compared to the nematic–isotropic surface tension in 5CB of  $\sim 2 \times 10^{-5} \text{ J m}^{-2}$ ; further work would appear to be fruitful.

**7. Structural forces in nematic films**

We now turn to the structural force between the two walls, which as shown in §4, is given by

$$\pi_D = -[F(\eta_m) - F(\eta_b)]. \tag{75}$$

The condition (44) shows that  $\pi_D$  is an increasing function of  $D$ , and is zero at  $D = \infty$ . Hence in this model  $\pi_D$  is always negative, or equivalently the plates attract each other.

We can also analyse the asymptotic behaviour in the large  $D$  limit. Because  $F'(\eta_b) = 0$ ,

$$F(\eta_m) - F(\eta_b) \sim (\eta_m - \eta_b)^2, \tag{76}$$

and from equation (46), we expect

$$\pi_D \sim \exp \left\{ \left[ -\frac{1}{2} F''(\eta_b) \right]^{1/2} D / \xi \right\}. \tag{77}$$

This exponential behaviour is a characteristic of the contact short-range potential assumed for the surface forces. Power law surface forces would give rise to a power law dependence of  $\pi_D$  upon  $D$  [22].

The nematic–paranematic transition can be thought of as taking place at constant  $t_{NI}$  by allowing  $D$  to vary. The disjoining pressure goes through a discontinuity at the transition. If  $\Delta t = t_{NP}(D) - t_{NI} > 0$  the high  $D$  phase is paranematic, but if  $\Delta t < 0$  the high  $D$  phase is nematic. In both cases, however,

$$\pi_D(D^-) < \pi_D(D^+) \tag{78}$$

and  $\pi_D(D)$  remains an increasing function of  $D$ . The attractive disjoining forces violate the mechanical stability condition (44); they could not be observed in a simple experimental context [15].

The discontinuity  $\Delta\pi_D = \pi_D(D^+) - \pi_D(D^-)$  along the coexistence line in  $(D^{-1}, t)$  space presents an interesting feature. In the asymptotic regime

$$\Delta\pi_D \sim \Delta F(\eta_m, t_{NP}(D)), \tag{79}$$

and hence from equation (50)

$$\Delta\pi_D \sim (s_I - s_N) \Delta t_{NP} \sim D^{-1}. \tag{80}$$

Thus initially  $\Delta\pi_D$  increases as  $D^{-1}$  increases. However, as  $D$  is further reduced the discontinuity goes through a maximum and decreases, finally disappearing at the critical point.

In figure 6 we present a typical plot of  $\pi_D$  against  $D$ , at constant  $t$ . We have chosen  $h_1 = 0.01$  and  $g = 0.15$ , the phase diagram of which is given in figure 1 (c); for these parameters  $t_{cr} = 0.0247$  and  $D_{cr}/\xi \approx 6$ . The plot is at  $t = 0.02 < t_{cr}$ . The significant features are the high  $D$  exponential behaviour, the rapid rise in  $\pi_D$  close to  $D_{cr}$ , and the lower  $d\pi_D/dD$  for smaller  $D$ . The large  $d\pi_D/dD$  in the region of  $D_{cr}$  is a critical effect indicating the closeness of the critical point; at the critical point this quantity diverges.

We would like to make contact with the experiment carried out by Horn *et al.* [15]. They measured the force between mica surfaces separated by the nematic liquid crystal 5CB in both planar and homeotropic orientations at room temperature. They found repulsive medium range structural forces and speculated that the modification of the order parameter near the surfaces was responsible for these forces. The repulsive structural forces cannot therefore be explained by the present model, confirming a prediction by Marčelja and Radić [23] who made an incomplete calculation using a simpler version of our model. In fact the experiment of Horn *et al.* was slightly more complicated than two parallel plates; in their experiment a drop of liquid crystal was placed between two cylindrical surfaces whose symmetry axes were parallel. However, this cannot change the qualitative picture. The attractive nature of the structural forces should be independent of the detailed form of  $V_s(\eta)$ , so long as it is assumed to be a contact potential. If  $V_s(\eta)$  had non-zero range this might make a difference. Repulsive structural forces have been predicted at short range [24], but these are

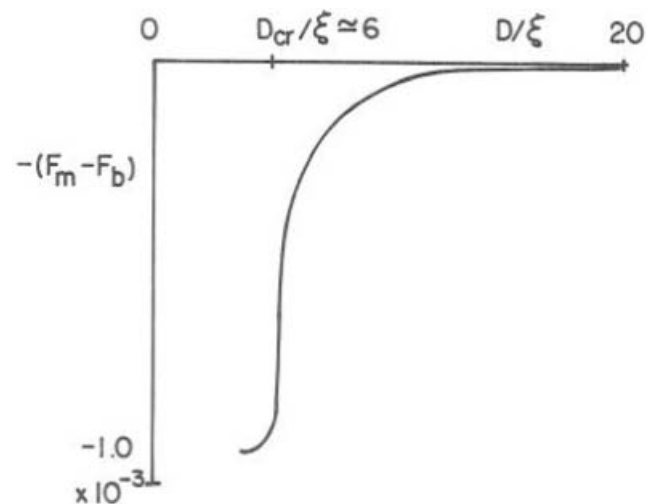


Figure 6. Disjoining force in the case  $g = 0.15$ ,  $h = 0.01$  at  $t = 0.2$  just below  $t_{cr} = 0.0247$ .

due to intermolecular correlations, and the range is much shorter than the experimental range. Evans *et al.* [12] studied the statistical mechanics of thin liquid films using a non-local density functional approach. In this system it is the density rather than the orientational order which changes, but otherwise there are strong analogies with the system we study.

