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Landau Theory at Extreme Pressures

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We give a detailed development of the construction of a Landau theory of high pressure phase transitions of the group–subgroup type, some results of which were announced in [A. Tröster, W. Schranz and R. Miletich, Phys. Rev. Lett. 88 55503 (2002)]. The order parameter driving the transition is defined with respect to a constrained background reference state obtained from separating the spontaneous strain from the bare elastic contribution. The theory is rewritten with respect to the undeformed laboratory state. The assumption of infinitesimal spontaneous strain leads to considerable simplifications. The general theory is illustrated on a simple example with quadratic-linear coupling between order parameter and strain.

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I. Introduction

In his pioneering work Landau [1] developed a free energy scheme to describe the thermodynamic properties of crystals near structural phase transitions that are of the group-subgroup type. The basic ingredient is the introduction of an order parameter (which can be one- or multicomponent, i.e. \( \eta \) or \( \eta_i \)) and the basic formula of the Landau theory is the expression for the thermodynamic potential considered as a function of the order parameter or order parameter components. The form of the Landau potential is restricted by symmetry considerations [2]. Allowing for spatial variations of the order parameter \( \eta(x) \) one arrives at the so called Landau-Ginzburg expression for the thermodynamic potential [3]. In the meantime this Landau-Ginzburg theory was successfully applied to a vast number of structural phase transitions in synthetic crystals [4] and minerals [5], incommensurate systems [6], quasicrystals, liquid crystals, complex fluids [7] and other soft matter systems. It was also extended to describe phase transitions which are not of the group-subgroup type, so called reconstructive phase transitions [8].

Most of these phase transitions are temperature induced, but there are also experiments on pressure induced structural phase transitions which are described by Landau theory. Examples can be found e.g. in [9–11]. There is however an important difference between temperature and pressure induced phase transitions. With increasing pressure one has to deal with two types of nonlinearities, i.e. geometrical and physical nonlinearities. At high pressures volume and lattice parameters start to deviate from a simple linear law, since the interatomic forces opposing further compression become stronger. This physical nonlinearity...
Landau Theory at Extreme Pressures

is usually described in terms of a so called equation of state $EOS$ given as $V = V(P)$. A rather often used one is the “Murnaghan EOS” [12] given as $V(P) = V_0(1 + K'_0 P / K_0)^{-1/K_0}$, where $K_0$ is the bulk modulus at $P=0$ and $K'_0 = \partial K / \partial P$ at $P = 0$. Of course the particular type of EOS depends on the physical details of the system and there are various EOS’s used in the literature [13–15]. Since at very high pressures the volume and axes changes can easily exceed 20% the corresponding strains entering the thermodynamic potential can no longer be treated as infinitesimal but one has to deal with finite strains. These nonlinearities make a consistent formulation of a Landau theory for high pressure phase transitions far from being simple. Another complication comes from the fact, that the known and experimentally tested EOS’s describe $V(P)$ and for a formulation of a Landau theory we need also the pressure dependence of the crystal axes, i.e. $a_i(P)$. Quite recently we have formulated a consistent Landau-type free energy based on a primary order parameter coupled to a finite strain with an elastic energy derived from an arbitrary EOS [16]. In a following series of papers [17, 18] we intend to address the problems in considerably more detail than it was done due to space limitations in Ref. [16].

The present work, which is devoted to a detailed discussion of the general construction of Landau theory coupled to finite strains, is organized as follows. In Section II we introduce some basic ingredients and notations of nonlinear elasticity. Section III contains the basic abstract construction of Landau theory coupled to finite strain measured with respect to a “background” reference state $\hat{X}_0(P)$. In building the theory, one is guided by the principle that the physics of the HPPT must be independent of the choice of deformed reference state (“laboratory system”) chosen to describe the relative deformation observed in a given experiment. In contrast to the case of temperature-parametrized Landau theory, a technical difficulty is overcome, which arises due to the fact that the order parameter itself must be defineable independently of a given elastic reference state. In Section IV the theory is reformulated in quantities as seen from the undeformed laboratory system $X$. Section V gives a discussion of the structural consequences that emerge in cases where the spontaneous strain is small enough to allow for being treated as infinitesimal. The paper closes with a short discussion and the worked-out example of a theory containing a scalar order parameter with quadratic–linear coupling to spontaneous strain.

II. General Concepts of Elasticity Theory

Let us first introduce some notation while recalling some basic notions of elasticity theory. For more details the reader should refer to classic textbooks, e.g. Refs. [23–27]. The whole formalism will be presented in the Lagrangian framework and for isothermal processes. For adiabatic conditions, the Helmholtz free energy $F$ would be replaced by the inner energy $U$, isothermal elastic constants by adiabatic ones and so on.

A. Basic Constructions

All through the present work we employ the Lagrangian picture, using one fixed coordinate system, usually defined by a set of 3 orthonormal base vectors chosen along convenient directions related to high symmetry directions of the (undeformed) crystal, to describe the deformation. Suppose that $X(m)$ denotes the resulting coordinates resembling the position of a mass particle $m$ in the supposedly undeformed elastic reference state of the body, which will also be called the “laboratory system” in the following. The set of all such coordinates
X(m) of its mass points m will be said to resemble an elastic reference state and is written as X.

