Abstract

These lectures focus on bifurcation analysis as a tool for studying phase transitions that occur in models of liquid-crystalline systems. We show how this approach bridges the gap between the phenomenological Landau theory and the — often intractable — full statistical mechanical treatment. Employing a “toy model” as a tutorial example the various ingredients of the technique are presented. Special attention is paid to the way in which one obtains information on the relation between the characteristics of the assumed interparticle interactions (shape, symmetry ...) and global properties of the phase transitions (order, symmetry of resultant phases ...). Finally a few more involved examples are discussed indicating how the approach can be applied to more realistic models and how it can serve as a complement to simulations.
1 Introduction

Liquid crystalline phase transitions (like most phase transitions) involve the phenomenon of symmetry breaking. In fact part of their interest derives from the diversity, and often subtlety, of the ways in which these systems upon cooling and/or compression stepwise lower their symmetry in order to span the gap between the high symmetry of the isotropic phase and the ultimate lowest symmetry crystalline phase. One almost feels that there is an underlying minimum principle at work that drives these systems to give up as little of their symmetry as the external conditions allow. Fortunately we possess, in the form of the Landau theory, a complete descriptive apparatus for symmetry-breaking phase transitions. The recipe to be followed is quite simple (i) select an order parameter being an observable that has specified transformation rules under the symmetry group of the high symmetry phase and whose values distinguish between the two phases (ii) generate an expansion of the relevant coarse-grained thermodynamic potential in terms of the order parameter around the high-symmetry phase. As an example consider the Isotropic-Nematic transition for which the order parameter is a symmetric, traceless, three-tensor $Q$ and the Landau expansion of the free energy takes the form

$$ F = F_0 + A \text{Tr}Q^2 + B \text{Tr}Q^3 + C_1(\text{Tr}Q^2)^2 + C_2 \text{Tr}Q^4 + ... \quad (1) $$

Under the assumption that the quadratic coefficient $A$ changes sign at the transition and the coefficients $B$ and $C_i$ are slowly varying we can then easily deduce the known properties of the I-N transition by calculating the minimum the free energy with respect to the order parameter. It should be noted that this procedure, although powerful, is both phenomenological and essentially \textit{a posteriori}. First of all the selection of the order parameter either requires prior knowledge of the macroscopic behaviour of the system or, barring that, a strong dose of physical intuition. One level down the coefficients in the expansion are either chosen to reproduce the expected behaviour or simply varied in order to probe the various possible transitions.

From the molecular point of view, where our only inputs are the particles that make up our system and the interactions between them, a few obvious questions immediately arise: (i) can we predict the order parameter and thus the symmetries of the resultant phase? (ii) can we calculate

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1For an up-to-date introduction see [26]
the analoga of the expansion coefficients $A, B...$ that determine the location and the nature of the transitions? In principle statistical mechanics should supply us with the answers to these questions. In practice, however, physics (like life itself) is not as easy as one would wish it to be. Consider the formulation of statistical mechanics closest in spirit to the situation at hand: classical density functional theory (CDFT). In this case we assume that we are supplied with the relevant thermodynamic potential as a functional of the one-particle distribution function $\rho^{(1)}(i)$, where $i$ is a shorthand for the degrees of freedom of a single particle e.g $i = (r, \Omega)$ for a rigid non-spherical particle, $r$ being the location of its center of mass and $\Omega$ its orientation with respect to a fixed reference frame. Some crude analogies with the Landau approach are apparent. First of all the equilibrium phase is selected through a variational principle. The $\rho^{(1)}(i)$ codes for the symmetries of the phase and thus plays the role of the order parameter. Finally the details of the functional implicitly specify the sought after expansion coefficients. The first problem we have to confront in this approach is that we do not know the true functional except possibly in terms of formal expansions, so we will be forced to make careful approximations that hopefully leave as much of the relevant physics as possibly. Next, even after making the necessary approximations, the variational principle will in general yield non-linear functional relations which are difficult to solve.

Part of the success of the Landau theory is based on the fact that it exclusively focuses on the description of the system near phase transitions, thus singling out the most interesting behaviour at the expense of a more microscopic description. The density functional formalism on the other hand does take into account the microscopic degrees of freedom, but in doing so introduces a level of complexity far beyond that of the Landau theory. The aim of these lectures will be to show how bifurcation analysis can help to bridge this gap, by studying the solutions of the variational principle for the density functional near its critical points. This technique allows us to extract the information relevant to two questions posed above i.e to determine the symmetry of the resultant phases and the nature and location of the phase transitions. Moreover it often yields to analytical treatment even in cases where only a minimum amount of information is supplied about the inter-particle interactions e.g just their symmetries, thus giving rise to predictions of a rather general nature valid for whole classes of systems.

I believe the ideas presented here are useful not just for theorists but also for those involved in simulating model liquid crystals. There are two
areas where bifurcation analysis can supply information of direct interest to a simulation:

**description** Solution of even the simplest model having the required symmetries will often yield the relevant order parameters that can be used to describe phases that are observed in the simulations.

**prediction** Analyzing a simple model for class of related particles and/or interactions can lead to predictions about the regions in the phase diagram where interesting behaviour can be expected, thus guiding the choice of systems to be simulated.

2 Generalities

2.1 Density functional theory

Starting point of the density functional theory for classical many-particle systems [3] is the observation that there exists a functional $W[\rho^{(1)}]$ of the one particle distribution function $\rho^{(1)}(i)$ with the following properties:

1. $W[\rho^{(1)}] \geq W[\rho^{(1)}_{eq}]$ where $\rho^{(1)}_{eq}$ is the equilibrium distribution.

2. $W[\rho^{eq}] = W_{eq}$ where $W_{eq}$ is the thermodynamic equilibrium value of the grand canonical potential.

These two properties together imply a variational principle for obtaining the full equilibrium properties of the system in question. The big surprise is that the variation is with respect to a quantity that depends only on the degrees of freedom of a single particle and not as one would expect with respect to an N-particle quantity. I should stress that there is no approximation involved here, and all many-particle correlations are correctly accounted for. In fact in a moment I will show how all higher order correlation functions can be generated from the functional itself. Since there is no such thing as a free lunch however, we must now face the downside of the theory: We have been told that the functional exists but have not been given any clue as how to construct it. Nevertheless we do know that it is has the following general structure (recall $W = F - \mu N$)

$$W[\rho^{(1)}] = F[\rho^{(1)}] - \mu \int d\rho^{(1)}(i)$$  \hspace{0.5cm} (2)
where the second term involving the chemical potential \( \mu \) is easily understood if one remembers that the equilibrium one particle distribution has the following normalization

\[
\int di \rho_{eq}^{(1)}(i) = N
\]

where \( N \) is the number of particles in the system. The first term represents the free energy of the system and can be expressed as

\[
\beta \mathcal{F}[\rho^{(1)}] = \int di \rho^{(1)}(i) \{ \ln V_T \rho^{(1)}(i) - 1 \} - \Phi[\rho^{(1)}]
\]

where the first part is the free energy functional for a non-interacting system, which contains the temperature dependent quantity \( V_T \) being the thermal volume of the system i.e. the product of the various thermal wavelengths associated with the kinetic degrees of freedom. As usual the sting is in the tail, here in the form of the functional \( \Phi \) that encapsulates all contributions due to interactions between the particles. When the particles in our system interact only pairwise through a potential \( v(i,j) \) this functional can, at least formally, be expanded in a generalized virial series using the language of diagrams \[9\]

\[
\Phi[\rho^{(1)}] = \text{Sum of all connected, irreducible diagrams with } \rho^{(1)} \text{ vertices and Mayer function bonds: } f(i,j) = e^{-\beta v(i,j)} - 1
\]