However, if the primary ordering force at the surfaces is dipolar, and only indirectly nematic through the coupling between polar and nematic order parameters, then repulsion between the walls is possible, as we now show. We write the free energy per unit volume as a function of a polar order parameter  $p$ , and ignore its dependence on the nematic order parameter  $\eta$ :

$$F(p) + \zeta^2 \left( \frac{dp}{dz} \right)^2 = \bar{F} + \frac{1}{2} a p^2 + \dots + \zeta^2 \left( \frac{dp}{dz} \right)^2, \quad (81)$$

where  $F$  is in general an even function of  $p$ ,  $a > 0$  implies that there is no spontaneous dipolar order, and for simplicity we take  $F(p)$  to have the simple form as in equation (81). We have introduced a dipolar correlation length  $\zeta$ . The polar order parameter  $p$  is in general a vector, but if the walls force  $p$  to be in the  $z$  direction, we take  $p = p_z$  to be a scalar. We shall not specify a particular form of the surface field  $V_s(p)$ , other than to observe that if the walls are identical,

$$p_s = p(0) = -p(D), \quad (82)$$

and  $p(z)$  is *antisymmetric* about  $z = D/2$ , by contrast with  $\eta(z)$  which is symmetric, and consequently  $p(D/2) = 0$ . The Euler–Lagrange equations for  $p$  and the crucial thermodynamic quantities can be written down by analogy with equations (27), (28), (40), (41), the equivalent equations for  $\eta$ ; we find

$$\zeta^2 \left( \frac{dp}{dz} \right)^2 = F(p) - F(0) + K_m^2 = F(p) - F_m, \quad (83)$$

where

$$K_m = \zeta \left( \frac{dp}{dz} \right)_{z=D/2}, \quad (84)$$

$$\phi = 2\sigma + (D/\zeta) F_m, \quad (85)$$

and the disjoining force is given by

$$\pi_d = -(F_m - F_b), \quad (86)$$

where the bulk free energy density  $F_b$  is

$$F_b = F(0). \quad (87)$$

Combining equations (83), (86) and (87) we obtain immediately

$$\pi_D = K_m^2 > 0, \quad (88)$$

or equivalently a *repulsive* long-range force between the plates. The large  $D$  behaviour of the disjoining force can be obtained from the analogue of equation (31),

$$\frac{D}{\zeta} \cong \int_0^{p_s} \frac{dp}{\sqrt{(\frac{1}{2} a p^2 + K_m^2)}}, \quad (89)$$

from which, combining equations (88) and (89),

$$\pi_D \sim \exp \left[ -\frac{1}{2} \left( \frac{1}{2} a \right)^{1/2} D/\zeta \right]. \quad (90)$$

In fact we expect both dipolar and nematic effects at the interfaces, which give rise to competing attractive and repulsive forces. A further complication might be the long-range nature of the electrostatic forces which interact with the dipoles. The crucial feature which ensures the repulsive force, however, is the anti-symmetry of the profile  $p(z)$  around the centre of the slab. The experimentally observed repulsive disjoining force is thus indirect evidence of the importance of surface dipolar forces, giving rise to surface dipole order. The dipolar forces do not need to be strictly electrical dipole forces; there is no evidence to suggest that mica is electrically active. However the molecules of 5CB do not have complete inversion symmetry along their major axis, and this may give rise to surface forces leading to dipolar surface order. We emphasize however that surface nematic order alone leads to an attractive disjoining force.

## 8. Conclusions

The primary aim of this study has been the investigation of the statistical mechanics of a directionally uniform nematic, in a thin slab between identical walls, in particular close to the nematic–isotropic transition. We have used a Landau–de Gennes mean field type theory with surface interactions of zero range. The theory is a one order parameter theory, and as such is applicable close to any order–disorder transition in a thin slab geometry. A secondary aim of this study has been to make a general contribution to the theory of the effects of finite size on first order phase transitions. We have also endeavoured, as some previous workers have not, to maintain contact between the results of the statistical mechanical calculations and more general thermodynamic considerations.

The theory predicts, almost universally, that in a finite slab the first order nematic–isotropic transition is shifted, and for sufficiently thin systems this first order

line terminates at a critical point. For large thicknesses the shift in transition temperature is inversely proportional to thickness, as predicted by the thermodynamic Kelvin approximation. For thinner systems the coexistence line is described by a Clausius–Clapeyron relation. In fact in many cases the asymptotic, large thickness result remains true even at lower thicknesses. The only exception, within the theory, to the generic phase diagram occurs when the walls are completely disordering; then there is no critical point. So long as this is not the case the high temperature isotropic phase is properly called a paranematic phase, because of the wall-induced order. This order can become quite significant close to the transition, in particular when the walls are wet by the nematic phase, and as the critical point is approached.

For many cases of partial wetting ( $\cos \theta \neq 0$  or  $\pi$ ) the walls are such as to slightly favour order when the bulk phase is disordered, but to disfavour order when the bulk is nematic. In the thick slab there will then be two possible shape profiles, one with increased and the other with decreased wall order. Although the nematic and paranematic profiles become identical at the critical point, in general the shape of the profile changes before the critical point, and depends on whether  $V_s'(\bar{\eta})$  is greater than or less than zero.

The statistical mechanics of the finite thickness system has a strong analogy with that of a nematic in an ordering field. Indeed, our results show that in the weak surface field regime the phase diagram of the finite system would be well predicted by averaging the surface fields over the whole system. The finite magnetic field critical point has not hitherto been experimentally accessible; the finite thickness effects are perhaps more so.

We have also studied the structural force between two walls. We find that surface nematic ordering gives rise to attractive forces between walls, but that the experimentally observed repulsion can only be understood in terms of surface dipole ordering.

The calculations of the asymptotic behaviour of various parameters in the large  $D$  limit should be directly amenable to experiment. We draw particular attention to behaviour of the discontinuity in the surface order parameter ( $\Delta\eta_0$  in §5) when the wall is such that one phase (either N or I) completely wets it. We find that in the large  $D$  limit, this discontinuity is normally inversely proportional to thickness (recalling that in a semi-infinite system it would be continuous). However the discontinuity is proportional to  $D^{-1/2}$  if the parameters at the wall are appropriate to a critical wetting transition. This includes the particular case of a wall wet by the isotropic phase. Such wetting is in a

sense less powerful, and unsurprisingly  $\Delta\eta_0$  is greater, i.e.  $D^{-1/2} > D^{-1}$ . Finally, of course, if the wall is not completely wet by either phase  $\Delta\eta_0$  remains finite at  $D^{-1}=0$ , which is larger still.

