GROUP THEORY OF THE LANDAU - THERMODYNAMIC THEORY OF CONTINUOUS PHASE TRANSITIONS IN CRYSTALS*

Joseph L. Birman
Physics Department
City College - City University of New York
New York, New York 10031

Abstract

A review is given of group-theory related aspects of the Landau-Thermodynamic Theory of continuous phase transitions in crystals. The review discusses developments of the theory during several time intervals. First interval: the 25 years (1937-62) after the theory was presented; Second interval (1962-77) covers the recent 15 years; Third interval (1977-) presents some possible directions for work in the future. Thus the first 40 years of this theory were characterized *inter alia* by elaborations and applications of the group theory aspects of the problem which Landau examined:

Given a system with group G;
What groups G', G'', ... may be achieved
by continuous transitions i.e. $G \to G', \ldots$?
What order parameters are consistent
with transitions $G \to G'$, or $G \to G''$, ...?

This review will emphasize group-theory related aspects of the theory.

*This work supported in part by NSF DMR76-20641-A01; ARO DAHC04-75-G-0052; FRAP-CUNY 11680.

1. Adspice (1937-1962)

This year 1977 marks the fortieth anniversary year of the seminal work by L.D. Landau[1] of 1937, in which he put forth a thermodyr heory of continuous phase transitions in crystals with symmetry consideratio. .aying an essential role. After forty years it seems appropriate to attempt at least some partial review of salient aspects of the theory namely: its basic principles, some clear illustrations of general applications and present status, and also one might presume to speculate on some directions for future work.

As given by Landau the theory contained two intertwined threads: a) a theory of symmetry change in continuous phase transitions and b) a theory of critical properties and thermodynamic functions near the transition. The first thread has been rather successful and has given rise to a continuing literature. It is the topic of this paper. The second thread has had a rather more mixed history: it is now known as "Mean Field Theory". Much current active work ("beyond" mean field theory) is now in process taking fluctuations and quantum corrections into account. Reviews of this literature exist[2] which can also serve as introduction. Later we make some brief remarks about the relationship between these two threads in the light of recent work.

The thermodynamic theory is concerned with transitions in crystals in which the physical state of the system changes continuously at the transition, but the symmetry changes discontinuously. To be precise: the total free energy Φ (Gibbs Function) of the system , is continuous, but discrete elements of symmetry are lost at the phase transition point. This appears to pose a dilemma: continuous transition but discrete change of a symmetry.

To resolve this "dilemma", Landau introduced two objects describing the system: the function Φ, and a density function ρ; the interplay between them plays a key role in the theory. We recapitulate his argument, first giving a one-dimensional model problem which focusses attention on some important aspects.

The Landau "Ansatz" and Model Problem: near T_c there exists a single "generalized Gibbs Potential" or "incomplete" Free Energy. Call this object $\Phi(T,P,c)$ where T and P are the temperature and pressure, and c is an "unconstrained" variable in Φ[3]. The order parameter c will be determined by minimizing Φ at each (T,P) :

c=0 implies "disordered" state (higher symmetry) $T>T_c$;

$c\neq 0$ implies "ordered" state (lower symmetry) $T<T_c$.

Further, near $(T_c P_c)$, assume that Φ can be expanded in powers of c

$$\Phi = \Phi_0 + \alpha c + Ac^2 + Bc^3 + Dc^4 + \ldots \qquad (1.1)$$

Assume $\alpha \equiv 0$, A>B>D> ...0 and A,B,... depend upon (T,P). Then Φ is a minimum if c=0. Consider now the first terms of the series: $\Phi \sim \Phi_0 + Ac^2$. If A<0 then $c\neq 0$ produces a minimum of Φ. Clearly the equation A(P,T)=0 determines the phase transition line separating regions with c=0 and $c\neq 0$. Now suppose $B\neq 0$, so $\Phi \sim \Phi_0 + Ac^2 + Bc^3$.

Evidently in this case $c \neq 0$ can always produce Φ_{MIN}, irrespective of the sign of A, i.e. the system will always be ordered and no phase transition can occur.

Consider this situation a little further, if B is present in general. It may be that <u>both</u> A and B vanish at a point in (T,P) plane, keeping the transition continuous:

$$A(P,T) = 0, \quad \text{and}$$
$$B(P,T) = 0 \tag{1.2}$$

Simultaneous vanishing produces a singular or "tricritical" point at (P_c, T_c). Otherwise if B is present and does not vanish with A, the ordered state $c \neq 0$ always is stable.

For a <u>normal</u> continuous transition $B \equiv 0$. As we shall see below this produces a symmetry restriction and has important symmetry consequence. Hence, to fourth order in c, the "normal" Landau free energy is

$$\Phi \sim \Phi_0 + Ac^2 + Dc^4 \; ; \tag{1.3}$$

$A(T,P) = 0$ gives the transition line.

Recall that in the <u>disordered</u> state $A>0$ and $D>0$, and Φ_{MIN} requires $c=0$, while in the <u>ordered</u> state $A<0$ and $D>0$ so $c \neq 0$ produces Φ_{MIN}.

This Landau Model Problem indicates schematically the structure of the theory.

The proper theory emerges in three dimensions; in which symmetry becomes manifest. First let us confront the question of how to define the symmetry of the system. Suppose there are atoms of a certain kind comprising the crystal. Let $\rho(\vec{r})$ be the probability that the atom is located at $\vec{r}$. The set of equivalent positions

$$\vec{r};\ \vec{r}' = P\vec{r};\ \vec{r}'' = Q\vec{r};\ \vec{r}''' = S\vec{r};\ \ldots$$

where $\rho(\vec{r}) = \rho(\vec{r}') = \rho(\vec{r}'') = \rho(\vec{r}''') = \ldots$ is obtained by transforming the initial position $\vec{r}$ into $\vec{r}'$, $\vec{r}''$, ... The linear operators

$$E,\ P,\ Q,\ S,\ \ldots$$

including the identity E form the symmetry group of the system. This group G is a space group. The usual notation for the space group elements (operators) is

$$P \equiv (\phi|\vec{t}) \text{ and } (\phi|\vec{t})\cdot\vec{r} \equiv \phi\vec{r} + \vec{t}$$

where ϕ is an orthogonal transformation: rotation, reflection, and $\vec{t}$ a translation perhaps including a fractional (non-integral) translation.