Finally, as promised earlier, this functional can be used to generate all direct correlation functions through the relation

\[
c^{(n)}(i_1, i_2, ..., i_n; \rho^{(1)}) = \frac{\delta^n \Phi[\rho^{(1)}]}{\delta \rho^{(1)}(i_1) \delta \rho^{(1)}(i_2) ... \delta \rho^{(1)}(i_n)}
\]

These in turn can be related through generalized Ornstein-Zernike relations to the more usual \( n \)-particle densities \( \rho^{(n)} \) \[5\], showing that the density functional indeed gives full description of \( N \)-body equilibrium system.

Suppose now that one way or the other (approximations, intuition, reading of sacred texts ...) we have managed to construct a functional relevant to the system we want to study. As a first step towards solving the variational problem to determine the equilibrium distribution we then look for the stationary distributions for which
\[
\frac{\delta \mathcal{W}[\rho^{(1)}]}{\delta \rho^{(1)}(i)} = 0 \tag{7}
\]
Inserting the general form of \(\mathcal{W}[\rho^{(1)}]\) we arrive at the following selfconsistency relation for the one particle distribution

\[
\rho^{(1)}(i) = \frac{1}{\mathcal{V}_T} e^{\beta \mu} \exp \frac{\delta \Phi[\rho^{(1)}]}{\delta \rho^{(1)}(i)} \tag{8}
\]
revealing the role that the first functional derivative of \(\Phi\) plays as a self-consistent effective one particle potential. As mentioned in the introduction this selfconsistency relation that determines the stationary distributions is a highly non-linear functional relation whose solution even in the simplest cases requires numerical treatment. The chemical potential \(\mu\) is easily eliminated from this equation using the normalization condition eqn. (3).

### 2.2 Bifurcation analysis

As stated before we are not going to try to solve the stationarity equation eqn. (8) in its full glory but instead concentrate on its behaviour in the neighbourhood of a symmetry breaking phase transition. The reason that we can do so is due to the fact that this type of phase transitions is associated with the appearance of multiple solutions to eqn. (8). The general mechanism by which such new solutions appear as the value of some external parameter in the functional is changed is that of a bifurcation i.e the new solution branch off from the originally stable solution. The new solution might immediately be the globally stable one in which case we have a continuous transition at the bifurcation point or it might be (initially) metastable with respect to the parent phase in which case one expects a first order transition, the bifurcation point marking the upper (or lower) limit of stability of the parent phase. In Figure 1 we have sketched these two scenarios. Bifurcation analysis has been developed by mathematicians in order to deal with these phenomena which are common to many types of non-linear equations and has found wide application mainly in the field of non-linear differential equations [3]. Applications to the physics of phase transitions have been attempted only on a much more modest scale [2], possibly because good examples were much

\[\text{for a review see: [14]}\]
Figure 1: Generic bifurcation diagrams. The $x$-coordinate $\lambda$ is the thermodynamic parameter that drives the transition and the $y$-coordinate a generic order parameter. The thick lines are the stable solutions while the dashed lines are meta- or unstable solutions. $\lambda_*$ identifies the bifurcation point. (a) A continuous transition. The transition takes place at the bifurcation point (b) A first-order transition. The transition takes place at $\lambda^c \neq \lambda_*$. 
less obvious. By the end of these lectures, however, I hope to have convinced
the reader that liquid crystalline phase transitions are a “bifurcators heaven”.

Let us now see how the analysis works in practice. First of all we choose
an external parameter in our functional the variation of which will drive
the system to undergo a phase transition. For definiteness, and since our
examples are all geared towards hard particle systems, we’ll take the number
density \( n = \frac{N}{V} \) where \( V \) is the volume of our system (\textit{mutatis mutandi} any
other parameter like the temperature, pressure, external fields etc. could have
been chosen). Next we need an initially stable solution of the stationarity
equation eqn. (8) that is at least defined for a range of densities that span
the transition, which we’ll call the reference solution \( \rho_0^{(1)} \). We then look for a
solution close the reference solution by introducing the following expansions
in the arbitrary parameter \( \epsilon \) around the, as yet undetermined, density \( n_0 \)

\[
n = n_0 + \epsilon n_1 + \epsilon^2 n_2 + ... \quad (9)
\]

and

\[
\rho^{(1)} = \rho_0^{(1)} + \epsilon\{\rho_1^{(1)} + n_1 \frac{d \rho_0^{(1)}}{dn} |_{n_0}\} + \epsilon^2\{\rho_2^{(1)} + \frac{1}{2} n_1^2 \frac{d^2 \rho_0^{(1)}}{dn^2} |_{n_0} + n_2 \frac{d \rho_0^{(1)}}{dn} |_{n_0}\} + ... \quad (10)
\]

By separating out the flow along the reference solution, the functions \( \rho_l^{(1)} \)
with \( l = 1, 2, ... \) represent the actual deviations from the reference solution
at every order in \( \epsilon \). Inserting these expansions into the stationarity equation
eqn. (8) and solving order by order in \( \epsilon \) we construct a solution that “creeps”
along the bifurcating solution branch. The bifurcation density \( n_0 \) itself will
be determined by the lowest order equation which describes the conditions
for the appearance of a non-zero initial perturbation \( \rho_1^{(1)} \). This lowest order
equation commonly referred to as the bifurcation equation turns out to be

\[
\rho_1^{(1)}(i) = \rho_0^{(1)}(i) \int dj \ c^{(2)}(i, j; \rho_0^{(1)}) \rho_1^{(1)}(j) \quad (11)
\]

Its structure becomes even clearer if we make the following substitutions

\[
\phi_1(i) = \rho_0^{(1)}(i) \frac{1}{4} \rho_1^{(1)}(i) \quad (12)
\]

\[
K_0(i, j) = \rho_0^{(1)}(i) \frac{1}{2} c^{(2)}(i, j; \rho_0^{(1)}) \rho_0^{(1)}(j) \frac{1}{2} \quad (13)
\]

\[3\]Actually we have discarded a term here which enforces the correct normalization to
zero of the perturbation for the system in a finite volume. This term, however, van-
ishes in the thermodynamic limit where the normalizations are automatically enforced by
symmetry alone.
yielding the symmetric representation

$$\phi_1(i) = \int dj K_0(i, j) \phi_1(j)$$

(14)

This is nothing but a generalized eigenfunction equation. Since the kernel $K_0$ depends solely on the properties of the reference phase $\rho_0^{(1)}$, we have all the necessary information to solve it. The eigenfunctions follow immediately from the global symmetries of the reference solution since the kernel $K_0$ is invariant under these, which fixes its eigenfunctions. The bifurcation density is determined as the minimum value of the density for which $K_0$ has an eigenvalue of unity. In the general case there will be a degenerate set of eigenfunctions satisfying eqn. (14) so that we will need more information to fix the true bifurcating eigenfunction(s) in order to determine the nature of the emerging phase. This information is, as we will see below, supplied by the next order equation in the hierarchy of bifurcation equations generated by the expansions eqn. (9) and eqn. (10).