We next ask in what way the modelling of the problem might be incomplete. The contact interactions at the wall are an approximation which will give rise to incorrect asymptotic behaviour of the disjoining pressure at large thicknesses. If the surface interactions are power-law like this could be serious; however liquid crystal orienting interactions may be short-range. In any event the experiments remain unexplained and further experiments are clearly desirable. Similar qualifications apply to the whole Landau–de Gennes formalism, but it has proved useful in other contexts.

Perhaps a larger problem is concerned with the effect of fluctuations. For the nematic–isotropic transition fluctuations are important even for bulk three-dimensional systems, in the sense that the Ginzburg criterion [25] is not satisfied close to the transition. Presumably this becomes even more important for a thin system which is becoming in some sense two dimensional. This may mean that the theory is unreliable from a quantitative point of view, especially for thinner slabs. However, presumably the qualitative picture remains viable. We note, however, that in a system of cylindrical or spherical pores, the fluctuations become sufficiently powerful to broaden the singularities associated with a first order phase transition. A mean field theory of the type used in this paper would be unable to treat this phenomenon. In the nematic case for such a geometry it would also no longer be possible to ignore director inhomogeneities.

Finally, we turn to directions for future research. First of all there is a need for further experiments. The experiments on the nematic–isotropic transition at finite thickness by Yokoyama *et al.* [7], while strongly suggestive, are by no means conclusive, and unambiguous observations of the finite thickness critical point are clearly desirable. Similarly there is a need for further experimental work on the disjoining pressure, especially in view of the possible competition between attractive and repulsive structural forces. On the theoretical side we emphasise that the present theory is in fact the simplest possible. More sophisticated attempts at modelling should include explicitly the possibility of density change close to walls and the full nematic ordering tensor. Intriguing phenomena may also result when the two walls are no longer identical, including the possibility that the ordering temperature may no longer be a monotonic function of thickness.

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- [19] The notation we adopt is consistent with that in the statistical mechanics literature; see, for example, M.E. Fisher, H. Nakanishi. *Phys. Rev. Lett.*, **49**, 1565; the temperature variable is  $t$  and the surface fields are  $h_1$  and  $g$ . For translation: Sheng's  $g$  [3] is essentially our  $h_1$ , Lipowsky and Gompper's [10]  $a_1$  is our  $g$ , and Fan and Stephen's  $\beta$  [17] is our  $t$  (1982).
- [20] These results are in slight disagreement with those of Sheng [3]. For  $g=0$  we find  $t_{cr}$  weakly decreasing with  $h_1$ , although independent in the simple approximation. By contrast Sheng [3] finds  $t_{cr}$  increasing with  $h_1$ . The effects are, however, small.
- [21] If we translate the notation of Sheng [3], we obtain for the parameters in equation (18):  $A^1=8.67 \times 10^4 \text{ J m}^{-3} \text{ K}^{-1}$ ,  $B=2.12 \times 10^6 \text{ J m}^{-3}$ ,  $C=1.74 \times 10^6 \text{ J m}^{-3}$ ,  $T^*=307.14 \text{ K}$ ,  $L=4.5 \times 10^{-12} \text{ J m}^{-1}$ ,  $\zeta=13.2 \text{ \AA}$ .
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## Appendix 1

### Derivation of the stability conditions

In this appendix we derive the stability conditions equations(38) and (39) used in the derivation of the equilibrium values of  $\eta_0$  and  $\eta_m$  in §4. We recall that these quantities are solutions of the equations  $\phi_{\eta_0}=0$ ,  $\phi_{\eta_m}=0$  where  $\phi(\eta_0, \eta_m)$  is described by equations(28) and (29). The stability equations, conditions that a minimum in  $\eta$  has been found, are

$$\phi_{\eta_0\eta_0} > 0, \quad (A1)$$

$$\phi_{\eta_0\eta_0}\phi_{\eta_m\eta_m} - \phi_{\eta_0\eta_m}^2 > 0. \quad (A2)$$

In fact the equation  $\phi_{\eta_m}=0$  yields an implicit relation between  $\eta_0$ ,  $\eta_m$  and  $D$ , and as a result equation (A 2) can be rephrased as

$$\frac{d^2\phi}{d\eta_m^2} > 0, \quad (A3)$$

where  $\phi$  is now thought of as being a function of the one variable  $\eta_m$ .

From equation (28) we derive

$$\phi_{\eta_0\eta_0} = 2\sigma_{\eta_0\eta_0}. \quad (A4)$$

Now from equation (29)

$$\sigma_{\eta_0} = \mp 2\sqrt{[F(\eta_0) - F(\eta_m)] + V'_s(\eta_0)}, \quad (A 5 a)$$

$$= 0. \quad (A 5 b)$$

Hence

$$\sigma_{\eta_0\eta_0} = \mp \frac{F_{\eta_0}(\eta_0)}{\sqrt{[F(\eta_0) - F(\eta_m)]}} + V''_s(\eta_0). \quad (A6)$$

We now substitute from equation (A 5) into equation (A 6), yielding

$$\sigma_{\eta_0\eta_0} = -\frac{2F_{\eta_0}(\eta_0)}{V'_s(\eta_0)} + V''_s(\eta_0), \quad (A 7)$$

$$= -\frac{2}{V'_s(\eta_0)} \left[ F_{\eta_0}(\eta_0) - \frac{1}{2} V'_s(\eta_0) V''_s(\eta_0) \right], \quad (A 8)$$

$$= -\frac{2}{V'_s(\eta_0)} \frac{\partial}{\partial \eta_0} \left[ F(\eta_0) - \frac{1}{4} (V'_s(\eta_0))^2 \right], \quad (A 9)$$

and hence from equation (32)

$$\phi_{\eta_0\eta_0} = 2\sigma_{\eta_0\eta_0} = -\frac{4F'_m(\eta_0)}{V'_s(\eta_0)}. \quad (A10)$$

