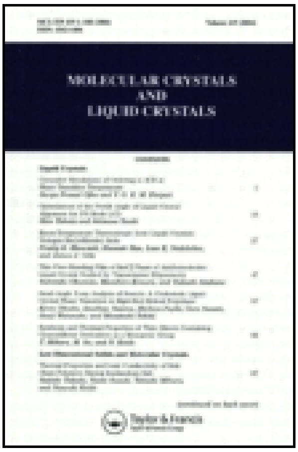

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Density Functional Theory of Liquid Crystal Phases

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DENSITY FUNCTIONAL THEORY OF LIQUID CRYSTAL PHASES

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Abstract A general discussion is given of the application of density functional theory of liquids to liquid crystal problems, with particular emphasis to the onset of smectic phases. Hard particle systems have long been used as useful paradigms of liquid crystal behaviour. In this paper we also present recent work on the phase diagram of hard spherocylinders, using a non-local density functional theory of a kind which has been successful in the study of hard sphere thermodynamics. We also discuss the effect of electric quadrupolar forces on the phase diagram of Onsager-like systems.

Keywords: phase transitions, smectics, theory, density functional

1. DENSITY FUNCTION THEORY IN LIQUIDS AND THE LIQUID-SOLID TRANSITION

In this section of the talk, we want to give a general background discussion of the use of the Density Functional Theory in Liquid Crystal problems. In the other sections of the talk we shall present some of our recent work on specific nematic and smectic systems. The Density Functional method is by now rather widespread. It would be misleading, indeed, to give a discussion which dwells solely in the liquid crystalline domain; the method has migrated to liquid crystal science from the theory of liquids, and in particular the theory of *inhomogeneous* liquids. There has also been, over the last few years, substantial progress in understanding the *freezing transition*, in which one considers solids as (extremely!) inhomogeneous liquids, and this progress is of great relevance, at least in principle, in the global understanding of the mesomorphic phases.

Two strategies which may be adopted by a statistical mechanician seeking the properties of a fluid are: i) calculate the partition function

$\mathcal{Z}$ (all relevant properties can then be found by taking suitable derivatives of $\mathcal{Z}$), or, ii) write down some suitable free energy as a function of some relevant important parameters and then minimise it. Both these strategies *are* of course in common use, and so it is of some interest to understand how they are connected. It is also well known that, in practice, *both* strategies can easily come badly unstuck; (i) because it is impossible to evaluate $\mathcal{Z}$, and (ii) because the free energy used in the minimisation is essentially *ad hoc*.

The physical properties of a fluid of N particles in volume V,in the presence of a potential $V(\mathbf{r})$ and at a chemical potential μ, is obtained by minimising the grand thermodynamic potential Ω, where, as usual:

$$\Omega = \mathcal{A} - \mu N \tag{1}$$

Now , in the presence of a potential $V(\mathbf{r})$, the density $\rho(\mathbf{r})$ is in fact *uniquely* determined, something that was proved first of all in the context of the theory of the (quantum) electron gas by Kohn and Sham[1] as long ago as 1965. The net result is that the Helmholtz free energy $\mathcal{A}$ can be written as a *functional** of the density $\rho(\mathbf{r})$:

$$\mathcal{A} = \mathcal{F}[\rho(\mathbf{r})] + \int \rho(\mathbf{r}) V(\mathbf{r}) d\mathbf{r}, \tag{2}$$

and where $\mathcal{F}$ is the *Free Energy Functional*. The resulting Euler-Lagrange equation is then:

$$\frac{\delta\Omega}{\delta\rho(\mathbf{r})} = \frac{\delta\mathcal{F}}{\delta\rho(\mathbf{r})} + V(\mathbf{r}) - \mu = 0 \tag{3}$$

This is an encouraging equation to have, since it is what people have been doing anyway, long before the formal theorem about the existence of a free energy functional was realised. On the other hand, in liquid (or any other!) problems, knowledge that $\mathcal{F}$ *exists*, is not of much help in *finding*

---

* One should not be afraid of functionals, although full mastery is clearly for the pure mathematician. What is important for us is that a functional is a function of a function. In fact a functional is the limit of a function of many variables. In this case the many variables are just the values of the argument function at each point. The branch of pure mathematics devoted to the study of these objects is known as *functional analysis*. A good account of how this theory is applied in the theory of fluids is given by R.Evans[2].