As the higher order equations from the bifurcation hierarchy in the general case rapidly become rather unwieldy if no appropriate shorthand is introduced, I will refrain from displaying any but rather make the following comments. First of all determining the equations is largely a matter of a lot algebra which can easily be automated using some form of symbolic processing. Second, and more important, they form a consistent scheme for successively solving for the unknown perturbations $n_i$ and $\rho_1^{(1)}$ i.e. the $k^{th}$-order equation contains only perturbations of order $\leq k$. Finally, as already mentioned above, most of the “juicy” information already follows from the first two equations in the hierarchy. That the technique can however be used to construct the bifurcating solution even quite far away from the bifurcation point is illustrated in the beautiful and pioneering paper by Kayser and Raveché on the Onsager model[12], a paper which in fact initiated my own involvement with bifurcation analysis.

2.3 The Onsager approximation

To escape slightly from the very general setting described in previous two subsections we will look somewhat closer at the Onsager approximation for hard particle systems. This approximation is of course widely used and is to hard particle systems what mean-field theory is to systems with soft potentials, an analogy which in fact goes quite deep [12, 13, 16]. Moreover, as far
as universal features of the phase transitions in such systems is concerned, it seems to be equivalent to a whole class of density functional theories currently in vogue\textsuperscript{[18]}. Dispensing for a moment with its justification, I just give its formulation in terms of the diagram expansion eqn. (5). It consists of keeping just the lowest order term in the expansion yielding the following form for the free energy density functional

$$\beta \mathcal{F}_{\text{Onsager}}[\rho^{(1)}] = \int di \rho^{(1)}(i) \{\ln V_T \rho^{(1)}(i) - 1\} + \frac{1}{2} \int di \int dj \rho^{(1)}(i) \rho^{(1)}(j) \chi(i,j)$$  \hspace{1cm} (15)

where I have introduced the characteristic function $\chi(i,j)$ taking on the value 1 when the particles overlap and 0 when they don’t, properties easily deduced from the form of the Mayer function and the fact that we are dealing with hard potentials. Anticipating some of the examples that are to follow we will consider only spatially homogeneous phases and restrict our attention to the orientational degrees of freedom. In this case the singlet distribution function takes on the form $\rho^{(1)}(i) = n \psi(\Omega)$ where $n$ is the number density and $\psi(\Omega)$ the orientational distribution function which has unit norm. All integrals over the spatial degrees of freedom can now be performed turning the Onsager functional into

$$\beta \mathcal{F}_{\text{Onsager}}[\psi] = \frac{1}{N} \int d\Omega \psi(\Omega) \{\ln \psi(\Omega) - 1\} + \frac{1}{2} n \int d\Omega \int d\Omega' \psi(\Omega) \psi(\Omega') \mathcal{E}(\Omega, \Omega') + \ln n V_T$$  \hspace{1cm} (16)

which by dividing out the number of particles $N$ allows us to pass painlessly to the thermodynamic limit. A central role is played by the excluded volume at fixed orientations

$$\mathcal{E}(\Omega, \Omega') = \int dr \int d\mathbf{r}' \chi(\mathbf{r}' - \mathbf{r}, \Omega, \Omega')$$  \hspace{1cm} (17)

This role becomes even more clear if we work out the bifurcation equations in this case for phases developing from the low density isotropic phase $\psi_0(\Omega) = \frac{1}{8\pi^2}$. The first two equations are

$$\psi_1(\Omega) = -\frac{n_0}{8\pi^2} \int d\Omega' \mathcal{E}(\Omega, \Omega') \psi_1(\Omega')$$  \hspace{1cm} (18)
and
\[ \psi_2(\Omega) = -\frac{1}{8\pi^2} \left\{ n_0 \int d\Omega' \mathcal{E}(\Omega, \Omega') \psi_2(\Omega') + n_1 \int d\Omega' \mathcal{E}(\Omega, \Omega') \psi_1(\Omega') - \right. \]
\[ \left. \frac{1}{2} n_0^2 \left\{ \int d\Omega' \mathcal{E}(\Omega, \Omega') \psi_1(\Omega') \right\}^2 - \frac{1}{8\pi^2} \int d\Omega' \left\{ \int d\Omega'' \mathcal{E}(\Omega', \Omega'') \psi_1(\Omega'') \right\}^2 \right\} \] (19)
showing how the problem, apart from the algebra, reduces to the knowledge of the eigenvalues and eigenfunctions of the pair excluded volume \( \mathcal{E}(\Omega, \Omega') \).

3 A tutorial example

3.1 Rods with restricted orientations

Rather than continuing the analysis in an abstract setting I would like to work through a simple example indicating along the way how the results tie in the general statements made above. Of course by using the big guns on such a small target one runs the risk of practicing overkill, but I feel the insight in the method gained through this procedure outweighs this risk.

The model I consider is the following “travesty” of a hard particle fluid: uniaxial inversion symmetric convex bodies whose symmetry axis can point in a restricted number of directions namely parallel to the axes of a \( d \)-dimensional Cartesian reference system. Allowing general values for the dimensionality \( d \) (rather than just the conventional \( d = 3 \)) gives us a bit more room to play with the model. Such restricted orientation fluids have already received quite a lot of attention in the past \[29, 21, 2\], so none of the results are going to come as a surprise. Furthermore, in the light of the remarks made in section 2.3, the discussion will be restricted to the Onsager approximation.