Hence from equations (A 1) and (A 10) we derive the condition (38)

$$\frac{F'_m(\eta_0)}{V'_s(\eta_0)} < 0.$$

We shall derive equation (39) by starting with the condition (A 3). From equation (28)

$$\frac{d\phi}{d\eta_m} = 2 \frac{d\sigma}{d\eta_m} + \frac{D}{\xi} \frac{dF(\eta_m)}{d\eta_m}, \quad (A 11 a)$$

$$= 0, \quad (A 11 b)$$

where equation (A 11 b) is the stationary condition, but can be thought of as the defining equation for a (locally defined) function  $D(\eta_m)$ . Then

$$\frac{d^2\phi}{d\eta_m^2} = 2 \frac{d^2\sigma}{d\eta_m^2} + \frac{D}{\xi} \frac{d^2F(\eta_m)}{d\eta_m^2}. \quad (A12)$$

However, using equation (A 11 b)

$$2 \frac{d^2\sigma}{d\eta_m^2} = -\frac{d}{d\eta_m} \left[ D(\eta_m) \frac{dF(\eta_m)}{d\eta_m} \right], \quad (A 13)$$

$$= -\frac{dD(\eta_m)}{d\eta_m} \frac{dF(\eta_m)}{d\eta_m} - D(\eta_m) \frac{d^2F(\eta_m)}{d\eta_m^2}, \quad (A 14)$$

and combining equations (A 12) and (A 14) we obtain

$$\frac{d^2\phi}{d\eta_m^2} = \frac{1}{\xi} [D - D(\eta_m)] \frac{d^2F(\eta_m)}{d\eta_m^2} - \frac{1}{\xi} \frac{dD}{d\eta_m} \frac{dF(\eta_m)}{d\eta_m}, \quad (A 15)$$

$$= -\frac{1}{\xi} \frac{dD}{d\eta_m} \frac{dF(\eta_m)}{d\eta_m}, \quad (A 16)$$

$$= -\frac{1}{\xi} \left[ \frac{dF(\eta_m)}{d\eta_m} \right]^2 \frac{dD}{d\eta_m} / \frac{dF(\eta_m)}{d\eta_m}. \quad (A 17)$$

Now, recalling equation (32)  $F_m(\eta_0) = F(\eta_m)$ , and changing the independent variable from  $\eta_m$  to  $\eta_0$ , we derive

$$\frac{d^2\phi}{d\eta_m^2} = -\frac{1}{\xi} \left[ \frac{dF(\eta_m)}{d\eta_m} \right]^2 \frac{D'(\eta_0)}{F'_m(\eta_0)}. \quad (A18)$$

Hence  $\frac{d^2\phi}{d\eta_m^2} > 0$  implies the relation (39)

$$\frac{D'(\eta_0)}{F'_m(\eta_0)} < 0.$$

## Appendix 2

In this appendix we discuss in more detail the behaviour of the graph of  $D(\eta_0)$ , derived from equations (31) and (32) and used in order to derive the phase diagram discussed in § 6. This will enable us to see more clearly the origin of the critical point within the theory, and we shall also see the connection between the graph of  $D(\eta_0)$  and the shape of the profile  $\eta(z)$ .

We consider first the simplest case of  $g=0$ ; in this case the wall always orders the liquid crystal, so  $\eta_0 > \eta_m$ . We also find  $\cos \theta > 0$  in the semi-infinite system, and from the Kelvin approximation  $t_{NP}(D)$  increases as  $D$  decreases in the asymptotic large  $D$  regime, a trend which in fact continues for smaller  $D$  right up to the critical point. In figure 7  $D(\eta_0)$  has been plotted for an increasing sequence of temperatures, starting at  $t_{NI}$  and terminating at the nematic-paranematic critical temperature  $t_{cr} = t_{NP}(D_{cr})$ .

The main features of these graphs can be understood as follows. For pedagogical reasons we start with figure 7(b), in which  $D(\eta_0)$  has three separate branches. The low  $\eta_0$  solution corresponds to the thin film of low adsorption regime, i.e. low  $\eta_0$  and low  $\eta_m = \eta_b$  in the  $D = \infty$  limit; the intermediate  $\eta_0$  solution corresponds to the semi-infinite case in which the surface is more or less nematic, but the bulk is isotropic (the so-called thick or wetting film solution,  $\eta_m$ , is still small); the high  $\eta_0$  solution corresponds to the nematic liquid. In all cases the physical solutions correspond to  $D(\eta_0)$  being a decreasing function of  $D'$ , this means that the smaller the system, the more the order, as expected for  $h_1 > 0$ . The regions where  $D(\eta_0)$  is an increasing function of  $\eta_0$  (the dotted lines) are unstable solutions. For  $h_1 \sim 0.12$  the nematic phase does not wet the wall and in general, the low  $\eta_0$  branch is more stable than the intermediate branch. However for  $h_1 > 0.12$  we do get wetting and the intermediate branch is more stable. As discussed in equation (54) at the finite  $D$  transition to the nematic

branch  $\Delta\eta_0 \sim D^{-1} \sim \Delta t_{\text{NP}}$ , indeed as  $t$  approaches  $t_{\text{NI}}$ , the wetting film solution for  $D=\infty$  approaches the nematic solution; this corresponds to the intermediate branch of  $D(\eta_0)$  narrowing and squeezing towards the upper nematic branch of  $D(\eta_0)$ , as can be seen in figure 7(a) where it has finally disappeared. On the other hand as  $t$  is increased the wetting film branch becomes progressively less stable and it disappears between figures 7(b) and (c) for  $D=\infty$ , as the unstable thin film  $D(\eta_0)$  branch hits the stable thick film branch. Thenceforth (figure 7(c)) the thick film only leaves a ghost at finite  $D$ , in the form of an intermediate maximum of  $D(\eta_0)$ . Eventually the bulk nematic phase becomes unstable at a temperature  $t_{\text{N}}^*$  ( $=\frac{1}{24}$  in our model for  $h=0$ ), and then only one branch of  $D(\eta_0)$  remains (cf. figure 7(d)). Notice however that a nematic phase still exists for low  $D$ , and the  $D=\infty$  solution has now become a maximum in  $D(\eta_0)$ . Finally in figure 7(e) at  $t=t_{\text{cr}}$ ,  $D(\eta_0)$  becomes monotonic with an inflexion point at  $\eta_0=\eta_0^{\text{cr}}$ . The phase transition between the low  $\eta_0$  and high  $\eta_0$  branches of  $D(\eta_0)$  disappears here, so this is the critical point.