Thus the space group G of the system is the invariance group of the probability density function $\rho(\vec{r})$: a typical element of G has the property

$$\rho((\phi|\vec{t})^{-1}\cdot\vec{r}) = \rho(\vec{r}). \tag{1.4}$$

In order that the space group G shall change (phase transition) we will require that $\rho(\vec{r})$ shall depend also functionally upon the order parameter $\{c\}$. Specifically we require:

$$\rho(\vec{r};\ \{c\}) \text{ shall be such that:}$$

$$\rho(\{c\} = 0) \to G$$

$$\rho(\{c\} \neq 0) \to G' \qquad (1.5)$$

where G' is a subgroup of G. Thus discrete symmetry elements are lost upon phase transition $G \to G'$.

The total Free Energy Φ in three dimensions is treated as in the Landau Model (one-dimensional) Problem. Now however the physical order parameter will be a set of objects $\{c\}$. Here

$$\{c\} \to \text{irred. rep. } D^{(j)} \text{ of G.}$$

That is the set $\{c\}$ is a basis for an irreducible representation D^j of G. (We discuss D^j for space groups below.) The interplay between the density function ρ and the Free Energy Φ, both functionally depending on $\{c\}$ is the key to Landau's theory. It is assumed that $\Phi(\{c\})$ is a continuous functional of $\{c\}$ near $(T_c P_c)$ and that $\Phi(\{c\})$ always satisfies the extremum condition for each T and P. Then

$$T>T_c\ ,\ \Phi_{MIN} \qquad \{c\} = 0 \to G$$

$$T<T_c\ ,\ \Phi_{MIN} \qquad \{c\} \neq 0 \to G'\ .$$

Consider group G. The set of all partner functions for all irreducible representations D^j of G is complete in the sense of symmetry. Thus any function can be expanded in this symmetry-complete set. Write the density $\rho = \rho_0 + \delta\rho$ and expand $\delta\rho$ in the set $\{D^j\}$ - omitting the trivial representation D^1 of G which is assumed included in ρ_0. Then

$$\rho(\vec{r}) = \rho_0(\vec{r}) + \delta\rho(\vec{r})$$

$$\delta\rho(\vec{r}) = \sum_{j\,k}{}' \; c_k^j \, \phi_k^j \, (\vec{r})$$

where j labels the irreducible representation, and k the partner, the prime denotes omission of D^1; the basis functions $\phi_k^j(\vec{r})$ transform as

$$P_S \, \phi_k^j \, (\vec{r}) = \phi_k^j \, (S^{-1}\vec{r}) = \sum_m D^j(S)_{mk} \, \phi_m^j$$

Usually it is more convenient to take the quantities c_k^j as bases rather than the functions ϕ_k^j .

By definition ρ is a scalar density or probability. Then the terms in $\delta\rho$ also are scalar.

The Free Energy Φ is now written as a series

$$\Phi = \Phi_0 + Af^{(2)}(\{c\}) + Bf^{(3)}(\{c\}) + \ldots$$

$$+ \sum_\gamma D_\gamma f_\gamma^4(\{c\}) + \ldots . \qquad (1.5)$$

Because Φ is a scalar invariant each term in the expansion must be G-invariant. Then $f^{(2)}(\{c\})$ is an invariant bilinear (quadratic) form in the components: c_1^j, c_2^j, $\ldots c_k^j$, $\ldots$. (fixed j). (The linear term is absent since j=1 is excluded.) If we consider the first two terms of the expansion it is immediate why only one irreducible representation is taken: each set $\{c^j\}$, $\{c^{j'}\}$, ... will produce an independent quadratic invariant A_j , $A_{j'}$, ... Following the Model Problem, from each such quadratic invariant we obtain a distinct equation $A(P,T) = 0$. If two such equations were present: $A_j(P,T) = 0$ and $A_j(P,T) = 0$ they would determine one (tricritical) point for the transition. The classical theory excludes this case (but see below).

Thus only the bases of a single irreducible representation D^j are used in $\delta\rho$ and in Φ.

If a trilinear invariant $f^{(3)}(\{c\})$ were present a second condition $B(P,T) = 0$ would occur again determining a point, along with $A(P,T) = 0$. The theory requires absence by symmetry of this term. In group theoretic terms

$$(D^j \otimes D^j \otimes D^j)_{SYM} \equiv D^j_{(3)} \not\supset D^1 \qquad (1.6)$$

where all representations refer to G.

To terms of fifth order

$$\Phi = \Phi + A\, f^{(2)}(\{c\}) + \sum_\gamma D_\gamma f_\gamma^{(4)}(\{c\}) \qquad (1.7)$$

where γ enumerates the distinct quartic invariants which can be constructed from the set $\{c\}$. The density function is

$$\rho(\vec{r}) = \rho(\vec{r}) + \sum_k{}' c_k^j \phi_k^j \equiv \rho(\{c\}) \qquad (1.8)$$

One manner of proceeding is to find all possible sets of extrema of Φ, by solving the set of equations:

$$\partial\Phi/\partial c_k^j = 0 \qquad k = 1 \ldots \ell_j \qquad (1.9)$$

Each such extremum is achieved by some non-zero subset of the $\{c_k^j\}$. Let one such set be $\{\bar{c}_k^j\}$. Then the density

$$\rho(\vec{r}) = \rho_0(\vec{r}) + \sum_k{}' \bar{c}_k^j \, \phi_k^j(\vec{r})$$

corresponds, and the invariance group $\bar{G}' \supset G$ is the new symmetry. The transition $G \to \bar{G}'$ is then predicted to be consistent with continuous change, with the order parameter $\{\bar{c}\}$. Note that the theory does not require this transition to be continuous, but permits it to be.