After a deformation, the coordinates of m will have changed to \( \hat{X} = \hat{X}(X) \). Accordingly, for varying m the triple \( \hat{X} = \hat{X}(X) \) defines a vector field on the space occupied by the deformed body, which will be said[28] to be in the new elastic reference state \( \hat{X} \). The displacement vector measured with respect to the reference state \( X \) is \( u(X) := \hat{X}(X) - X \). The spatial variation of deformation is represented by the matrix of deformation gradients \( \alpha \) with components

\[
\alpha_{ik}(X) := \frac{\partial \hat{X}_i}{\partial X_k}
\]  

(1)

For later use, we also introduce the matrix \( \xi := \alpha^{-1} \). In terms of \( \alpha_{ik}(X) \), two different measures of strain can be introduced:

- The linearized strain tensor \( \bar{e} := \alpha - 1 \) with components

\[
\bar{e}_{ik}(X) := \alpha_{ik}(X) - \delta_{ik}
\]  

(2)

- The Lagrangian strain tensor \( e := \frac{1}{2} (\alpha^+ \alpha - 1) \) with components

\[
e_{ik}(X) := \frac{1}{2} \left( \sum_n \alpha_{ni}(X)\alpha_{nk}(X) - \delta_{ik} \right)
\]  

(3)

Notice that \( e \) can also be written as \( e := \frac{1}{2} (\bar{e} + \bar{e}^+ + \bar{e}^+ \bar{e}) \) with components

\[
e_{ik}(X) = \frac{1}{2} \left( \bar{e}_{ik}(X) + \bar{e}_{ki}(X) + \sum_n \bar{e}_{ni}(X)\bar{e}_{nk}(X) \right)
\]  

(4)

A deformation is called homogeneous, if all coefficients \( \alpha_{ik}(X) \equiv \alpha_{ik} \) are constants, which is the case we will focus on below. We emphasize the trivial fact that both strain tensors can always be defined, no matter if the deformation under investigation is “small” or “large”. Generally, \( e(X) \equiv 0 \) vanishes identically throughout the body if and only if the deformation is a pure rigid body motion, i.e. a translation and rotation respecting all distances between particles in the body. Up to such trivial manipulations of the body, the Lagrangian strain tensor \( e \) completely determines the deformation and has a clear-cut geometrical meaning, representing the change in distance between any two mass points of the system due to the deformation (cf. e.g. Ref. [24]). However, being symmetric, the 6 independent components of \( e \) of an inhomogeneous strain can only determine the 9 independent components \( \alpha \) by obeying a set of integrability conditions, the so-called compatibility relations [23]. For homogeneous strain these relations are trivially satisfied. In fact, the “missing” 3 components of \( \alpha \), which can be arranged into the tensor

\[
\omega_{ij} := \frac{1}{2} (\alpha_{ij} - \alpha_{ji})
\]  

(5)

describe rotations. If \( \alpha \) is symmetric, \( \alpha \) is calculated from \( e \) as

\[
\alpha = \sqrt{2e + 1} = 1 + e - \frac{1}{2}e^2 + \ldots
\]  

(6)
In components this means
\[ \alpha_{ij} = \delta_{ij} + e_{ij} - \frac{1}{2} \sum_k e_{ik} e_{kl} + \ldots \] (7)

In contrast, while the linear nature of \( \bar{e} \) comes in handy at times, for large deformations it is not an appropriate measure of strain[29]. For instance, \( \bar{e} \equiv 0 \) in general does not imply \( e \equiv 0 \).

The relative volume change or reduced volume accompanying the deformation is
\[ J(\alpha) := \frac{V[\hat{X}]}{V[X]} = \det \alpha \] (8)

In an abuse of language the deformation is termed infinitesimal, if the difference between the tensors \( \bar{e} \) and \( e \) can be numerically neglected.

Let \( F(\hat{\epsilon}; \hat{X}) \) denote the system’s Helmholtz potential in the deformed state \( \hat{X} \), in which one measures the deformation gradient tensor \( \hat{\alpha} \) with resulting Lagrangian strain \( \hat{\epsilon} = (\hat{\alpha}^+ \cdot \hat{\alpha} - 1)/2 \). The stress \( \tau = \tau[\hat{X}] \) induced by the strain \( e \) relative to the undeformed reference state \( X \) accompanying this deformation, which is physically measured measured in \( \hat{X} \), is known as the Cauchy stress and is calculated from \( F(\hat{\epsilon}; \hat{X}) \) as
\[ \tau_{ij}[\hat{X}] = \frac{1}{V[X]} \frac{\partial F(\hat{\epsilon}; \hat{X})}{\partial \hat{\epsilon}_{ij}} \bigg|_{\hat{\epsilon}=0} \] (9)