The situation is slightly different for  $h_1 \approx 0.024$ , for then there is no boundary transition and only one possible value of  $\eta_0$  for  $D=\infty$ , implying the absence of the left-hand branch in figures 7(a) and (b). Figure 7(b) is thus directly followed by figure 7(d). Otherwise the picture is qualitatively the same. In all these cases the low temperature solution is the nematic branch. If  $t$  is increased at fixed  $D$  the solution jumps to another branch at a phase transition temperature  $t_{\text{NP}}(D) > t_{\text{NI}}$ . For  $D \leq D_{\text{cr}}$ , on the other hand, this is no longer possible and there is no phase transition.

We now examine what happens as we turn on progressively a surface disordering effect. The crucial quantity to monitor is  $\eta_0^*$ , defined by

$$V'_s(\eta_0^*) = -h_1 + g_1\eta_0^* = 0. \quad (\text{B1})$$

The two points to bear in mind, from equations (26) and (27), are that the sign of  $V'_s(\eta_0)$  gives the sign of  $(d\eta/dz)_{z=0}$ , and that  $(d\eta/dz)$  is monotonic for  $0 < z < D/z$ . From this we conclude that if  $\eta_m > \eta_0^*$ , then  $\eta_m > \eta_0 > \eta_0^*$ , and conversely if  $\eta_m < \eta_0^*$  then  $\eta_m < \eta_0 < \eta_0^*$ . There are now three cases, depending on the size of  $\eta_0^*$ . We list and discuss them in order of increasing surface disorder, or equivalently, decreasing  $\eta_0^*$ .

In case (i)  $\eta_0^* > \eta_{\text{N}}(t_{\text{NI}}) = \frac{2}{9}$ . Then because  $\eta_{\text{N}}(t)$  is a decreasing function of  $t$ , the surface potential is ordering both in the nematic phase and in the isotropic phase in the region of  $t_{\text{NI}}$ . The structure of  $D(\eta_0)$  is now very similar to that in figure 7, and  $t_{\text{NP}}(D) > t_{\text{NI}}$  as in that case also. There is one slight difference. Because  $\eta_0 > \eta_m$ , but also  $\eta_0 < \eta_0^*$  in order to maintain the monotonicity of  $\eta(z)$ , as  $D \rightarrow 0$ ,  $\eta_0 \rightarrow \eta_0^*$ . Because of the similarity of this case to the simple ordering case we do not show a separate diagram for this.

In case (ii)  $\eta_0^* < \eta_{\text{N}}(t_{\text{NI}})$ , but  $\cos\theta > 0$ . In this model  $\cos\theta=0$  corresponds to  $h_1 = g\eta_c = g/9$  [1]. A metastable bulk nematic continues above  $t_{\text{NI}}$  with  $\eta_{\text{N}}(t)$  decreasing with  $t$ , until it reaches bulk instability at  $t_{\text{N}}^*$  ( $=\frac{1}{24}$  for  $h=0$  in this model), by which point  $\eta_{\text{N}}$  has reached  $\eta_{\text{N}}^*$ ; in this model  $F(\eta)$  has an inflexion point at  $\eta_{\text{N}}^* = \frac{1}{6}$ . The crucial region of interest is above  $t_{\text{NI}}$ , because  $t_{\text{NP}}(D) > t_{\text{NI}}$ . We consider case (ii (a)):  $\eta_{\text{N}}(t_{\text{NI}}) > \eta_0^* > \eta_{\text{N}}^*$ , and case (ii (b)):  $\eta_{\text{N}}^* > \eta_0^* > \eta_c$

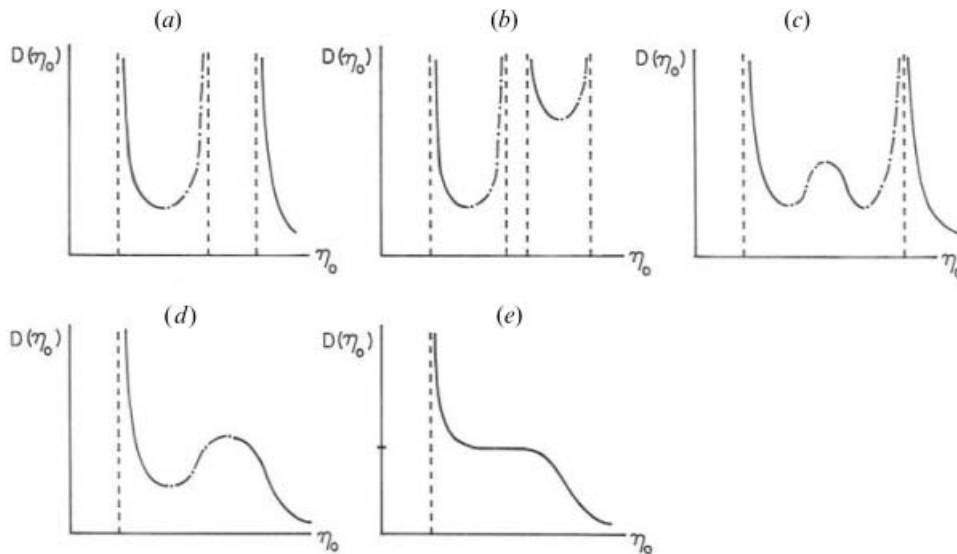


Figure 7. Graphs of  $D(\eta_0)$  as temperature is increased for  $g=0$ . (a)  $t=t_{\text{NI}}$ ; (b)  $t_1 > t_{\text{NI}}$ ; (c)  $t_2 > t_1$ ; (d)  $t_3 > t_2$ ; (e)  $t=t_{\text{cr}}$ .

separately. In both cases, however, we observe that at  $t_{NI}$ ,  $V_s'(0) < 0$  in the isotropic phase and so as far as the isotropic phase is concerned the surface orders, but  $V_s'(\eta_N(t_{NI})) > 0$ , and hence from the point of view of the nematic phase the surface is disordering.