So far the theory implicitly assumes the crystal structures G and G' to be spatially homogeneous. Lifschitz first investigated this requirement carefully.[4] To exclude inhomogeneity it should be impossible to construct an invariant from bilinear products of the c_k^j and their spatial derivatives. The two which come to mind are the antisymmetric bilinear:

$$\{c_k^j \, \partial c_\ell^j/\partial x - c_\ell^j \, \partial c_k^j/\partial x\} \sim J_{[2]}$$

and the symmetric bilinear

$$(c_k^j \, \partial c_\ell^j/\partial x + c_\ell^j \, \partial c_k^j/\partial x) \equiv \partial/\partial x \; (c_k^j \, c_\ell^j) \sim J_{(2)}$$

But if $J_{(2)}$ were in the Free Energy (density) ϕ then the total free energy $\Phi \sim \int \phi dv$ merely gains a constant. However if $J_{[2]}$ were present then an extremum of Φ would occur consistent with spatial variation of the order parameter i.e. a non-homogeneous crystal. To eliminate this possibility Lifschitz introduced the condition

$$D^j{}_{[2]} \otimes D^{(\nabla)} \not\supset D^1$$

If this Lifschitz condition is obeyed then only spatially homogeneous solutions would result.

Now a brief review of the theory of space group irreducible representations can be given.[5] The space group G is a discrete subgroup of the Euclidean group involving discrete orthogonal and inhomogeneous (translation) transformations. Let T be the group of lattice translations: it is a normal subgroup of G. Then G can be decomposed as

$$G = T + (\phi_2|\tau_2) \; T + \ldots + (\phi_h|\tau_h) \; T$$

and $G/T = P$ is the crystal class or "point group of the space group". The fractional τ may be zero or not. T is an Abelian group (actually product of three Abelian groups

-- one for each cartesian direction) and is reduced via a set of Bloch Functions $\psi^{(\vec{k})}$, such that

$$(\varepsilon|t_L)\ \psi^{(k)} = e^{i\vec{k}\cdot t_L}\ \psi^{(k)} = D^{(k)}(\varepsilon|t_L)\ \psi^{k}$$

where t_L is a lattice translation. The matrix

$$D^{(k)}(\varepsilon|t_L) \equiv e^{i\vec{k}\cdot t_L}$$

is a one dimensional irreducible representation. The complete set of inequivalent $\vec{k}$ (mod $2\pi B_H$ where B_H is a reciprocal lattice vector in the dual space to T) spans the First Brillouin Zone. The set of $\vec{k}$ form a quasicontinuum. Now for each $\vec{k}$ in the zone, determine the subset of rotations $\phi(k)$ with property

$$\phi_\alpha(k) \cdot \vec{k} = \vec{k} + 2\pi\vec{B}_H \qquad \alpha = 1,\ldots,\ \ell_k$$

This set defines a group

$$P(k) \equiv \varepsilon, \phi_2(k), \ \ldots\ , \ \phi_{\ell_k}(k).$$

which is the "point group of wave vector $\vec{k}$". Now determine the irreducible ray (projective) representations of P(k) with factor system $r \equiv \exp(i\vec{k}\cdot t_L)$ where $\vec{t}_L$ is the lattice translation which occurs in forming (in G) the product of coset representatives:

$$(\phi_\alpha|\tau_\alpha)\ (\phi_\beta|\tau_\beta) = (\varepsilon|t_L)(\phi_{\alpha\beta}|\tau_{\alpha\beta})$$

$$\phi_{\alpha\beta} = \phi_\alpha\phi_\beta\ ;\ t_L \equiv \phi_\alpha\tau_\beta + \tau_\alpha - \tau_{\alpha\beta}$$

These irreducible ray representations become the allowable "little" group irreducible representations of the space group G(k), where

$$G(k) = T + (\phi_2(k)|\tau_2)\ T + \ldots + (\phi_{\ell_k}(k)|\tau_{\ell_k})T$$

and $\quad G(k)/T = P(k).$

The irreducible ray representations of P(k) with the correct factor system are acceptable irreducible representations of G(k) which we call $D^{(k)(m)}$. Then using the decomposition

$$G = G(k) + (\phi_s|\tau_s)\ G(k) + \ldots$$

where $(\phi_s|\tau_s) \not\in G(k)$, the full space group irreducible representation $D^{(*k)(m)}$ is obtained by induction:

$$D^{(\vec{k})(m)} \text{ of } G(k) \uparrow D^{(*k)(m)} \text{ of } G$$

Note that globally the irreducible representations of G are characterized by a "star" of inequivalent wave vectors

$$*\vec{k} \equiv \{\vec{k}, \phi_\alpha \cdot k, \ldots\}$$

and a little group index m. Locally one has a canonical wave-vector $\vec{k}$, and a little group index m. In many cases, vide infra, k can be treated as a quasi-continuous variable labelling a function.

Recapitulating: in order to apply to crystals, the earlier notation D^j should be replaced by $D^{(*k)(m)}$ for irreducible representations of G. The {c} need to carry labels relevant to partners which span $D^{(*k)(m)}$.