Let us label the allowed orientations of the particles by \( s \), where it will turn out to be convenient to let \( s \) range from 0 to \( d-1 \). The excluded volume between two particles with fixed orientations has an exceedingly simple form
\[ \mathcal{E}(s, s') = e_\parallel \delta(s, s') + e_\perp (1 - \delta(s, s')) \] (20)
Because the particles are convex and non-spherical the excluded volume \( e_\parallel \), when they are parallel is smaller than the corresponding quantity, \( e_\perp \), when they are not. Remember that all the orientations are mutually orthogonal so that, given the symmetry of the particles, all non-parallel directions are
equivalent as far as the excluded volume is concerned. Introducing the dimensionless number density \( \eta = n(e_\perp - e_\parallel) \) we can write down the density functional as

\[
\frac{\beta W[\psi]}{N} = \sum_{s=0}^{d-1} \psi(s) \{ \ln \psi(s) - 1 \} - \frac{1}{2} \eta \sum_{s=0}^{d-1} \sum_{s'=0}^{d-1} \delta(s, s') \psi(s) \psi(s') + \\
\ln \mathcal{V} n + \frac{1}{2} ne_\perp - \beta \mu \sum_{s=0}^{d-1} \psi(s) 
\] (21)

The chemical potential here just serves as a Lagrange multiplier which is used to obtain the correct normalization of the orientational distribution, and will be eliminated immediately. We therefore find, after performing the variation with respect to \( \psi \), the following selfconsistency equation

\[
\psi(s) = \frac{\exp \eta \sum_{s'=0}^{d-1} \delta(s, s') \psi(s')} {\sum_{s'=0}^{d-1} \exp \eta \sum_{s''=0}^{d-1} \delta(s', s'') \psi(s'')} 
\] (22)

This equation might be \textit{deja vu} for some readers, since it is nothing but the mean-field equation for the d-state Potts model on an arbitrary lattice if we identify \( \eta = \beta z J \) where \( J \) is the coupling constant and \( z \) the coordination number of the lattice. Note that the isotropic solution \( \psi_0 = \frac{1}{d} \) which plays the role of reference phase, is a solution at all densities.

### 3.2 Analysis

Instead of rederiving the bifurcation equations from the start we can use the general results of section 2 for the Onsager case, if we make the following changes: (i) replace all integrations over the orientation \( \Omega \) by sums over the discrete variables \( s \) (ii) replace every factor \( 8\pi^2 \) by \( d \) being the “volume” of the discrete orientation space and (iii) replace the excluded volume \( E(\Omega, \Omega') \) by \( -\delta(s, s') \) and, finally, (iv) change all references to the number density \( n \) into the dimensionless density \( \eta \). This results in

\[
\psi_1(s) = \frac{\eta_0}{d} \sum_{s'=0}^{d-1} \delta(s, s') \psi_1(s') 
\] (23)
\[ \psi_2(s) = \frac{1}{d} \left\{ \eta_0 \sum_{s'=0}^{d-1} \delta(s, s') \psi_2(s') + \eta_1 \sum_{s'=0}^{d-1} \delta(s, s') \psi_1(s') + \frac{1}{2} \eta_0^2 \left\{ \left( \sum_{s'=0}^{d-1} \delta(s, s') \psi_1(s') \right)^2 - \frac{1}{d} \sum_{s'=0}^{d-1} \left\{ \sum_{s''=0}^{d-1} \delta(s', s'') \psi_1(s'') \right\}^2 \right\} \right\} \] (24)

which are the analogs of the equations eqn. (18) and eqn. (19).

Ignoring for the moment that first bifurcation equation is actually trivial in this case (we are faced with the daunting task of diagonalizing the identity matrix !), we are going to take a round-about way by exploiting the symmetries of the reduced excluded volume \( \delta(s, s') \) to obtain a complete set of eigenfunctions. This procedure prepares the way for later applications where the symmetries of the excluded volume will play a crucial role in the analysis. Instead of exploiting the full symmetry, which is that of the symmetric group \( S_d \) of all permutations of \( d \) objects, we can get away with just the subgroup formed by the cyclic permutations \( C_d \). The irreducible representations of this abelian group are the functions

\[ \phi_k(s) = e^{2\pi i ks} \quad k = 0, 1, \ldots, d - 1 \] (25)

They form an orthogonal set under the innerproduct defined by

\[ \langle \phi_i, \phi_j \rangle = \sum_{s=0}^{d-1} \phi_i^*(s) \phi_j(s) = d \delta(i, j) \] (26)

where the * denotes complex conjugation. The reduced excluded volume has the simple expansion

\[ \delta(s, s') = \frac{1}{d} \sum_{k=0}^{d-1} \phi_k(s) \phi_k^*(s') \] (27)

which is the completeness relation for the irreps of \( C_d \). Combining these two relations one sees that every \( \phi_k \) with \( k = 0, 1, \ldots, d - 1 \) is an eigenfunction of the reduced excluded volume with eigenvalue unity. Note, however, that \( \phi_0 \), being the identity representation of \( C_d \), is just a constant and therefore proportional to the isotropic distribution \( \psi_0 \), so should not be included in the bifurcating eigenfunction, whose general form thus becomes

\[ \psi_1(s) = \sum_{k=1}^{d-1} c_k \phi_k(s) \] (28)

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Inserting this form into the bifurcation equation eqn. (23) one immediately obtains the bifurcation condition

\[ \frac{\eta_0}{d} = 1 \] (29)

which fixes the bifurcation density \( \eta_0 = d \). We now know when the bifurcation occurs, but are still in the dark as to what exactly happens, since the coefficients \( c_k \) in the general form of the bifurcating eigenfunction are as yet undetermined, reflecting the fact that the \( \phi_k \) form a degenerate set of eigenfunctions of the reduced excluded volume. Having exhausted the first bifurcation equation, this is clearly the point where the second bifurcation equation eqn. (24) comes in. The fact that this equation can be used for the purpose at hand without solving for its unknowns is due to two surprises. The first surprise is that we can eliminate the unknown second order perturbation \( \psi_2 \). The key ingredient to this elimination is the following identity

\[ \langle \phi_k, \psi_2 \rangle = \eta_0 \frac{d}{d - 1} \sum_{s=0}^{d-1} \sum_{s'=0}^{d-1} \phi_k^*(s) \delta(s, s') \psi_2(s') \] (30)

which is valid for any \( k = 0, 1, \ldots, d - 1 \). This identity, which one easily checks in this special case, follows from a general property of the excluded volume, namely that it is invariant under the interchange of the two particles involved (in more formal terms this means that it can be interpreted as a hermitian operator on the space of single particle distributions equipped with a suitable inner product). The recipe is now as follows: take the inner product of eqn. (24) with any of the \( \phi_k \) with \( k = 1, \ldots, d - 1 \) and use the identity given above to equate the left hand side to the first term on the right hand side. This leaves \( d - 1 \) equations involving the unknowns \( c_k \) and \( \eta_1 \). Skipping the intermediate algebra these equations can be written as

\[ \frac{2\eta_1}{d^2} c_k = - \sum_{l=1}^{d-1} \sum_{m=1}^{d-1} \delta_{k, (l + m) \mod d} c_l c_m \] (31)

The second surprise is that one can scale away the prefactor containing the unknown first perturbation in the density \( \eta_1 \) (provided it is non-zero, of course) by changing to variables \( b_k = -\frac{d^2}{2\eta_1} c_k \) yielding the simplified equation

\[ b_k = \sum_{l=1}^{d-1} \sum_{m=1}^{d-1} \delta_{k, (l + m) \mod d} b_l b_m \] (32)
This equation is not as bad as they come and we can find $d$ solutions to it labeled by $n = 0, 1, \ldots, d - 1$

$$b_k^{(n)} = \frac{1}{d-2}e^{\frac{2\pi i nk}{d-2}}$$  \hspace{1cm} (33)