$\mathcal{F}$.

In order to find $\mathcal{F}$, one must resort to other stratagems. Let us first confine interest to uniform fluids. What in fact we need is *another* theory of fluids. Most theories of simple fluids start with the *hard sphere* fluid. Using the Percus-Yevick integral equation theory[3], Carnahan and Starling[4] came up with the following equation of state:

$$\mathcal{F} = N\psi(\rho); \tag{4a}$$

$$\psi = \psi_{\mathrm{ideal}} + \Delta\psi \quad , \tag{4b}$$

where the ideal part of the free energy is given by the usual perfect fluid form:

$$\psi_{\mathrm{ideal}} = k_B T \; \mathit{ln} \; \rho V_Q \; , \tag{4c}$$

and the excess free energy $\Delta\psi$ is given by:

$$\Delta\psi = \frac{(4 \; -3\eta)}{(1 \; - \; \eta)^2} \, k_B T \; , \tag{4d}$$

where in these formulae T is the absolute temperature, k_B is Boltzmann's constant, V_Q is a constant depending on temperature, and η is the *packing fraction*, i.e. the proportion of the volume occupied by fluid particles.

In all of this, there is no minimisation at all, although of course we have constructed $\mathcal{F}$ *ex post facto*. We note in passing that in order to pass from the free energy of a hard body fluid to that of a fluid with realistic interactions one generally uses *perturbation theory*[5]; one makes a functional expansion of the free energy $\mathcal{F}$, not now as a functional of ρ (which is kept constant), but as a functional of the interparticle potential $V(\mathbf{r}-\mathbf{r}')$.

Non-Uniform Fluids

A mathematical result of great importance in this area, and one which comes at first as something of a surprise, is the connection between the free energy functional (or rather its functional derivatives) and the *direct correlation function* c(r), first introduced as long ago as 1913 by Ornstein and Zernike[6].This result states that if the total functional $\mathcal{F}$ can be divided into an ideal part and an excess part, as in equation 4(b) above:

$$\mathcal{F} = \mathcal{F}_{\mathrm{ideal}} + \Delta\mathcal{F} , \tag{5}$$

then
$$\frac{\delta^2 \Delta\mathcal{F}}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')} = -k_B T\ c(\mathbf{r}-\mathbf{r}'). \tag{6}$$

The Ornstein-Zernike direct correlation function, we may recall, was introduced in order to take account of explicitly *short-range* interactions in a fluid, and is related to the usual fluid pair correlation function by the *Ornstein-Zernike* equation:

$$g(\mathbf{r}) - 1 = h(\mathbf{r}) = c(\mathbf{r}) + \rho\int c(\mathbf{r}')h(\mathbf{r}-\mathbf{r}')\ d\mathbf{r}'. \tag{7}$$

What this result enables us to do is carry out a *functional Taylor expansion* in order to derive $\mathcal{F}[\rho+\delta\rho(\mathbf{r})]$:

$$\Delta\mathcal{F}[\rho+\delta\rho(\mathbf{r})] - \Delta\mathcal{F}[\rho] = - \frac{1}{2}\ k_B T\int c(\mathbf{r}-\mathbf{r}')\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{8}$$

The quantity $c(\mathbf{r})$ is then calculable using one's favourite integral equation method, or by using some other approximation such as perturbation theory[7]. We shall not dwell at great length on the problems of calculating $c(\mathbf{r})$, other than to remark that for many purposes one may think of the direct correlation function as playing the same role with respect to the *free energy* as the interparticle potential plays with respect to the *energy*. In particular, at low densities the leading order approximation to the direct correlation function is given by the Mayer f-function:

$$c(\mathbf{r}) \sim f(\mathbf{r}) = \exp(\ -V(\mathbf{r})/\ k_B T\ ) - 1\ . \tag{9}$$

Forms of the Density Functional

The free energy functional is *non-local*, i.e. it is not merely the integral of a function of $\rho(\mathbf{r})$ at each point. Let us examine the form of a few popular forms.