This brings the Landau theory to the end of the first period of development which (in the writer's opinion) is marked by the appearance of the clear and masterful summary of the theory given in Lyubarski's text.[6]

According to Lyubarski an "active" space group irreducible representation $D^{(*k)(m)}$ is one satisfying the two major conditions of the theory which we now rewrite

$$D^{(*k)(m)}_{(3)} \not\in D^{(1)} \qquad \text{(Stability)} \quad \text{I}$$

$$D^{(*k)(m)}_{[2]} \otimes D^{(\nabla)} \not\in D^{(1)} \qquad \text{(Homogeneity)} \quad \text{II}$$

The basis functions of such active representations taken as the set {c} can be used in constructing Φ and ρ. Together with the requirement that the lower symmetry group G' shall be a subgroup of G

$$G \subset G' \qquad \text{(Broken Symmetry)}$$

these three statements epitomize the theory.

During this period (1937-1962) there were many applications of the theory to different crystal space groups. Most of these were to "Zellengleich" or T preserving transitions i.e. no increase of translational periodicity. These applications required only order parameters belonging to wave vector $\vec{k} = (0,0,0) \equiv \Gamma$ for which the ordinary representations of the point group suffices. A discussion of most important cases, with applications to ferroelectrics was given by Indenbom.[7]

Using the restrictions imposed by the conditions I, II, Lifschitz[4] gave a gen-

eral analysis of non-T preserving transitions, and Lyubarski summarized general restrictions on active representations, which we briefly review. In order that a representation $D^{(*k)(m)}$ shall be active the stability criterion I can be first applied. A necessary condition that the condition I is satisfied can be obtained by an examination of what we have called "wave vector selection rules". Thus if $D^{(*k)(m)}$ shall contain an invariant representation $D^{(\Gamma)(1)}$, it must be that in the symmetrized third power of $D^{(*k)(m)}$ there shall be contained any representation with zero (Γ) wave vector, and conversely. Consequently we examine the wave vector decomposition of the symmetrized cube:

$$(*k)_{(3)} = \sum_j \oplus \; *k_j$$

If on the right hand side Γ is absent then the representation is acceptable according to criterion I. If Γ is present one must go further to examine whether the identity or trivial representation $D^{(\Gamma)(1)}$ is contained in $D^{(*k)(m)}_{(3)}$. We have given procedures[5a] for carrying out these reductions elsewhere. By way of introduction it may be noted that the product of two stars

$$*k \circledast *k' = \sum \oplus \; *k''$$

is the set of all stars *k'' whose components satisfy

$$k''_\alpha = k_\beta + k'_\gamma$$

where all possible components $k_\alpha + k'_\gamma$ are used in forming the sums. So also the square

$$*k \circledast *k \equiv (*k)_2$$

and cube can be defined. To take account of multi-dimensional small representations, i.e. if $\ell_m > 1$ replace $(*k) \to (\ell_m *k)$. Then the symmetrized product is

$$(\ell_m *k)_{(3)} = \frac{1}{6}\,[\ell_m^3 (*k)_3 \oplus 3\ell_m^2 (*k) \circledast (*2k) \oplus 2\ell_m (*3k)]$$

and reduction can proceed easily. In this way individual stars can be examined for obeying I.

It turns out to be somewhat more direct to employ II and to derive general rules for active-acceptable representations. But (vide infra) condition II is more controversial and contrary to the earlier literature one should apply this condition separately from I. Again, wave vector rules can be first employed to determine if Γ

arises in the antisymmetric square:

$$(\ell_m * k)_{[2]} \equiv 1/2\ [\ell_m^2(*k)_2 - \ell_m(*2k)].$$

Again, even if Γ does arise, in the reduction of the stars on the right hand side, it must be investigated further whether the vector representation $\Gamma^{(v)}$ (which equals $\Gamma^{(15-)}$ in the cubic O_h group for example) appears. Of course a sufficient condition for $\Gamma^{(v)}$ to be absent is the absence of Γ in the reduction of $(\ell_m * k)_{[2]}$.

Further investigation of the homogeneity condition II has been carried out by Lifschitz and Lyubarski who worked out some general results for two types of situations which (borrowing from the older literature) we may call "Zellengleich" (phase transitions which do not change the translational symmetry) and "Klassengleich" (phase transitions which do not change the point group of the space group or "class" symmetry). An epitome of their results is: transitions changing lattice periodicity can occur using basis functions ψ_k with components of $\vec{k}$ equal to 1/2, 1/3, 1/4 of the reciprocal lattice vectors and producting doubling, trebling or four-fold increase in translational periodicity. A further cited result is that if P(k) is one of the following point groups: C_1, D_2, S_4, D_3, C_{3h}, then the corresponding basis set $\{\psi_{km}\}$ can be used for the construction of the density $\delta\rho$.

A general result is that a transition from $G \to G'$ may occur as second order consistent with the conditions I and II, if G' is a subgroup of index 2 of G:

$$G \subset G' \quad \text{and} \quad [G : G'] = 2$$

This is because there is a one-dimensional irreducible representation of G which, on the elements of the coset xG' ($G = G' + xG'$) has negative value to the value on the elements of G'. Such a representation evidently has no cubic invariant and, being one dimensional has no antisymmetric square containing a vector.

2. Respice (1962-1977)

A theme which is implicit in the Landau theory concerns the nature of the order parameters or set of basis objects which underlie the phase transition in question. As an example, consider the last statement regarding possible phase transitions to a subgroup G' of index 2. Although there exists an acceptable (= active) representation we must question if this representation is physically meaningful. Thus: can it "drive" the transition $G \to G'$? The answer could be obtained by constructing a successful dynamical model.

From a group theory-physics viewpoint the matter can be encapsulated in another statement or criterion:

The order parameters should correspond to a physical tensor field.