Putting it all together we find $d$ acceptable bifurcating eigenfunctions $\psi_1$

$$\psi_1^{(n)}(s) = \sum_{k=1}^{d-1} c_k^{(n)} \phi_k(s)$$

$$= -\frac{2\eta_1}{d^2(d-2)} \sum_{k=1}^{d-1} e^{\frac{2\pi i k(n-s)}{d-2}}$$

$$= -\frac{2\eta_1}{d^2(d-2)} (d\delta(n, s) - 1)$$  \hspace{1cm} (34)

The last identity brings us to our goal since it shows that the bifurcating solution is uniaxially symmetric about the ordering axis labelled by $n$, the fact that there are $d$ such solutions simply reflects the fact that the axes are all equivalent. We can thus conclude that we are dealing with an isotropic to nematic transition. Since we have assumed that $\eta_1 \neq 0$, we must be dealing with a first order transition (the case depicted in fig.1.b). Indeed in order for $\psi_1$ to represent enhancement of order in a certain direction we must have $\eta_1 < 0$ consistent with the “bending back” of the solution i.e. the creation of a v.d. Waals loop in the equation of state. The solution presented here is clearly valid only for $d \geq 3$. The case $d = 2$ is special and a glance at the equations shows that in this case we must have $\eta_1 = 0$, the fingerprint of a continuous transition (see fig 1.a). This should come as no surprise since the model for $d = 2$ is nothing but the Ising model, in one of its many disguises.

This is a good point to reflect on what we have achieved so far. Starting from the defining equations of our model we have derived by purely analytical means the location of the bifurcation point, an upper limit to the stability of the isotropic phase, as a function of the dimension and the parameters $e_{\parallel}$ and $e_{\perp}$ that describe the interactions between the particles involved. Moreover we have determined the order of the phase transition involved as well as the nature of the resultant phase. “Big deal, most of this was intuitively clear anyway”, I hear the skeptical reader say. Very true, of course, for the extremely simple model discussed here. However, the method, although devoid of intuition, is also free of prejudice and works just as well in more
complicated situations where intuition might not be of any help. I also hope that the reader has gotten some flavor of how the method focusses on rather general properties of the model being studied; most conclusions follow from the properties of the reduced excluded volume which is a quantity heavily constrained by symmetry- and other physical requirements. It is this feature which allows it to deal with whole classes of particles and/or interactions many detailed features of which need not be given in order to obtain the type of results we are after.

3.3 Connection with Landau theory

As mentioned in the introduction the combination of density functional theory and bifurcation analysis shows some analogy to the Landau theory of phase transitions. I would here like to pursue this analogy in some detail for the “toy model” just introduced. The bridge between the two theories is formed by the invariant expansion the distribution function involved. In our case where we have assumed a global $C_d$ symmetry the correct set of basis functions are the irreps $\phi_k$ defined in the previous subsection. The general form of the distribution function therefore is

$$\psi(s) = \sum_{k=0}^{d-1} a_k \phi_k(s)$$

(35)

Since $\psi$ must be normalized to unity we have the following constraint on the expansion coefficients $a_k$

$$\sum_{s=0}^{d-1} \psi(s) = \langle \phi_0, \psi(s) \rangle = da_0 = 1$$

(36)

This leaves the set $\{a_k\}_{k=1,\ldots,d-1}$ as free parameters. One more constraint is the fact that the distribution function must be real yielding the relation $a_k^* = a_{d-k}$.

The isotropic phase $\psi_0$ is characterized by

$$a_0 = \frac{1}{d}, \quad a_k = 0 \quad k = 1, \ldots, d - 1$$

(37)

making the set $\{a_k\}_{k=1,\ldots,d-1}$ a good candidate for an order parameter. By construction they also transform irreducibly under the symmetry group $C_d$ of the isotropic so that they indeed form a set of order parameters in the
sense of Landau [26]. The next step is to introduce the expanded form of
the distribution function in the free energy functional eqn. (21) and expand
with respect to the order parameters assuming that they are small, as is the
case near a phase transition. To third order in the $a_k$ we find

$$
\frac{\beta F}{N} \equiv f = f_0 + \frac{1}{2} d(d - \eta) \sum_{k=1}^{d-1} a_k^* a_k - \\
\frac{1}{6} d^2 \sum_{k=1}^{d-1} \sum_{k'=1}^{d-1} \sum_{k''=1}^{d-1} a_k a_{k'} a_{k''} \delta_{(k+k')} \text{mod} d, d-k'' + \ldots
$$

(38)

From the vanishing of the coefficient of the term quadratic in the order pa-
rameters we immediately recover the bifurcation condition $\eta = d$. Moreover,
if we ignore for the moment the presence and influence of higher order terms
in the expansion and differentiate with respect to the $a_k$ in order to mini-
mize the free energy, we recover equations equivalent to eqn. (31), leading
to the result that the solution has the expected uniaxial symmetry. In this
way one obtains exactly the same information as one got from the first two
bifurcation equations. The last step, however, can hardly be called system-
atic, and one would really need a more sophisticated analysis in terms of
the algebraically independent invariants along the lines of Prokrovskii and
Kats [20] to establish the claimed result. The source of this problem is the
fact that we are expanding the functional at a fixed value of the density. The
density, in contrast to the $\epsilon$-parameter in the bifurcation analysis, is not such
a good measure of the distance to the bifurcation and does not allow us to
separate the successive perturbations to the reference phase that determine
the properties of the emergent phase.

Expanding the free energy functional in a suitable set of order parameters
thus leads to a problem formally equivalent to the Landau expansion but
with the big difference that the coefficients in the expansion explicitly contain
microscopic information about the particles and their interactions. Although
the procedure outlined above leads to the same information, I feel that from a
calculational point of view the systematics of the bifurcation analysis applied
to the stationarity equations rather than to the functional are clearly to be
preferred.
4 Applications

In this section we will look at some applications of bifurcation analysis to more (or less) realistic models of liquid crystals. No attempt is made to review all aspects of the models discussed, but rather to indicate how the analysis reveals the salient aspects of the phase transitions involved and how these compare to results obtained by simulations. First of all the “nematic” to smectic A transition in a system of perfectly aligned hard rods is discussed. Although perhaps a somewhat artificial model it is nevertheless historically important in the sense that it was the first system for which conclusive evidence [24] was obtained that purely repulsive interactions can lead to liquid crystalline phases beyond the traditional nematics, a possibility that up till then had been actively dismissed by most workers in the field. This discovery has given a new lease on life on hard particle models in liquid crystal research, which is a welcome development both for simulators and theorists alike. Next the class of biaxial hard particles is taken on. Here the analysis really comes alive, since it allows us to infer many important properties of the phase diagram without resorting to a specific calculation on a single model. Finally I look towards the future and discuss some current projects and thoughts about future developments.