The *Cahn-Hilliard*[8] form might be thought to be the most weakly non-local:

$$\mathcal{F} = \int \{\ f[\rho(\mathbf{r})] + \frac{1}{2}\ K\ (\nabla\rho)^2\ \}\ d\mathbf{r}, \tag{10}$$

where $f[\rho]$ is the free energy density of a uniform fluid at density ρ, and K is a (possibly density-dependent) parameter designed to make sure that the long wavelength response of the fluid is correct.Thus f will have been calculated using some other theory of fluids. One would have been tempted to use a *local* functional, such as, for instance, the first term in the expression (10) above. However, it easy to see that this cannot be correct, for then, for instance, the liquid-vapour interface should be infinitely thin; there is no price to pay passing in an infinitely small length from one minimum of Ω to the other at the coexistence chemical potential. Notice, however, that appealing as this recipe is, it can't always be applied in a mathematically rigorous fashion. Cahn and Hilliard used this recipe to calculate the surface free energy at an interfacebetween coexisting phases of an alloy; however the function f only *exists* if there a potential $V(\mathbf{r})$ which will enforce this particular constant ρ - and such a V *doesn't* exist in a coexistence regime - by definition, indeed, otherwise it wouldn't be in a coexistence regime! This is not to say that such an approach is useless, of course (very good agreement with experiment can sometimes be obtained, and we know by now not to take too much notice of formal mathematics in practical applications), but it does at least dictate caution!

Another plausible form is the *perturbation theory form*[9]*:*

$$\mathcal{F} = \int f_{hs}[\rho(\mathbf{r})]\,d\mathbf{r} + \frac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'\,\rho(\mathbf{r})\rho(\mathbf{r}')V_{LR}(\mathbf{r}-\mathbf{r}'), \qquad (11)$$

where f_{hs} is the hard sphere free energy functional, and V_{LR} is the long-range part of the potential which induces interesting effects, such as the liquid-vapour phase transition.

This is in fact a (only slightly more sophisticated!) modern version of the 19th century van der Waals theory of fluids. It does however lead to a dramatic improvement in the predictive power - all essentially because the space avoiding features of the hard sphere fluid are better treated. The *problem* is that the direct correlation function is wrongly predicted. This has dramatic consequences when one is trying to treat the growth of wetting layers[10] and other adsorption problems. Trying to improve the direct correlation function in such a way that one describes correctly *both* the short-range structure of the fluid close to a wall *and* the growth of thick adsorbed layers, has turned out to be major headache.

Freezing

A traditional view of the liquid solid-transition considers *melting*, and asks the question of why vibrations can destroy, in a self-consistent way, the well-ordered lattice structure of a solid. This is the viewpoint of the solid-state physicist. But from the point of view of the liquid physicist this question is the wrong way round. The liquid physicist asks, not why melting, but rather, why *freezing*? What happens to the uniform fluid state in order that the self-consistent static density fluctuations which make up a crystal lattice are set up? There are other features of the solid state that are not amenable to this type of formulation (e.g. why do liquids flow and solids don't, which is the layman's appreciation of the difference), but this way of looking at the problem will be sufficient for us for now. Incidentally we should be aware that form the liquid crystal scientist's point of view, this question is crucial, for very often the *sine qua non* of the liquid crystal chemist is the suppression of freezing rather than the promotion of mesogenicity (after all to first approximation all liquid crystal molecules are long and thin!).

There is in fact a long history of attempts to construct theories of freezing in this vein. The first modern-looking theory is due to the great American chemist J.G. Kirkwood[11]and his school. The modern theory of freezing in simple fluids is due to Ramakrishnan and Yussuff[12] and Haymet and Oxtoby[13]. The basic idea is that of any mean field theory; the presence of an atom at a given site increases the probability of particles in a shell a distance R away (near the first maximum of g(r)), and this increased probability feeds back to increase the probability of finding a particle at the first site. If the feedback is positive a lattice is set up. How is one to formalise this? The crucial insight is that near the freezing transition the *structure* of the solid and of the coexisting liquid are close, and thus the free energy of one may be reached from the other by perturbation theory.More formally:

$$\text{SOLID} = \text{FLUID} + \text{DENSITY FLUCTUATION} \qquad (12)$$

or, using eq.(8)

$$\mathcal{F}[\rho_{\mathrm{solid}}] = \mathcal{F}_{\mathrm{ideal}}[\rho_{\mathrm{solid}}] + \Delta\mathcal{F}[\rho_{\mathrm{liquid}}] - \frac{1}{2} k_B T \int c(\mathbf{r}-\mathbf{r}')\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')d\mathbf{r}d\mathbf{r}', \qquad (13)$$

where

$$\begin{aligned}\delta\rho(\mathbf{r}) &= \rho_{\text{solid}}(\mathbf{r}) - \rho_{\text{liquid}} \\ &= \Delta\rho + \sum \rho_{\mathbf{q}}\, e^{i\mathbf{q}.\mathbf{r}} .\end{aligned} \qquad (14)$$

This approach works....well, in fact too well as it turned out[14].The idea is that the perturbation should be *weak*; only a few values of **q** in the Fourier expansion should be required, and the effective potential at each point is given not by the interparticle potential, but by the c(**r**). But in practice, although taking only a few **q** did work, closer examination showed that in the region of the lattice sites $\delta\rho$ was getting *very* large; very many **q**'s were required for the self consistency to work well, and from a computational point of view, minimisation of Ω involved very slow convergence indeed.

The results were promising, but yet substantial problems remained. What was to be done? Well, if $\delta\rho$ gets large, is there a way to avoid perturbation theory and evaluate $f[\rho(\mathbf{r})]$ locally? But here we also have a problem, because the local densities are getting *so* large that a uniform fluid at this density would be too dense to pack, or equivalently $f \to \infty$! The problem, in a nutshell, is how to *extrapolate* reliably from a region which we understand (the liquid), to one we don't (the solid), when it is clear that there is *some* close resemblance between the two phases.

One fruitful way out of the dilemma involves setting up a more sophisticated non-local density functional than before. In the *Weighted Density Approximation*[15] we suppose that the effective density at a point is not the *actual* density $\rho(\mathbf{r})$, but rather a *weighted* density $\bar{\rho}(\mathbf{r})$, where $\bar{\rho}$ is some density suitably averaged over a region about **r**. This wouldn't be much use if we weren't able to concoct a recipe for carrying out the weighting, but fortunately, because functional derivatives of $\mathcal{F}$ give c(**r**), and we have integral equation theories for that quantity, we are in business. Thus now:

$$\mathcal{F} = \mathcal{F}_{\text{ideal}} + \int \rho(\mathbf{r})\Delta\psi[\bar{\rho}(\mathbf{r})]\, d\mathbf{r}, \qquad (15)$$

with

$$\bar{\rho}(\mathbf{r}) = \int w(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}', \qquad (16)$$

and where $w(\mathbf{r};\bar{\rho})$ is the *weight function* . At this stage let us not pursue the details of this theory (or rather group of theories, for each set of workers have their own favourite weight function, and reasons why their *particular* choice of weight function is more sophisticated than that of competing workers). Let us merely remark that good results have been obtained for freezing thermodynamics, and that, even at liquid-solid coexistence, where one would expect the solid particles to be *least* localised about their lattice points, the ratio ρ_{max}/ρ_{min} over a unit cell in the solid is of the order of 10^8; this is *extraordinarily* large when one keeps in mind that we are using the liquid to extrapolate properties of the solid.

2. APPLICATION TO LIQUID CRYSTAL PHASES

Once we pass from simple liquids to liquid crystals, life becomes considerably more complicated, because now we have a free energy functional $\mathcal{F}$ as a functional of $\rho(\mathbf{r},\omega) = \rho f(\mathbf{r},\omega)$, where $\rho(\mathbf{r},\omega)$ is the density as a function of orientation and position, and $f(\mathbf{r},\omega)$ is the orientational distribution function for the molecules (which may itself, of course, be a function of position). We can identify a plethora of liquid crystal phases - nematic, smectic A or C, and solid phases with orientational order - not to mention the more exotic smectic or chiral phases. What we shall do in this section is give a very quick review of what has been done (this will include a reinterpretation of the classic theories of liquid crystal science) and then pass to our own recent work (which we do not any way claim to be definitive!).