This criterion was introduced by the present author.[8]

The condition of spatial homogeneity (II) of the phase resulting from the transition came under renewed investigation in this period owing to two factors: one experimental, the other theoretical. The experimental discovery is: transitions to helicoidal magnetic structures, forbidden if II is satisfied. These structures are characterized by long wavelength displacements from the ideal crystalline order: each atom is only slightly displaced from its ideal location but overall a wave-like displacement occurs. A period of controversy (not yet satisfactorily resolved) ensued. Dzaloshinsky[9a] produced an argument for the validity of the homogeneity criterion; Goshen, Mukhamel and Shtrikman[9b] discussed it further, as has Mikaelson[10] later. This reformulation proceeds by using a "wave packet" type argument. Consider the density

$$\delta\rho(\mathbf{r}) = \sum_{k_0 \le k \le k_0 + \delta k} \sum_{\substack{m \\ \alpha}} c_\alpha^{(*k)(m)} \psi_\alpha^{(k)(m)}(\mathbf{r}) \tag{2.1}$$

in which we use functions of one irreducible representation $\psi_\alpha^{(k)(m)}$ and neighboring irreducible representations belonging to some region of $\vec{k}$ space around k_0. Then the coefficient of the quadratic term in the expansion of Φ, which becomes zero at the phase transition line: $A(T,P) = 0$, should already be a minimum (extremum) by symmetry with respect to the only quasicontinuous variable in the problem namely, $\vec{k}$. Considering $A^{(\vec{k})(m)}$ as a function of $\vec{k}$, the condition for an extremum is $(\partial A^{(k)(m)}/\partial k\big|_{k_0}) = 0$, and can be analyzed group theoretically.[5a] Only points, lines, planes of high symmetry permit such an extremum. Then if $*\vec{k}_0$ is the extremum star (wave vector $\vec{k}_0$ the homogeneity condition is, for that $\vec{k}_0$:

$$A^{(\vec{k}_0)(m)}(P,T) = 0 \tag{2.2}$$

Investigation[9b] shows that for the $\vec{k}_0$ consistent with the extremum the homogeneity

condition (II) is satisfied; or equivalently: there is no term of the form $a_\alpha\, b_\beta\, k_\gamma$ in the expansion of Φ, where $a_\alpha(b_\beta)$ are real (imaginary) parts of $c^{(k_0)(m)}$ and $\alpha\beta\gamma$ are cartesian components.

According to this analysis helicoidal structures arise if the k for which $A^{(k)(m)} = 0$ is not a symmetry-determined extremum but "accidental" i.e. arbitrary k. Then linear terms $(k_0 + \kappa)$ may appear and (κ small) a slow modulation of long wave length can occur with wavelength $\lambda_{MOD} = 2\pi/|\kappa|$. This reworking of the Lifschitz "homogeneity" constraint seems to serve two purposes. Firstly by relieving the absolute constraint II it permits the appearance of long-wave modulated (helicoidal) structures. Secondly it now establishes a subclassification: phase transitions with order parameter $\vec{k}_0$ corresponding to a symmetry-determined minimum $A^{(k_0)(m)}$ satisfy II and thus prohibit modulated structures; phase transitions for which the wave-vector of the order parameter is not symmetry determined (i.e. $A^{(k)(m)} = 0$ for a k determined by the dynamics) is consistent with helicoidal (modulated structures). A further elaboration of this approach was recently given by Mikaelson.[10]

A second objection which has been made to the homogeneity condition is of a different nature. Dimmock[11] pointed out that including both the sets $\{c_\alpha^j\}$ and gradients $\{\partial c_\alpha^j/\partial x_n\}$ enlarges the symmetry set beyond the original formulation of the theory. Recall, the role played by use of a single irreducible representation D^j is to ensure that only a single $A^j(P,T)$ changes sign at $(T_c P_c)$. Now when the basis set is enlarged, by including representations $D^j \otimes D^{(v)}$ additional $D^{j'}$ occur so the theory no longer concerns a single D^j. It does not appear that this objection has been satisfactorily dealt with.

A recent extension of the Lifschitz type of argument has been given by Hornreich, Luban, Shtrikman[12]. Recall the Landau "model problem" (1.1), but now let us allow for spatial inhomogeneity by taking higher order derivatives into account. Passing to Fourier Space (i.e. by Fourier Transform) this implies permitting the free energy functional Φ to be wave-vector dependent. In the model problem let k be the wave number so ($\partial c/\partial x \sim kc$; $\partial^2 c/\partial x^2 \sim k^2 c^2$; ...). Then the lowest order non-vanishing terms in expansion of Φ can be included by permitting the coefficient A in (1.1) to be k dependent as:[12]

$$A^{(k)(j)} = A_0 + \alpha k^2 + \beta k^4 \qquad (2.3)$$

which includes effectively terms in Φ of order $(\partial^2 c/\partial x^2)^2$. The "normal" continuous transition requires $A^{(k)(j)}$ to change sign — we may assume $A^{(k)(j)}$ is already the "necessary minimum". Then the equation $A^{(k)(j)} = 0$ determines a critical k_0. Thus let $\alpha>0$, and $\beta>0$ in (2.3) which assures that $A^{(k)(j)}$ will be a stable extremum at $k=0$. When $\alpha<0$ the minimum occurs at

$$k_0 = (-\alpha/\beta)^{\frac{1}{2}} \qquad (2.4)$$

and the minimum $A^{(k)(j)}$ with respect to k is $A^{(k_0)(j)}$; the phase transition line $T_\lambda(P)$ is given by

$$A^{(k_0)(j)} = A_0 - \alpha^2/\beta = 0 \qquad (2.5).$$

$\alpha = 0$ determines the transition point (P_L, T_L), known as the Lifschitz Point. The novel qualitative feature here is the "critical k". The theory predicts that a continuous transition occurs first to a region with k=0, then at the Lifschitz Point the wave vector begins to increase continuously: thus a modulated (helicoidal) structure occurs with temperature-dependent k_0. The model free energy has the form

$$\Phi \sim \Phi_0 + Ac^2 + b_2k^2c^2 + b_4k^4c^2 + Dc^4 + \ldots \qquad (2.6)$$

where b_m are constants, and $b_1 \equiv 0$; $b_3 \equiv 0$.