4.1 Parallel hard rods

Consider a fluid of hard cylinders perfectly aligned along a given direction which we will identify with the $z$-axis of our coordinate system. Without further justification we adopt the Onsager approximation [16]. More elaborate functionals have been constructed for this model [28, 19], but these do not lead to qualitatively different results. The characteristic function of the excluded volume of two cylinders at a relative separation $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ is given by

$$\chi(\mathbf{r}) = \Theta(\sigma^2 - x^2 - y^2)\Theta(L - |z|)$$

(39)

where $\sigma$ and $L$ are the diameter and the length of the cylinders respectively and $\Theta(\cdot)$ denotes the Heavyside function. The analog of the first bifurcation equation eqn. (11) is given by

$$\rho_1(\mathbf{r}) = -n \int d\mathbf{r}' \chi(\mathbf{r} - \mathbf{r}')\rho_1(\mathbf{r}')$$

(40)
where as before $n$ is the number density of the spatially homogeneous “nematic” phase formed by the low density system. Since the characteristic function is invariant under global translations, the sought after eigenfunction must be a plane wave $\phi_q(r) = \exp i q \cdot r$. Inserting this into the equation we find the bifurcation condition

$$1 = -2\pi \sigma^2 Ln_j(q\parallel L) \left( \frac{J_1(q\perp \sigma)}{\frac{2}{7} q\perp \sigma} \right)$$

where $j_0$ is a spherical Bessel function and $J_1$ an ordinary one and we have decomposed the wavevectors in its components along and perpendicular to the alignment axis. This equation as it stands is heavily underdetermined. Fortunately we can use the physical requirement that we should look for the smallest density at which there exists a solution, since this is where the low density spatially disordered phase becomes unstable. Given this requirement there is just one relevant solution

$$n_0 = 0.7321 \sigma^{-2} L^{-1}$$
$$q_{\parallel,0} = 4.493 L^{-1}$$
$$q_{\perp,0} = 0$$

which describes the onset of a smectic density wave along the alignment axis. Knowing the nature of the bifurcating solution simplifies the further analysis because it allows us to parametrize the one particle density as

$$\rho(r) = n \left( 1 + \sum_{l=1}^{\infty} a_l \cos(lqz) \right)$$

In order to perform the bifurcation analysis to higher order we insert this parametrization into the stationarity equation and make the following expansions

$$n = n_0 + \epsilon n_2 + \epsilon^2 n_2 + \ldots$$
$$a_l = a_{l,0} + \epsilon a_{l,1} + \epsilon^2 a_{l,2} + \ldots \quad l = 1, 2, \ldots$$
$$q = q_0 + \epsilon q_1 + \epsilon^2 q_2 + \ldots$$

Without going into details I just quote the most important results: (i) The free energy of the smectic phase for $n > n_0$ is indeed lower than that of the nematic phase, showing that the bifurcation leads to a thermodynamically
stable phase (ii) \( n_1 = 0 \), so the predicted phase transition is second order in full agreement with the simulation results. Of course, the Onsager approximation is too crude to get quantitative results comparable to the simulations. One improvement suggested in ref. [16] is to add more terms in the diagram expansion of the free-energy. Carrying out this program up to the fourth order diagrams one finds the following values for the critical packing fraction \( \eta = \frac{1}{4} \pi \sigma^2 Ln \) and the wavelength \( \lambda \) of the smectic modulation at the transition

\[
\eta_c^{(4)} = 0.37 \quad \lambda_c^{(4)} = 1.34L 
\] (45)

These values compare favourably to the simulation results

\[
\eta_{c}^{MC} = 0.36 \quad \lambda_{c}^{MC} = 1.27L 
\] (46)

### 4.2 Biaxial particles

Most of the convex hard particles which have been studied as models for liquid crystals have the property of being uniaxially symmetric i.e possess an axis of rotational symmetry. They therefore seem doomed to form, if anything, nematic phases which also possess this same symmetry, at least as the first stage of symmetry breaking from the low-density isotropic phase. Particles in general, however, are not uniaxially symmetric. How does this influence the formation of the nematic phase? Under what conditions can phases with lower symmetry develop from the isotropic phase? It is this type of questions that is ideally suited for an attack by bifurcation analysis. The example to be discussed here is what happens if the particles have biaxial symmetry of the type \( D_{2h} \), which is the symmetry group of a rectangular box with at least one of its sides different in length than the other two. Since \( D_{2h} \) is a subgroup of \( C_{\infty h} \), this class of particles contains all the uniaxially symmetric, inversion invariant, models as well so comparisons with previous results are easy. Examples of such particles are general ellipsoids and spheroid-platelets [15] which have the well-studied ellipsoids of revolution and spheroid-cylinders as special cases respectively. We again call on the Onsager approximation to illustrate the working. This is not really a heavy restriction since I have recently shown [18] that the results about to be presented

---

\[\text{In fact there exists a large, but unfortunately rather impenetrable, mathematical bibliography on the relationship between symmetry breaking and bifurcations. For a recent review supposedly aimed at a more physical audience see [7]}\]
hold without change for a large class of functionals that comprises most of
the ones proposed in the literature e.g. scaled particle theory [4] and more
recently the Smoothed Density Approximation [10]. The common element
of all these approximations is that the dependence of the excess free energy
of the system on the orientational distribution of the molecules is described
in terms of the distribution averaged excluded volume
\[ E_{\text{ave}}[\psi] = \frac{1}{2} \int d\Omega_1 \int d\Omega_2 \psi(\Omega_1) \psi(\Omega_2) E(\Omega_1, \Omega_2) \] (47)
which is also the second virial coefficient in a density expansion of the free
energy. As it turns out all symmetry related properties of the phases that
develop from the isotropic phase are determined solely by the properties of the
excluded volume \( E(\Omega_1, \Omega_2) \) regardless of the precise form of the functional. Of
course the more “non-universal” features of the transitions, like the location
of the bifurcations, do depend on the specific functional.

Let’s start then by analyzing the properties of the excluded volume of two
particles with fixed orientations that follow from symmetry considerations
alone. First of all global rotational invariance dictates that it should be a
single argument function \( E \) of the relative orientation \( \Omega = \Omega_2^{-1} \Omega_1 \) of the two
particles only, or
\[ E(\Omega_1, \Omega_2) = E(\Omega) \] (48)
Symmetry with respect to the interchange of the two particles involved imply
that the function \( E(\Omega) \) is invariant under taking the inverse of its argument
\[ E(\Omega^{-1}) = E(\Omega) \] (49)
This last property, together with the fact that the excluded volume is a real
quantity, implies that the excluded volume interpreted as an operator using
the following prescription
\[ E[f](\Omega_1) = \int d\Omega_2 E(\Omega_1, \Omega_2) f(\Omega_2) \] (50)
is hermitian on the space of real valued functions of orientation equipped
with the following innerproduct
\[ \langle f, g \rangle = \int d\Omega f(\Omega) g(\Omega) \] (51)
This property, as mentioned in the section on the tutorial example, is a crucial
ingredient of the analysis. Finally we have to implement the \( D_{2h} \) symmetry
of the particles themselves. If \( g_1 \) and \( g_2 \) arbitrary elements of this symmetry group interpreted as a rotation and/or inversion, then we must require the following identity

\[
E(\Omega_1 g_1, \Omega_2 g_2) = E(\Omega_1, \Omega_2)
\]  