The classic theories of the nematic state are the Maier-Saupe theory[16] (for thermotropics) and the Onsager theory[17] (for hard body interactions). Both of these theories take the general form:

$$\mathcal{F}_{\text{nematic}} - \mathcal{F}_{\text{isotropic}} = \mathcal{F}_{\text{ideal}} + \frac{1}{2}\int V_{\text{eff}}(\mathbf{r}-\mathbf{r}',\omega,\omega')\Delta\rho(\mathbf{r},\omega)\Delta\rho(\mathbf{r}',\omega')d\mathbf{r}d\mathbf{r}'d\omega d\omega', \quad (17)$$

where $\Delta\rho(\mathbf{r},\omega) = \rho(\mathbf{r},\omega) - \rho/4\pi$ is the 'orientational part' of the density, and V_{eff} is an effective potential constructed either by considering long-range dispersion forces (in the Maier-Saupe case) or by considering volume exclusions in the virial expansion (in the Onsager case). If we look at the structure of these theories with the benefit of modern understanding of fluid theories, we see that in both cases the effective potential should really be replaced by $-k_BTc(\mathbf{r}-\mathbf{r}',\omega,\omega')$, where c is the direct correlation function discussed in the first part of the talk.[18,19] But there our problems start, because whereas in simple fluids with spherical molecules there are years of experience in testing out approximations for $c(r)$ -integral equations, perturbation theory, series expansions and so on - for mesogenic molecules there is much less, and what there is, is largely numerical[20]. So necessarily going beyond Onsager in any sophisticated way is likely to prove tough going. Actually, Onsager theory is a low density approximation, and is exact in the limit of very long rods; it turns out that if one compares Onsager theory with more exact calculations, one gets remarkably good answers. We note in passing, that our general belief about thermotropics is that they result from a complex interplay between shape ('steric effects') and longer-range attractive interaction, and the work of Cotter and colleagues[21] and by Gelbart and colleagues[22] in the 70s and early 80s also falls into the general category of density functional theories, although these authors didn't use this explicit terminology.

Smectics

It is in discussing the inhomogeneous smectic phases that some of the more sophisticated considerations about non-locality that we introduced in the first part of the talk may become relevant in the liquid crystal context. Let us first discuss, in a more general way, the origin of smectogenicity. There has been much work on the thermodynamics of hard body fluids over the years since Onsager's seminal work in 1949. This partly because of the evident experimental interest, but also because hard body systems present a 'clean' theoretical problem; there is no more modelling to be done. It has long been clear that a rod-like molecular shape is an important precondition of nematogenicity, but it is equally clear that most liquid crystals are not *simply* hard rods - they are biaxial, they have flexible tails at the end and sometimes even in the middle, sometimes even they have (what looks like to this mathematical physicist!) twiddly bits hanging off the side. And long hard chemical experience tells us that all these factors play a rôle in the liquid crystalline properties. Until recently most chemists would have sworn that it is the existence of flexible tails which governs the existence of a smectic phase. And surely this cannot be entirely wrong, for these flexible tails *must* inhibit true crystal formation.

It was therefore long part of the conventional wisdom that hard rods, although forming a nematic phase easily, do not form smectic phases. This intuition was further consolidated by the realisation that a system of *perfectly aligned ellipsoids* also cannot form a smectic phase, because the statistical mechanics of that system is the same as that of a hard sphere fluid (a mapping can easily be made by simply stretching one coordinate). Of course, the fluid of perfectly aligned ellipsoids is not the *spontaneously* aligned nematic, but it seems highly plausible that if the nematic order parameter is high (as it is in the Onsager nematic), the two systems will have closely analogous behaviour. In particular, because of the presumed coupling between the smectic and nematic order parameters, one expects that the real nematic will be *less* inclined to order smectically.