Let us now pass to three dimensions. The requirement that $b_1 \equiv 0$ is seen to be equivalent to the original Lifschitz homogeneity condition. The condition that $b_3 \equiv 0$ when translated into three dimensional form allowing for c to be generalized to the set $\{c_k^j\}$ is [12]

$$D^j_{[2]} \not\supseteq D^{(V)}_{(3)} \not\supset D^1 \qquad (2.7)$$

(This condition is sufficient, but perhaps not necessary, for the term: $b_3k^3c^2$ [generalized to three dimensions] to be absent). Hornreich and co-workers have identified certain magnetic systems which seem to exhibit a Lifschitz Point; this subject is now being actively investigated.

Let us now return to other developments of the thermodynamic theory. As explained above in the Landau approach[1][6] one is obliged to find all possible extrema of the set of equations (1.9); each such extrema gives a permitted density via (1.10). Further consideration shows that one can use the group theory directly, by-passing this procedure.

Let the set $\{\bar{c}_k^j\}$ be one possible set of solutions of (1.9), so (1.10) is the corresponding density and $\bar{G}'$ the new symmetry (invariance) group which is a subgroup of G. Then the representation D^j, basis $\{c_k^j\}$ of G, contains a subset $\{\bar{c}_k^j\}$ of G, which is perforce a basis for the trivial representation D' of $\bar{G}'$. Group theoretically

$$D^j \text{ of } G \downarrow D^1 \text{ of } \bar{G}' \qquad \text{(Subduction)}.$$

The subduction criterion is evidently contained in the Landau theory: it was first explicitly recognized and used by the present author[13]. Clearly all possible ex-

trema of Φ i.e. sets $\{\vec{c}^{j}_{k}\}$ satisfy the subduction criterion. Conversely if D^{l} of G' induces D^{j} of G then D^{j} is acceptable: the Froebenius Reciprocity Theorem obliges the multiplicities (induction/subduction) to be the same. Thus the subduction criterion is necessary and sufficient in order that D^{j} of G should be acceptable-active.

If D^{j} of G $\downarrow$ D^{l} of G' and <u>only</u> D^{l} then G' is normal in G.

The subduction criterion has been used for transitions in symmorphic and non-symmorphic crystals[14], and was recently applied by Izyumov[15].

Extending the subduction criterion, the present author, with Goldrich[16], proved a chain criterion for the chain of subgroups

If G'' C G' C G; and
D^{j} of G $\downarrow$ D^{l} of G' (once) and
D^{j} of G $\downarrow$ D^{l} of G'' (once):
Then G $\rightarrow$ G'' is eliminated.

By (once) is meant: once and only once.

It might be worth remarking that the subduction criterion and the chain criterion were intended to be used with the Landau stability criterion, and (in appropriate cases) with the Lifschitz homogeneity criterion. No claim was made regarding validity of the subduction/chain subduction criterion apart from the thermodynamic theory.

In this context the work of Ascher[17] is relevant. He proposed a "Maximal Subgroup" condition which (in simplest terms) asserts that if a chain of possible subgroup transitions exists (G'' C G' C G) then a continuous transition occurs to the maximum subgroup. Ascher has recently[17] emphasized the independence of his condition from thermodynamic theory: in that sense it is purely group theoretical. In some cases this maximal subgroup condition is equivalent to the chain subduction criterion.

It is clear that polynomials (in the bases $\{c^{j}_{k}\}$)which are invariant under space group G play an essential role in the Landau Theory. The free energy Φ (see 1.3)) is a sum of such G-invariant polynomials. It is well known that any G-invariant polynomial can be expressed as an algebraic form in a limited number of them, namely the Integrity Basis of representation D^{j} group G. For example, for group $G = O_h = m3m$ (octohedral point group, order 48), the three dimensional representation $D^{(4)}$ based on $(\vec{r} \equiv (x,y,z))$has integrity basis which can be written:

$$J_2 = (x^2 + y^2 + z^2) \; ; \; J_4 = (x^4 + y^4 + z^4); \; J_6 = x^2 y^2 z^2$$

and any polynomial invariant is an algebraic form: $f(J_2, J_4, J_6)$. Gufan and Sakhnenko[18] seem to have been the first to suggest formulating the thermodynamic theory

directly in terms of the integrity basis ab initio, by expanding Φ in the integrity basis. In certain cases of large dimensionality dim $D^j > 4$ they find different predictions of the theory using the integrity basis ab initio. The difference resides in the fact that higher order invariants will be expressible in terms of different numbers of arbitrary coefficients (the A,B,D, of equ. (1.3)) compared to the direct Taylor-like expansions in the usual theory. It would be useful to have additional investigations of this point which may have important physical consequences.

In any event it is very useful to have the integrity basis available for all groups G of interest. At the V^{th} Colloquium, Michel[19] reviewed the theory of G-invariant polynomials and gave a complete listing of the integrity basis for the fundamental representation of all molecular and crystal point groups: i.e. the faithful irreducible representations (for example $D^{(4)}$ for O_h) of all 32 crystallographic point groups plus the icosahedral groups I and I_h. The corresponding group algebra was discussed by Patera and Winternitz[20]. Recently the present writer and Jaric[21] presented some results on invariant theory (calculation of the Molien Function) for full space group irreducible representations which will be useful inter alia for Landau theory.