In figure 8 we show a number of plots of  $D(\eta_0)$  for increasing values of  $t$  in case (ii (a)). In figure 8(a), close to  $t_{NI}$ , there are two branches of  $D(\eta_0)$ . The left-hand branch is the isotropic branch. The physical part of this branch has  $D$  decreasing with  $\eta_0$ , corresponding to increased order at the surfaces. The right-hand branch is the nematic branch, but on this branch as  $\eta_0$  decreases, so does  $D$ , corresponding to disordering surfaces. On this branch as  $\eta_0 \rightarrow \eta_N^*$ ,  $D \rightarrow 0$ . There is also an unstable  $\eta_0 = \eta_0^*$  (for all  $D$ ) branch, as can be seen from equations (26) and (27). The unstable part of the isotropic branch also hits  $\eta_0 = \eta_0^*$ , and terminates there, at a finite value of  $D$ , because the change of sign of  $(d\eta/dz)$  at  $\eta_0 = \eta_0^*$  destroys the solution. However as  $t$  increases  $\eta_N(t)$  decreases, eventually reaching  $\eta_0^*$  in figure 8(b). The surface is now neutral with respect to the nematic phase, and ordering with respect to the isotropic phase. The right-hand branch of  $D(\eta_0)$  is thus squashed into the line  $\eta_0 = \eta_0^*$ . As  $t$  is further increased the nematic branch has  $D$  increasing with decreasing  $\eta_0$ ,

consistent with  $\eta_N(t) < \eta_0^*$  and ordering interfaces (cf. figure 8(c)). Note that  $D(\eta_0^*)$  remains zero. The progression from figure 7(c) to 8(d) is analogous to that from figure 7(b) to (d) in the case of continuous wetting: the bulk nematic is destabilized. Finally (not shown) a critical point is reached, by analogy with figure 7(e).

Schematic order parameter profiles for the coexisting phases within the slab for case (ii (a)) are shown in figure 9. In figure 9(a) the paranematic phase is more ordered near the walls, but the nematic phase is less ordered near the walls, corresponding to the respective branches of  $D(\eta_0)$  in figure 8(a). In figure 9(b) the paranematic phase remains more ordered near the wall, but the nematic profile is more constant, corresponding to  $D(\eta_0^*)$  in figure 8(b). However in figure 9(c) both profiles are more ordered close to the wall, corresponding to subsequent pictures in figure 8, and remaining true at the critical point.

In figure 10 we present plots of  $D(\eta_0)$  for case (ii (b)), for temperatures increasing from  $t_{NI}$  to  $t_{cr}(D)$ . Figure 10(a) represents the situation at (and just above)  $t_{NI}$  and is analogous to figure 8(a). We remark that in this figure the turning point of  $D(\eta_0)$  takes place for  $\eta_{max} < \eta_0 < \eta_0^*$ , where  $\eta_{max}$  is the point at which  $F(\eta)$  has

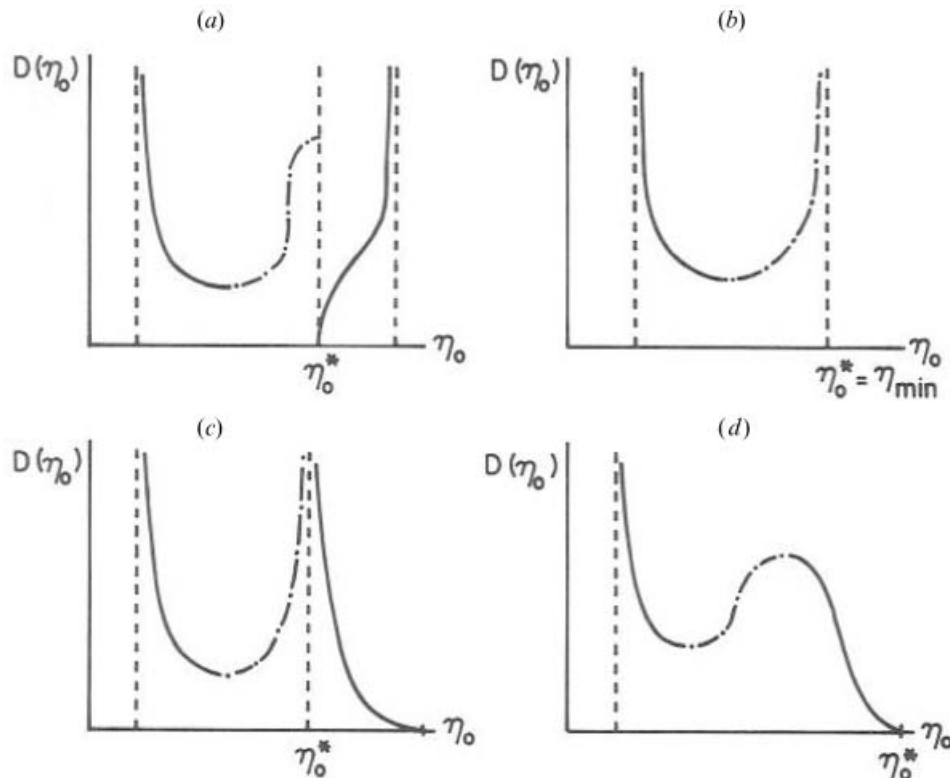


Figure 8. Graphs of  $D(\eta_0)$  for  $\cos \theta > 0$ ,  $g \neq 0$ ; case (ii (a)) in the text. (a)  $t = t_{NI}$ ; (b)  $t = t_1^* > t_{NI}$ ; (c)  $t_1^* < t < t_N^*$ ; (d)  $t_N^* < t < t_{cr}$ .