There was therefore great surprise when the computer simulations of Stroobants *et al*[23] showed that perfectly aligned spherocylinders do indeed form a smectic phase (and it was later found that this is also true for the freely rotating nematic phase). The difference in shape between hard ellipsoids and spherocylinders , though often thought of as a trivial detail, in fact is crucial to the phase behaviour. With hindsight one can find chemical intuition to justify this datum (in terms of particles in different layers 'fitting together')! A rather good quantitative explanation of the Monte Carlo data has been given by Mulder[24] using the simplest possible theory. In this theory one uses the free energy functional given by the equivalent in a smectic context of eq(17), and uses a slightly modified version[18,22] of the low density approximation for $c(\mathbf{r},\omega,\omega')$:

$$c(\mathbf{r},\omega,\omega') = (1-\eta)^{-1} f_{\mathrm{Mayer}}(\mathbf{r},\omega,\omega') \quad . \tag{18}$$

One then conducts an an analysis of the *stability* of the nematic phase against spontaneous density fluctuations. The results are startlingly good; the onset of smectic behaviour is predicted to take place at a packing fraction $\eta \cong 0.36$ (simulations $\eta \cong 0.35$) and λ/L, the ratio of the smectic wavelength to the rod length, is predicted to be 1.398 at the transition (1.28 in the simulation).

Our own recent work on the onset of smectic behaviour lies in two areas. The first calculation[25] concerns the onset of the smectic A phase for hard spherocylinders for finite (and rather small) D/L (D is the diameter of the rods). The second calculation[26] is concerned with the existence of smectic C phases and the molecular preconditions for this.

Phase Diagram for a system of Hard Spherocylinders

This calculation is an attempt to generalise the Tarazona non-local density functional theory to smectic liquid crystals. Unfortunately, fruitful as this approximation is in understanding freezing the generalisation to liquid crystals is not obvious (Tarazona himself[27] has suggested another possibility). Our approach is somewhat *ad hoc;* our hope is that, as these systems come under more intensive theoretical and computational study, evidence will emerge as how to best describe them.

We start with a functional

$$\mathcal{F}[\rho(\mathbf{r},\omega)] = \mathcal{F}_{\text{ideal}} + \mathcal{F}_{\text{excess}} \; . \tag{19}$$

$\mathcal{F}_{\text{ideal}}$ is treated exactly; the following expression is used for $\mathcal{F}_{\text{excess}}$:

$$\mathcal{F}_{\text{excess}} = \int \rho(\mathbf{r})\Delta\psi[\bar{\rho}(\mathbf{r})]\, d\mathbf{r} \; . \tag{20}$$

The weighted density is given by:

$$\bar{\rho}(\mathbf{r}) = \int w(\mathbf{r}-\mathbf{r}';\, [\ell(\omega)])\; \rho(\mathbf{r}')\, d\mathbf{r}' . \tag{21}$$

The weight function itself is given by:

$$w(\mathbf{r};[\ell]) = -\frac{1}{2B_2^I} \int f_{\text{Mayer}}(\mathbf{r},\omega,\omega')\; \ell(\omega)\ell(\omega')\; d\omega d\omega' , \tag{22}$$

where B_2^I is the second virial coefficient of the isotropic fluid. Finally the excess free energy function itself is given by:

$$\beta\Delta\psi[\rho] = \rho B_2^I + \beta\Delta\psi^{CS}[\eta] - 4\eta. \tag{23}$$

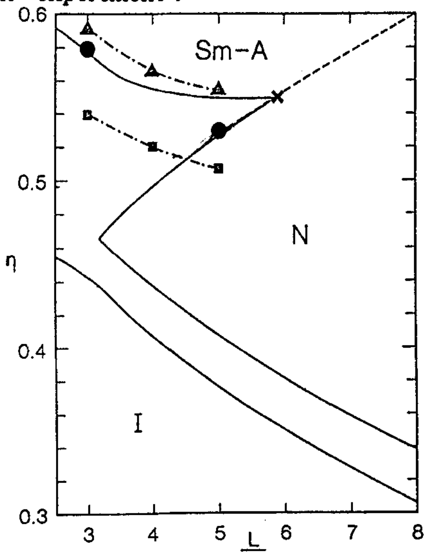
The superscript CS stands for Carnahan-Starling. We shall not discuss here the detailed reasons for choosing this set of recipes, save to say that the intention is a free energy which matches closely the Onsager free energy at low densities and high L/D, and which reduces to the Carnahan-Starling formula when L/D = 0. There is thus implicitly an intention to interpolate smoothly between the hard sphere and hard rod limits. This free energy is thsn minimised with respect to possible nematic and smectic order parameters for different η and L/D. A summary of the results is given in Fig 1.