Another recent development of the theory applies to structurally complex crystals for example those of non-symmorphic space group symmetry. In many cases such crystals can be considered as comprising independent, interpenetrating, sublattices. Each such sublattice is characterized by some sub-space group of the entire space group. In work of Agyei and the writer[22] a sublattice approach was devised. The main physical idea is that one or more sublattices are responsible for the phase transition and that these sublattices can be used to define an "effective space group" for the transition: G_{eff} where

$$G' \subset G_{eff} \subset G$$

Thus G_{eff} is an intermediate group: it is a subgroup of G and supergroup of G'. The order parameter for the transition will be classified under G_{eff} and the criteria of the theory will be applied as if the working group were G_{eff}. In order to connect with the usual treatment one is essentially assuming that Φ can be decomposed into a sum of sublattice contributions plus a small inter-sublattice part, which can be neglected in first approximation:

$$\Phi = \sum \Phi_{SL} + \sum \Phi_{INT} \sim \sum \Phi_{SL}$$

The theory can then encompass a situation in which the same physical order parameter can satisfy all the sublattice criteria for continuous transition using group G_{eff} but fails to (i.e. predicts a first-order transition) for the actual space group G. Such transitions were denoted "weakly first order". Further investigation is needed to establish the validity and applicability of this subgroup approach.

This review has been concerned with group theory principles of the Landau theory, particularly in respect to non-magnetic crystallographic transitions. With few exceptions most of the work described here can be taken over to the magnetic case. A key new feature for magnetism is the presence of the anti-unitary motion-reversal operator θ. The structure of the magnetic space group will include both unitary and anti-unitary symmetry operations: in some cases the full space-time symmetry group $\mathcal{G}$ has the form $\mathcal{G} = G + \theta G$; other types of magnetic symmetry groups differ. A review of the theory as applied to magnetic transitions including the operator θ was given by Cracknell[23].

Among many actual applications of the Landau theory to systems of physical interest there are to ferroelectrics[24]; to the phase transition -- superconducting transition in A-15 structure (O_h^3-Pn3m) alloys[25] and other alloys[26]; to systems exhibiting charge-density wave (CDW) superlattice instability transitions[27]; to phase transitions in liquid crystals[28]; and to order-disorder transitions in absorbed systems[29]. Literature citations are given to some recent publications of each type which I have found useful. A reader can quickly pass to a chain of references and I hope gain access to the other applications[30].

3. Prospice (1977 -)

Any predictions about the future are certainly speculative, but non-the-less may be useful.

A safe prediction is that there will be continued applications of those parts of the theory based fairly closely upon thermodynamics. Thus, new, different and more complex condensed matter systems will be investigated for symmetry-allowed continuous transitions, using the theory straightforwardly.

A highly interesting new development in principle in the theory has been reported at this VIth Colloquium by Michel and Mozrzymas[31]. They used a combination of invariant theory and Morse theory to classify types of extrema of G-invariant polynomials (up to 6th degree in some cases) and thus they obtain the broken symmetry directly without explicit computation of minima. The latter feature is also true of the subduction criterion, but it seems that the use of Morse Theory can be a powerful additional tool in the Landau analysis.

As a final remark we shall now return our consideration to the starting point of the Landau theory: the intertwined threads of symmetry change and theory of critical properties in continuous transitions. In recent work several groups have taken up this problem in the framework of so-called renormalization group calculations[32], of critical properties. The steps in this work are: a) construction of a G-invariant Hamiltonian H based upon a set of order parameters $\{c_k^j\}$ deemed significant to the transition; b) repeated application of the scaling-rescaling transformation of the renormalization group; c) location of fixed points (if any) of the renormalization group transformation to give the fixed-point Hamiltonian H*; d) computation of critical properties from H*.

Typically[33] this proceeds by constructing a starting Hamiltonian H which is a functional of the order parameters $\{c_k^j\}$ - treated as fields. The structure of the starting H is familiar from the expression (1.5):

$$H = -\sum [r f^{(2)}(\{c\}) + f^{(2)}(\{\nabla c\})]$$

$$- \sum_{\gamma} u_\gamma f_\gamma^{(4)}(\{c\}).$$

where r, u_γ are interaction constants in this so-called LGW (Landau, Ginzburg, Wilson) Hamiltonian, γ enumerates independent 4th degree invariants. It is conventional to denote $H(r,u_\gamma)$. The rescaling (Renormalization group)transformation: T when repeatedly applied may ultimately give "fixed points":

$$T \cdot T \cdot \ldots H(r,u_\gamma) = H(r^*, u_\gamma^*)$$

where r^*, u_γ^* are in the "parameter space". Such fixed points can be classified as "stable" or "unstable".

It develops that Hamiltonians for certain order parameters (certain irreducible representations of particular space group G) do not possess stable fixed points. It has been proposed that in such a case the transition will be first-order i.e. not continuous even if the same order parameters {c} do satisfy the usual group theory criteria (stability, subduction). Hence the conjecture that:

> A stable fixed point is necessary for continuous transition, in addition to the other group theory criteria.

Are we on the verge of a new reunification of symmetry and dynamics of phase transitions, which would extend Landau's work to include quantum effects of fluctuations? It seems likely that interesting investigations are to be expected [34].

Acknowledgements

Many colleagues have kindly sent me references to the literature, reprints and preprints, and have shared their viewpoints with me. I wish to thank especially Drs. Abrahams, Agyei, Aizu, Ascher, Boccara, Cracknell, Dzyaloshinsky, Dvorak, Gufan, Hornreich, Indenbom, Ishibashi, Izyumov, Jaric, Litvin, Michel, Mikhelson, Mozrzymas, Opechewski, Patera, Solyom, Tolédano and Winternitz, in this regard. The views expressed in this paper are mine and the above mentioned authors may disagree with some.

Most of all I want to warmly thank Prof. H. Callen who first suggested to me (in 1965) that the Landau theory had many interesting facets which could be profitably examined.