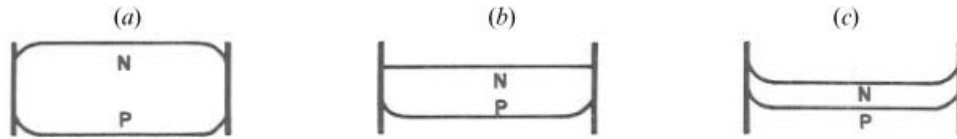


Figure 9. Coexisting profiles for the case described in figure 8. N is the nematic profile; P is the paranematic profile. (a)  $t < t_1^*$ ; (b)  $t = t_1^*$ ; (c)  $t > t_1^*$ . At  $t = t_{cr} > t_1^*$  the two profiles become identical.

a maximum. This can be seen from equation (32), which shows that  $F(\eta_m)$  and  $\eta_m$  have turning points close to but slightly above the maximum of  $F(\eta_0)$ , and from equation (31) which gives  $D$  in terms of an integral between  $\eta_m$  and  $\eta_0$ . Thus we expect a qualitative change when  $\eta_{max}$ , which is an increasing function of  $t$ , reaches  $\eta_0^*$ , at a temperature  $t^*$  (cf. figure 10 (b)). At  $\eta_0^*$  the governing equations are satisfied for arbitrary  $D$ , and

$$\lim_{\eta_0 \rightarrow \eta_0^*} D(\eta_0) = \lim_{\eta_0 \rightarrow \eta_0^*} D(\eta_0).$$

As  $t$  is increased further,  $\eta_0^*$  is now less than  $\eta_{max}$ , and so there is a region of instability on the right-hand branch of  $D(\eta_0)$  (cf. figure 10 (c)), and a region of what might still be called nematic stability (for small  $D$ ) on the left-hand branch of  $D(\eta_0)$ . Finally (cf. figure 10 (d))

the kink in the branch of  $D(\eta_0)$  disappears at a critical point.

The profiles  $\eta(z)$  corresponding to figure 10 are the same as those in figure 8 corresponding to case (ii (a)). Thus the profiles corresponding to figure 10 (a) are shown in figure 9 (a); the exceptional case corresponding to figure 10 (b) is shown in figure 9 (b), and figure 9 (c) represents the profiles of figure 10 (c).

We now consider case (iii) for which  $\cos \theta < 0$ , and  $0 < \eta_0^* < \eta_c$ . The surface disorder has now increased sufficiently to depress the ordering transition in a finite system. The relevant region to examine is now  $t < t_{NI}$ . Graphs of  $D(\eta_0)$  are shown, now in order of decreasing temperature, in figure 11. The features of this set of graphs are analogous to those of figure 10. Close to  $t_{NI}$  (cf. figure 11 (a))  $\eta_0^* < \eta_{max}$ ; there is a left-hand paranematic branch of  $D(\eta_0)$  extending to  $D=0$  at  $\eta_0^*$ ,

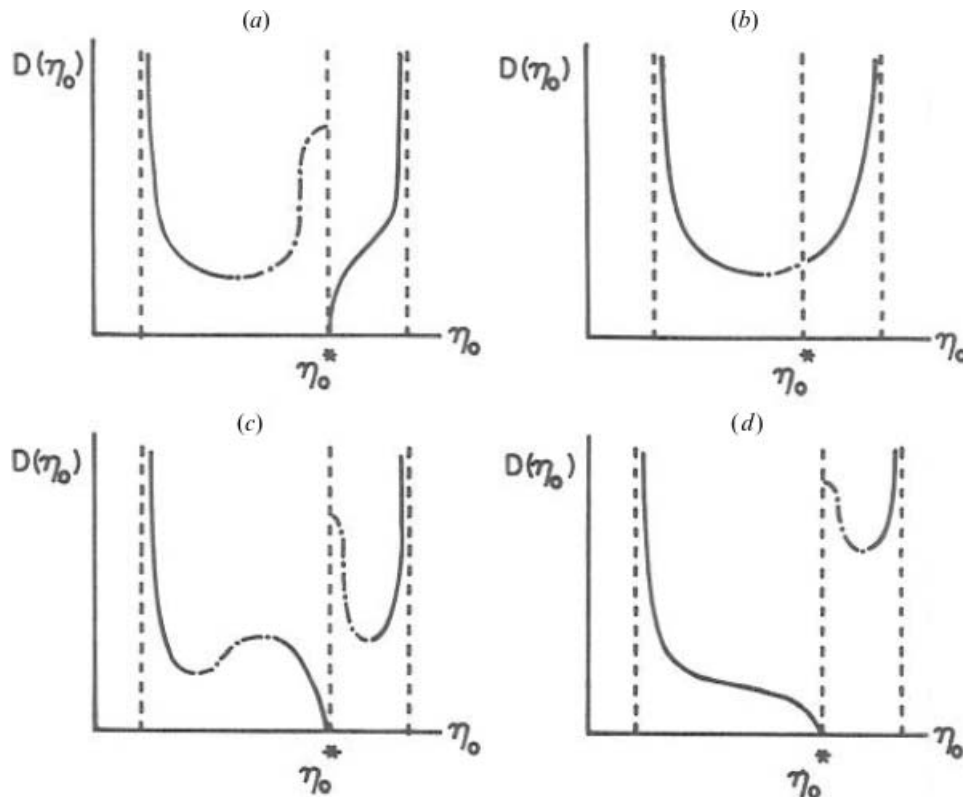


Figure 10. Graphs of  $D(\eta_0)$ ,  $g \neq 0$ , case (ii (b)) in the text. (a)  $t = t_{NI}$ ; (b)  $t = t^* > t_{NI}$ ; (c)  $t = t_1 > t^*$ ; (d)  $t = t_{cr} > t_1$ .