(52)
to hold, or equivalently

\[
E(g_2^{-1} \Omega g_1) = E(\Omega)
\]  

(53)
A set of functions of the relative orientation that have the above symmetries can be obtained from the usual Wigner rotation matrices \( D_{m,n}^{(l)} \) by the following projection

\[
\Delta_{m,n}^{(l)}(\Omega) \propto \sum_{g_1 \in D_{2h}} \sum_{g_2 \in D_{2h}} D_{m,n}^{(l)}(g_2^{-1} \Omega g_1)
\]  

(54)
which if one works this out yields the, suitably normalized, functions

\[
\Delta_{m,n}^{(l)} = (\frac{1}{2}\sqrt{2})^{2+\delta_{m,0}+\delta_{n,0}} \left( D_{m,n}^{(l)} + D_{-m,n}^{(l)} + D_{m,-n}^{(l)} + D_{-m,-n}^{(l)} \right)
\]  

\[ l = \text{even} \quad m, n \geq 0 \text{ and even}
\]  

(55)
Putting it all together we can expand the excluded volume as

\[
E(\Omega_1, \Omega_2) = \sum_{l,m,n} \left( \frac{2l+1}{8\pi^2} E_{l,mn} \Delta_{m,n}^{(l)}(\Omega_2^{-1} \Omega_1) \right)
\]  

(56)
where the prime reminds us of the restrictions on the indices \( l, m \) and \( n \). Moreover, the particle interchange symmetry implies that the expansion coefficients are symmetric in the indices \( m \) and \( n \) i.e \( E_{l,mn} = E_{l,nm} \). In this way we have milked all the information from the various symmetry constraints that apply to the excluded volume achieving a considerable reduction in the number of parameters that enter into the problem.

The next step in the program is to solve the lowest order bifurcation equation (cf. eqn. \([13]\)). This involves some explicit properties of the functions \( \Delta_{m,n}^{(l)} \), the details of which need not concern us here. The most important point is that these functions for a fixed value of the angular momentum index \( l \) form \((\frac{l}{2}+1)^2\)-dimensional invariant subspaces under the operation eqn. \([50]\) and that every eigenvalue is \((\frac{l}{2}+1)\)-fold degenerate. For reasons explained earlier on, we are looking for the eigenvalue that will yield the smallest value of the bifurcation density. Given the assumptions made — convexity, and more importantly pure \( D_{2h} \) symmetry so no cubic symmetry — this relevant
eigenvalue will be found in the subspace with \( l = 2 \), which describes the most coarse scale deviations from isotropicity. The result for the bifurcation density is

\[
n_0 = -\frac{8\pi^2}{\frac{1}{2}(E_{2,00} + E_{2,22}) - \frac{1}{2}\sqrt{(E_{2,00} + E_{2,22})^2 + 4E_{2,02}^2}}
\]  

(57)

while the two degenerate eigenvectors \( \phi_0 \) and \( \phi_2 \) are given by

\[
\phi_0 = e_0\Delta^{(2)}_{0,0} + e_2\Delta^{(2)}_{0,2} \\
\phi_2 = e_0\Delta^{(2)}_{2,0} + e_2\Delta^{(2)}_{2,2}
\]

(58)

where the coefficients are the following explicit functions of the expansion coefficients

\[
e_0 = -\frac{E_{2,02}}{\sqrt{E_{2,02}^2 + \tau^2}} \\
e_2 = \frac{\tau}{\sqrt{E_{2,02}^2 + \tau^2}}
\]

\[
\tau = \frac{1}{2}(E_{2,00} - E_{2,22}) + \frac{1}{2}\sqrt{(E_{2,00} - E_{2,22})^2 + 4E_{2,02}^2}
\]

(59)

Note that the bifurcation density and the eigenfunctions are completely determined by the three expansion coefficients \( E_{2,00}, E_{2,02} \) and \( E_{2,22} \) of the excluded volume. This is reasonable since, intuitively, a convex particle of \( D_{2h} \) symmetry has three independent dimensions that fix its coarse-scale shape (cf. the side lengths \( a, b \) and \( c \) of a rectangular box). Since the absolute volume of the particle is irrelevant, and can be absorbed into a redefined density, there are effectively only two free parameters that describe the specific shape (for the rectangular box one could take the ratios \( \frac{a}{c} \) and \( \frac{b}{c} \) for instance).

Finally, we have to determine the actual bifurcating eigenfunction, in order to learn what the symmetry of the new phase is. We know that it is a linear combination of the degenerate eigenfunctions obtained from the lowest order bifurcation equation

\[
\psi_1 = c_0\phi_0 + c_2\phi_2
\]

(60)

Following the procedure already outlined in the tutorial example we can determine the unknown coefficients \( c_0 \) and \( c_2 \) by using the second order bifurcation equation eqn. (19). The interested reader can find the details in
the original reference [17]. Amazingly enough, the result depends only on the sign of a single quantity

\[ \nu = e_0(e_0^2 - 3e_2^2) \]  \hspace{1cm} (61)

where the \( e_n \) are the components of the degenerate eigenfunctions \( \phi_m \) on the basis \( \Delta_{m,n}^{(2)} \). We distinguish the following cases

\[ \nu > 0 \] The solution has uniaxial symmetry and describes the ordering of the major axis of the particle in a preferential direction i.e a rod-like nematic phase which we denote by \( N_+ \). The transition to this phase will be of first order.

\[ \nu = 0 \] The solution has the \( D_{2h} \) symmetry of a biaxial nematic phase \( N_{\text{biax}} \). The transition to this phase is of second order.

\[ \nu < 0 \] The solution again has uniaxial symmetry but now describes the ordering of the minor axis of the particle in a preferential direction i.e a disk-like nematic phase \( N_- \). The transition is again of first order.

The particles for which \( \nu = 0 \) form lines of Landau bicritical points in the shape-density phase diagram being the endpoints of the first order transition lines to the rod- and disk-like nematic phases and marking the four-phase coexistence of the isotropic, rod-like, disk-like and biaxial phases. The solutions to the equation \( \nu = 0 \) can be given explicitly in terms of the excluded volume expansion coefficients \( E_{2,mn} \) as

\[ E_{2,02} = 0, \quad E_{2,00} - E_{2,22} > 0 \]  \hspace{1cm} (62)

and

\[ |E_{2,02}| = -\frac{1}{2}\sqrt{3}(E_{2,00} - E_{2,22}) \]  \hspace{1cm} (63)

The fact that there are two equations reflects the underlying arbitrariness of the choice of the remaining two axes of the particle fixed frame once the primary axis is chosen. A generic impression of a slice of the phase diagram in the neighbourhood of such a point is sketched in figure 2. The existence of these bicritical points can be understood by considering the following “thought experiment” on a system of rectangular blocks with two side lengths \( c > a \) considered fixed and third \( b \) considered variable. We start with \( b = a \) where the particle is an effectively uniaxial rod clearly
Figure 2: Generic phase diagram in the neighbourhood of the $I - N_{(+)} - N_{(\text{biax})} - N_{(-)}$ multicritical point. x-axis: parameter describing shape of particle. y-axis: density. The full lines are continuous transitions while the dashed lines bound the coexistence region of first order transitions.
disposed to forming a rod-like nematic. If we now gradually increase $b$ until $b = c$ we end up again with an effectively uniaxial shape but now clearly disk-like and bound to form a nematic phase where the normal to the disk will be ordered. The two types of nematic order $N_+(\cdot)$ and $N_-(\cdot)$ cannot be transformed continuously into each other so another phase must intervene, which perforce has a lower symmetry. This leads to the conclusion that there must be at least one intermediate value of $b$ for which the particle is neither enough rod-like nor disk-like to form the corresponding phases. A duality argument first proposed by Straley [23] which maps rods into equivalent disks can then then be used to show that there is a unique value of $b$ for which this intermediate phase is accessible from the isotropic phase.