The crucial points which concern the onset of smectic behaviour to note in Fig.1 are : a) there is a continuous nematic-smectic A phase transition for L/D>5.9; b) there is a first-order nematic-smectic A transition for 3.2<L/D<5.9 and c)for L/D<3.2 the nematic phase disappears altogether. There is thus a nematic-smectic A *tricritical* point at η=0.55, L/D=5.9, and an isotropic-nematic-smectic A *triple* point at η =0.46, L/D=3.2. We find that the packing fraction at the nematic-smectic A continuous transition *increases* as a function of L/D, though we have not been able, for numerical reasons, to follow this transition all the way to L/D=∞. We may remark, however, that this qualitative trend seems implausible , and, indeed, Somoza and Tarazona[27] have cogently argued against this. They find, however, a tricritical point at L/D=50, which also seems implausible. An interesting feature of this phase diagram, which we have not so far examined, is the value of L/D at which all liquid crystalline phases disappear, and only true crystalline phases remain.

Ordering in a fluid of parallel cylinders with quadrupolar interaction

Many mechanisms have been proposed to account for the existence of the smectic C (and, indeed, other tilted phases). Two (presumably not exclusive) possibilities are (i) the existence of biaxiality or polar orderin the mesogens; the smectic C phase is then induced by an interaction between a smectic A phase and phase biaxiality induced by the molecular biaxiality , or (ii) the existence of intermolecular forces which induce smectic C order *without* destroying the cylindrical symmetry of the molecules. A popular idea in the 1970s[28], revived recently in a rather qualitative way by Barbero and Durand[29], is that quadrupolar interactions may play just this rôle.

We have therefore studied a model fluid of perfectly aligned cylinders, with electric quadrupoles of strength q placed at the centres of these cylinders. The free energy of this system is described using essentially the Onsager theory for the effects of volume exclusion and then taking account of the effects of the quadrupoles in perturbation theory using the random phase approximation popular in the theory of liquids. For further details we refer the reader elsewhere[26]. The results of this calculation, which are summarised in Figure 2, are instructive. We find the possibility of a nematic, a smectic A and a smectic C phase, with the smectic C phase occurring at higher quadrupole moment, or, equivalently, at lower temperatures. The smectic phases occur at higher packing fractions. An amusing feature is that at these higher densities there is a region in which the *high* temperature phase is a smectic A, the *intermediate* temperature phase is a smectic C, but the *low* temperature phase is a nematic, apparently breaking the rule that ordering increases as temperature is decreased. It seems likely however that this anomalous feature will disappear in a more realistic model which allows free rotations. For in such a case the nematic order parameter would be coupled to the smectic order parameter; at lower temperatures the nematic order parameter would be higher, and this would in turn promote low temperature smectic order. Another feature of our results which seem to depend on the specific model of *parallel* cylinders is that all our phase transitions are continuous; it can easily be shown, however that if other order parameters interact with the smectic order parameter, the phase transition can become first order. A particularly attractive feature of the model that we study here is that, however unrealistic it is as a model of a real liquid crystal, it is relatively simple to simulate, and thus to compare theory with 'experiment'.