References

(1) L.D. Landau, Phys. Z. Soviet. 11, 26, 545 (1937) (trans. in L.D. Landau "Collected Papers" ed. D. ter Haar, Pergammon (1965) also L. Landau, E. Lifschitz "Statistical Physics" (Pergammon Press).

(2) See the contribution by J.M.J. van Leeuwen to this Colloquium (these Proceedings) for literature citations. Also "Critical Phenomena" ed. C. Domb, M. Greene Vol 6 (Academic Press 1977).

(3) H. B. Callen "Thermodynamics" (Academic Press, New York).

(4) E.M. Lifschitz, Soviet Journal of Physics 6, 61; 251 (1942).

(5a) J.L. Birman: "Theory of Crystal Space Groups and Infra-Red and Raman Processes of Insulating Crystals" Handbuch der Physik Vol 25/2b (Springer-Verlag 1974).

(5b) C.J. Bradley, A.P. Cracknell: "Mathematical Theory of Symmetry in Solids" (Oxford University Press 1972).

(6) G. Ya. Lyubarski: "Application of Group Theory in Physics" (Pergammon Press).

(7) V.L. Indenbohm, Kristallografia 5, 115 (1960).

(8) J.L. Birman, Phys. Rev. Lett. 17, 1216 (1966).

(9a) I.E. Dzyaloshinsky, Sov. Phys. JETP 19, 960 (1964).

(9b) S. Goshen, D. Mukhamel, S. Shtrikman, Int. J. Magnetism 6, 22 (1974).

(10) A. Michelson, Phys. Rev. B. (in press 1977).

(11) J.O. Dimmock, Phys. Rev. 130, 1337 (1963).

(12) R. Hornreich, M. Luban, S. Shtrikman, Phys. Rev. Lett. 35, 1678 (1975) and private communication); A. Michelson, Phys. Rev. B, 16, 577 (1977).

(13) J.L. Birman, Phys. Rev. Lett. 17, 1216 (1966); Y. Gufan, F.T.T. 13, 225 (1971).

(14) B. Lavrencic and T. Shigenari, Proceedings IInd Int'l. Group Theory Colloquium (Nijmegen 1973); and Solid State Comm. 13, 1329 (1973), Ferroelectrics 8, 451 (1974);

(15) Yu. A. Izyumov, Uspekhi Fiz Nauk 118, 53 (1976).

(16) F.E. Goldrich and J.L. Birman, Phys. Rev. 167, 528 (1968).

(17) E. Ascher, Helv. Phys. Acta 39, 446 (1966), Phys. Lett. 20, 352 (1966), J. Phys. C (1977).

(18) Y.M. Gufan, V.P. Sakhnenko, Sov. Phys. JETP 36, 1009 (1973); also Sov. Phys. JETP 42, 728 (1976) and references therein, to earlier work.

(19) L. Michel, Proc. Vth Int'l. Colloquium on Group Theory Methods in Physics (Academic Press, New York 1977-8). See also references in this paper.

(20) J. Patera, P. Winternitz, J. Chem. Phys. 65, 2725 (1976).

(21) M. Jaric and J.L. Birman, (these Proceedings and J. Math. Phys. 18, 1456 (1977).

References continued

(22) A. Agyei and J.L. Birman, phys. stat. solidi (b) 80, 509 (1976); ibid b 82, 565 (1977).

(23) A.P. Cracknell, J. Lorenc, J.A. Przystawa, J. Phys. C 9, 1731 (1976) and papers referred to there.

(24) A.P. Levanyuk, D.G. Sannikov, Usp. F.N. 112, 561 (1974), and F.T.T. 18, 423 (1976); also V. Janovec, V. Dvorak, J. Petzett Czech. J. Phys. B 25, 1362 (1975); P. Toledano, J. Toledano, Phys. Rev. B 14, 3097 (1976).

(25) M. Jaric and J.L. Birman, Phys. Rev. B 16, (1977).

(26) See ref. 16.

(27) Y. Ishibashi, and V. Dvorak, J. Phys. Soc. Japan (1977); W.L. McMillan, Phys. Rev. B 14, 1496 (1976).

(28) V.L. Indenbohm, S.A. Pikin, E.B. Laginov, Kristallografiya 21, 1093 (1976).

(29) E. Domany, M. Scheck, J.S. Walker, Phys. Rev. Lett. 38, 1148 (1977).

(30) A discussion of many applications of Landau theory, and also some microscopic dynamic models and approaches is given in: N. Boccara "Symétries Brisées" (Hermann, Paris (1976)).

(31) L. Michel, I. Mozrzymas (Proceedings this Colloquium).

(32) See literature citations in refs.2 and G. Tovlovse and P. Pfevty "Introduction au Groupe de Renormalization...", Presses Universitaire (Grenoble (1976); J. Wiley (1977)).

(33) D. Mukhamel, Phys. Rev. Lett. 34, 481 (1975); D. Mukhamel, S. Krinsky, Phys. Rev. B 13, 5065, 5078, and 5086 (with P. Bak) (1976); S.A. Brazovskii, I.E. Dzaloshinskii, JETP Lett. 21, 164 (1975), Sov. Phys. JETP 43, 1178 (1976); V.A. Alessandrini, A.P. Cracknell, J.A. Przystawa, Comm. on Phys. 1, 51 (1976); I.E. Dzaloshinsky, JETP (1977).

(34) See discussions of "Asymptotic Symmetry" inter alia in A.Z. Patashinsky and V.L. Pokrovski, Sov. Phys. Usp. 20, 30 (1977) [UFN 121, 55 (1977)], in M.E. Fisher, Rev. Mod. Phys. 46, 597 (1974); and especially in E. Brézin, J.C. le Guillov and J. Zinn-Justin, Phys. Rev. B10, 892 (1974).