Sphero-platelets are to date the only particles for which the expansion coefficients $E_{2,mn}$ have been calculated analytically and the equation $\nu = 0$ determining the “bicritical” particles solved explicitly. This solution suggests strongly that asymptotically in a regime where the largest dimension of the particle is much larger than the smallest dimension ($c \ll a$) the intermediate dimension $b_*$ of the “bicritical” particle is approximately the geometric mean of the other two

$$b_* \sim \sqrt{ac}$$

This prediction was recently verified in the first extensive simulation on a system of biaxial particles—in this case general ellipsoids—performed by Allen [1]. This result is all the more noteworthy since it shows that the results obtained on these symmetry related questions in the type of approximations treated here remain relevant to the full statistical mechanics of the problem. This supports some of the ideas I have presented regarding the “universality” of results obtained from the bifurcation analysis even of highly approximate free energy functionals.

In summary we have managed to determine for a whole class of convex hard particles the properties of the phases that are reached by phase transitions from the low density isotropic phase, as predicted by a whole class of free-energy functionals. In order to apply the analysis to any specific particle in this class one needs as input only three numbers: $E_{2,00}, E_{2,02}$ and $E_{2,22}$. It is precisely this generality and economy of description, which focusses only on those parameters in the problem which are relevant to the properties of the actual transitions, which make bifurcation analysis such an attractive tool in the study of symmetry-breaking phase transitions.
4.3 . . . and beyond

The question of which problem to tackle next using the techniques described here is difficult since we are faced with an *embarras de choix*. The phenomenology of liquid crystals has grown so immensely during the last two decades that the possibilities seem inexhaustible. I’ll therefore restrict myself to two directions. The first is interesting also from a methodological point view, while the second concerns qualitatively new and hitherto unexpected phases.

The first category of problems concerns the transitions from already ordered phases. All the examples treated in these lectures were transitions from the totally disordered state. The general theory, however, deals equally well with these order-order phenomena. Good examples are the nematic-smectic transition in a system of freely rotating rods and the as yet not completely understood sequence of phase transitions in the parallel hard cylinder- and spherocylinder systems. Both these problems have already been studied in the past (*N* − *SA* transition: [22, 19], parallel hard rods: [25, 11]), but I believe the last word has not been spoken yet. In the case of the nematic-smectic transition, for instance, it has up to now always been assumed that the smectic fluctuation that appears at the transition is decoupled from the orientational order. Technically speaking this means that a smectic fluctuation of the form

\[ \psi_1(z, n) = \psi_0(n) \cos qz \]  \hspace{1cm} (65)

is introduced by hand, where \( n \) denotes the unit vector along the particle’s symmetry axis and \( \psi_0 \) is the orientation distribution function of the parent nematic phase. This assumption is already suspect on purely physical grounds, since we expect enhancement of the nematic order inside the smectic layer due to the increased local density there. This suspicion is confirmed if we apply the general form of the first bifurcation equation eqn. (11) to this problem. We find that the bifurcating solution has the initial form

\[ \psi_1(r, n) = \phi_q(n) \cos q \cdot r \]  \hspace{1cm} (66)

where the function \( \phi_q \), which describes the lowest order response of the orientational distribution to the smectic density wave, is a solution of the following equation

\[ \phi_q(n) = -n\psi_0(n) \int d\mathbf{n}'\hat{c}_0^{(2)}(q, n, n')\phi_q(n') \]  \hspace{1cm} (67)
which contains the fourier transform $\hat{c}_0^{(2)}$ of the direct pair correlation in the nematic phase. Although linear, this is a highly non-trivial equation, mainly because its kernel is, even in the Onsager approximation, a complicated function of its arguments. Solving it would, among other things, give a first principles demonstration that the smectic density wave is indeed parallel to the nematic director.

The second interesting development is the evidence for the existence of a so called cubic phase in a system of hard cut-spheres by Frenkel and co-workers \[6, 27\]. This is a phase, which possibly has long range cubic orientational order without, however, long-range positional order (it is of course highly structured locally). Not only is the type of order new but it also surprising that uniaxially symmetric bodies like the cut-spheres can form homogeneous phases of lower symmetry, in this case that of the cubic group $O_h$. Since the evidence suggest that this phase develops spontaneously from the isotropic phase without any intermediate nematic, it would seem feasible to understand its creation using bifurcation analysis of a suitable functional. As a preparatory exercise we are currently studying a model system that is guaranteed to show a cubic phase, albeit through a different mechanism. This model is that of the so called Onsager crosses, introduced by Frenkel \[6\] to study the possibilities of the formation of liquid crystals with exotic symmetries. The model consist of particles composed of three mutually orthogonal infinitely thin hard rods that are connected to each other in their centers of mass so as to form a rigid cross.

5 Conclusions

At the end of this short guide to the application of bifurcation analysis to the study of liquid crystal phase transitions, it seems fitting to put the technique once more in perspective. First of all it is useful to bear in mind that it is indeed a tool and not a theory. In the context discussed here, formulating a theory is equivalent to specifying a free energy functional. There is no general recipe for this process of theory formation although we are guided by criteria like simplicity and unbiasedness (you should take care not to put in by hand what you want to get out!). The Onsager approximation for hard non-spherical particles scores well on these points, which, apart from the fact that it also yields interesting results, accounts for its ongoing and well-deserved use. Bifurcation analysis, on the other hand, is just a technique
for obtaining some of the consequences of a given theory by analyzing the non-linear equations that describe the predicted equilibrium phases. It is, however, a rather powerful technique, and I hope to have given the reader some impression of this in these lectures. More specifically it focusses exclusively on the most interesting aspect of any theory viz. its predicted phase transitions and their properties. If a theory can be compared to an oyster, then bifurcation analysis is one of those smart little implements that break it open in order to get at the pearl, being the phase transition. Given the continued activity in the field and the ever increasing knowledge obtained by computer simulations on well defined model systems, I feel confident that bifurcation analysis is just at the beginning of its “product life-cycle” in liquid crystal research.

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