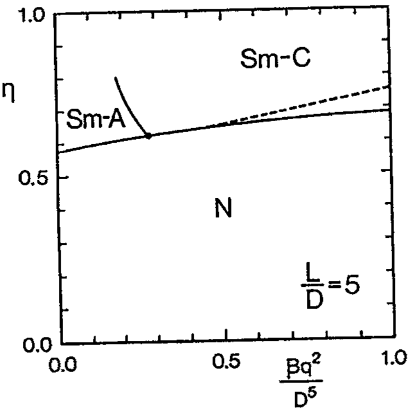


Fig.2. Phase diagram of Hard Cylinder plus Quadrupole system discussed in text.Note that $\beta q^2/D^5$ is temperature scale for this system

Fig.1. Phase Diagram of hard spherocylinder fluid in $(L/D,\eta)$ plane. Full lines correspond to first order transitions; continuous lines to continuous transitions.Circles are simulation results from ref 23. Squares and triangles are theoretical results on η at N-Sm A boundary from ref 27.

3. SUMMARY

Density functional theories have been increasingly used to describe the properties of many types of fluids, including liquid crystals. While most models up to now have been relatively simple, we may expect attempts totake account of models of greater complexity which will describe the relationship between molecular detail and quantitative features of mesomorphic phase diagrams.

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REFERENCES

1. W. Kohn and L.J. Sham, *Phys.Rev.* **140**, A1133 (1965).
2. R. Evans, *Adv. Phys.* **28**, 143 (1979).
3. J.K. Percus and G.J. Yevick, *Phys.Rev.* **110**, 1 (1957).
4. N.F. Carnahan and J.G. Starling, *J.Chem. Phys.* **51**, 635 (1969).
5. J.D.Weeks, D.Chandler and H.C. Andersen, *J.Chem.Phys.* **54**, 5237 (1971).
6. L. Ornstein and F. Zernike, *Proc.Acad.Sci.Amsterdam* **17**, 793 (1914).
7. see e.g. J-P. Hansen and I.R. McDonald, Theory of Simple Liquids (Academic Press, New York, 2nd edition 1986).
8. J.G. Cahn and J.E. Hilliard, *J.Chem.Phys.* **28**, 258 (1958).
9. C. Ebner, W.F. Saam and D.Stroud, *Phys.Rev.A* **14**, 2264 (1976).
10. R. Evans, P. Tarazona and U.Marini Bettolo Marconi, *Mol.Phys.* **50**, 993 (1983)
11. J.G. Kirkwood and E. Monroe, *J.Chem.Phys.* **8**, 845 (1940).
12. T.V. Ramakrishnan and M.Yussouff, *Phys.Rev.B* **19**, 2775 (1979).
13. A.D.J. Haymet and D.W. Oxtoby, *J.Chem.Phys.* **74**, 2559 (1981).
14. A.D.J. Haymet, *Ann.Rev.Phys.Chem.* **38**, 89 (1987).
15. P. Tarazona, *Mol.Phys.* **52**, 81 (1984).
16. W. Maier and A.Saupe, *Z.Naturf.* **13**, 564 (1958).
17. L. Onsager, *Ann.N.Y.Acad.Sci.* **51**, 627 (1949).
18. J. Stecki and A. Kloczkowski, *J.Phys (Paris)* **40**, C3-360 (1979).
19. T.J. Sluckin and P. Shukla, *J.Phys.A* **16**, 1539 (1983).
20. A. Perera and G.N. Patey, *J.Chem.Phys.* **89**, 5861 (1988).
21. M.A. Cotter and D.C. Wacker, *Phys.Rev.A* **18**, 2669,2676 (1978).
22. W.M. Gelbart and A. Ben Shaul, *J.Chem.Phys* **77**, 916 (1982).
23. A. Stroobants, H.N.W. Lekkerkerker and D. Frenkel,*Phys.Rev.A* **36**, 2929 (1987).
    J.A.C.Veerman and D.Frenkel, *Phys.Rev.A* **41**, 3237 (1990).
24. B. Mulder, *Phys.Rev.A* **35**, 3095 (1987).
25. A. Poniewierski and T.J. Sluckin, *Phys.Rev A* to be published (1991).
26. A. Poniewierski and T.J. Sluckin, *Mol. Phys.* to be published (1991).
27. A. Somoza and P. Tarazona, *Phys.Rev.A* **41**, 965 (1990).

28. e.g. R.G. Priest, *J.Chem.Phys.* **65**, 408 (1976).
29. G. Barbero and G. Durand, *Mol.Cryst.Liq.Cryst.* **179**, 57 (1990).