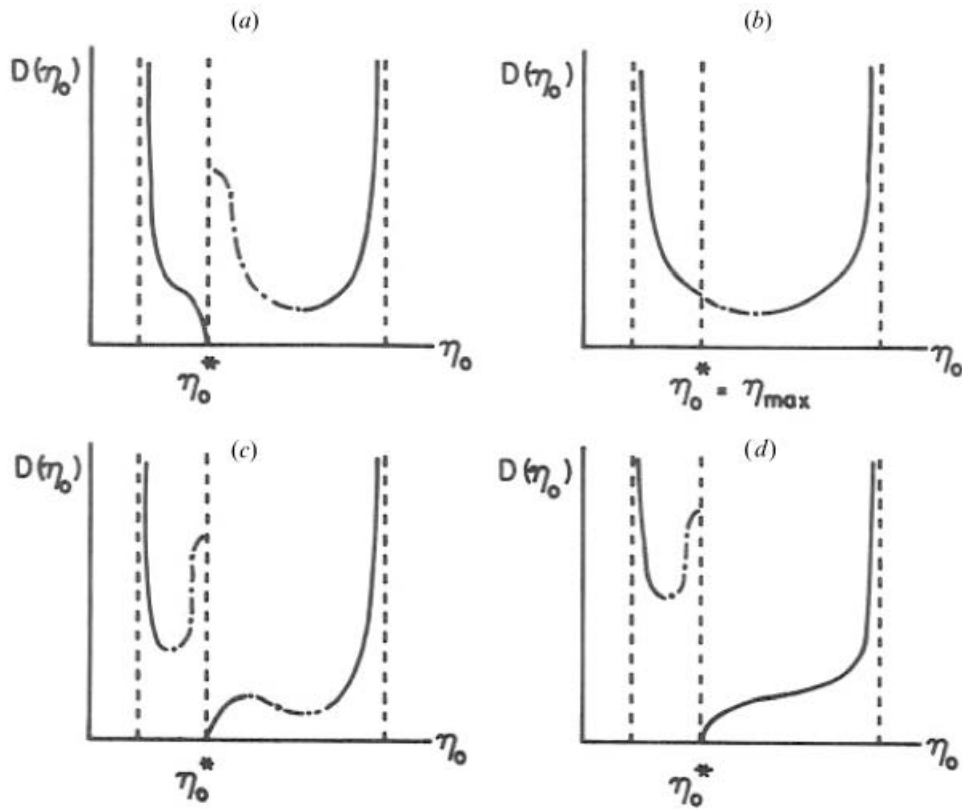


Figure 11. Graphs of  $D(\eta_0)$ ,  $\cos \theta < 0$ . (a)  $t = t_{NI}$ ; (b)  $t = t^* < t_{NI}$ ; (c)  $t = t_1 < t^*$ ; (d)  $t = t_{cr} < t_1$ .

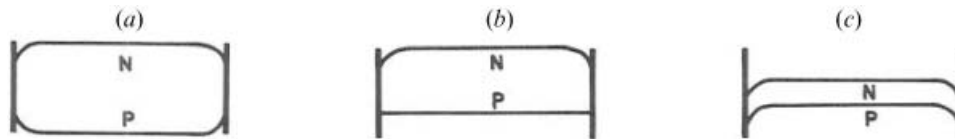


Figure 12. Coexisting profiles for case described in figure 11. (a)  $t_{NI} > t > t^*$ ; (b)  $t = t^*$ ; (c)  $t^* > t > t_{cr}$ .

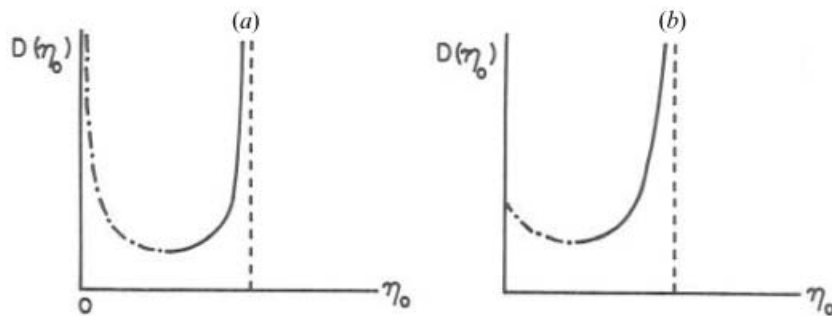


Figure 13. Graphs of  $D(\eta_0)$  for a disordering surface  $h_1 = 0$ , (a)  $0 < t < t_{NI}$ ; (b)  $t < 0$ .

and a right-hand nematic branch of  $D(\eta_0)$  which becomes unstable close to  $\eta_0^*$  and terminates at a finite value of  $D$  at  $\eta_0^*$ . As  $t$  is decreased  $\eta_{\max}$  decreases and reaches  $\eta_0^*$  (cf. figure 11(b)), there is then an exchange of stability between the two branches and part of the paranematic branch lies to the right of  $\eta_0^*$  (cf. figure 11(c)). Finally the kink in  $D(\eta_0)$  disappears at a critical point (cf. figure 11(d)).

The coexisting profiles corresponding to these graphs are shown in figure 12. In figure 12(a), near  $t_{\text{NI}}$ , as in the previous cases there is a nematic phase slightly disordered near the wall and a paranematic phase ordered close to the wall, corresponding to figure 11(a). Figure 12(b) corresponds to the situation in figure 11(b); for sufficiently small  $D$  the paranematic profiles have  $\eta(z) = \eta_0^*$ . Then the coexisting profiles in figure 12(c) are both less ordered near the wall; this is consistent with both profiles corresponding to  $\eta_0$  on the right hand branch of  $D(\eta_0)$ .

Finally we come to the case  $h_1 = 0$ , when the surface is purely disordering. Depending on the value of  $g$  the isotropic phase wets one wall partially ( $-1 < \cos \theta < 0$ ) or completely ( $\cos \theta = -1$ ). Complete wetting occurs if  $g > \frac{1}{3}$ . Plots of  $D(\eta_0)$  for  $0 < t < t_{\text{NI}}$  and  $t < 0$  are shown in figure 13(a) and (b), respectively. For  $0 < t < t_{\text{NI}}$  there are two solutions:  $\eta_0 = \eta_m = 0$  and a second solution which is the stable branch of  $D(\eta_0)$ . For complete wetting the right-hand asymptote approaches  $\eta_0 = 0$  as  $t \rightarrow t_{\text{NI}}^-$ . From figure 13(a) it is clear that there is no critical point for  $t > 0$ . For  $t < 0$ ,  $D(\eta_0)$  is finite and  $D'(\eta_0)$  is negative. There is thus no critical point here either, except in the purely formal limit of  $t_{\text{cr}} = -\infty$ , at which  $D(\eta_0 = 0) = 0'(\eta_0 = 0) = 0$ . We remark that below  $t = 0$  the bulk isotropic phase is unstable. However for a finite system with low enough  $D$ , the  $\eta(z) = 0$  phase can be stabilized, even though it corresponds to a local maximum of  $F(\eta)$ , because then  $\sigma = 0$ .