Taking an expansion of \( F(\hat{\epsilon}; \hat{X}) \) to second order in the Lagrangian strain \( \hat{\epsilon} \), we obtain the elastic constants measured in the deformed state \( \hat{X} \) as
\[ C_{ijkl}[\hat{X}] := \frac{1}{V[X]} \frac{\partial^2 F(\hat{\epsilon}; \hat{X})}{\partial \hat{\epsilon}_{ij} \partial \hat{\epsilon}_{kl}} \bigg|_{\hat{\epsilon}=0} \] (10)

This yields the Taylor series
\[ F(\hat{\epsilon}; \hat{X}) = V[\hat{X}] \left( \sum_{ij} \tau_{ij}[\hat{X}] \hat{\epsilon}_{ij} + \frac{1}{2} \sum_{ijkl} C_{ijkl}[\hat{X}] \hat{\epsilon}_{ij} \hat{\epsilon}_{kl} + O(\hat{\epsilon}^3) \right) \] (11)

Higher order elastic constants are defined similarly.

**B. Transformation Properties**

Strain between two deformed states of a body is a relative concept, and a “deformation” of a system is always defined with respect to another “undeformed” state of it. As there are usually always external forces acting on the system, e.g. gravity, air pressure etc., even the laboratory state of an experimental high pressure specimen could still be regarded as “deformed.” It is therefore a vital theoretical requirement that the physical content of the description of a deformed state of a given system should remain the same under any change of elastic reference state.

We now study the superposition of homogeneous deformations. Let \( X \xrightarrow{e} \hat{X} \) and \( \hat{X} \xrightarrow{\bar{e}} \hat{\hat{X}} \) denote two successive homogeneous deformations with accompanying Lagrangian strains \( e \) and \( \bar{e} \), respectively. Then the Lagrangian strain tensor \( \eta \) of the
superposition $X \xrightarrow{\eta} \hat{X}$ satisfies the nonlinear relation

$$\eta = e + \alpha^+ \cdot \hat{\epsilon} \cdot \alpha$$ \hspace{1cm} (12)

where again $\alpha$ denotes the deformation gradient matrix corresponding to $e$. In components this means

$$\eta_{ik} = e_{ik} + \sum_{mn} \alpha_{mi} \hat{\epsilon}_{mn} \alpha_{nk}$$ \hspace{1cm} (13)

The relation inverse to (12) is obviously

$$\hat{\epsilon} = \xi^+ (\eta - e) \xi$$ \hspace{1cm} (14)

In components:

$$\hat{\epsilon}_{ik} = \sum_{mn} \xi_{mi} (\eta_{mn} - e_{mn}) \xi_{nk}$$ \hspace{1cm} (15)

These relations bear important consequences. In fact, since physically the Helmholtz free energy must be invariant with respect to the choice of reference state, it must satisfy the identity

$$F(\hat{\epsilon}; \hat{X}) \equiv F(e + \alpha^+ \cdot \hat{\epsilon} \cdot \alpha; X)$$ \hspace{1cm} (16)

or

$$F(\hat{\epsilon}; \hat{X}) \equiv F \left( e_{kl} + \sum_{mn} \alpha_{mk} \hat{\epsilon}_{mn} \alpha_{nl}; X \right)$$ \hspace{1cm} (17)

A short calculation therefore yields the result

$$\tau[\hat{X}] = \frac{1}{J[\alpha]} \alpha^+ \cdot T(e) \cdot \alpha$$ \hspace{1cm} (18)

or

$$\tau_{ij}[\hat{X}] = \sum_{mn} \frac{\alpha_{mi} T_{mn}[X] \alpha_{nj}}{J[\alpha]}$$ \hspace{1cm} (19)

where the Piola-Kirchhoff stress tensor of the second kind

$$T_{mn}[X] := \frac{1}{V[X]} \frac{\partial F(e; X)}{\partial e_{mn}}$$ \hspace{1cm} (20)

is thermodynamically conjugate to $e$ in $X$. For completeness we also record the inverse relation

$$T(e) = J[\alpha] \xi^+ \cdot \tau[\hat{X}] \cdot \xi$$ \hspace{1cm} (21)

In components

$$T_{ij}[X] = J[\alpha] \sum_{mn} \xi_{mi} \tau_{mn}[\hat{X}] \xi_{nj}$$ \hspace{1cm} (22)
A Cauchy stress $\tau$ is said to exert hydrostatic pressure $P$ if it is diagonal with $\tau_{ij} = -P\delta_{ij}$. More generally, the hydrostatic component of a Cauchy stress $\tau$ and its corresponding traceless deviatoric stress $\tilde{\tau}$ will be defined by $\tau := -(1/3)\text{tr}\,\tau = -(1/3)\sum_i \tau_{ij}$ and $\tilde{\tau} := \tau + \tau.\bar{\cdot}$. A Cauchy stress $\tau$ is termed uniaxial along the axis $k$ if it can be written $\tau_{ij} = -P\delta_{ij}\delta_{jk}$ for a suitable choice of rectangular coordinates.

III. Definition of Landau Theory

In the following we will investigate phase transitions of the group-subgroup type in the framework of a Landau theory with elastic couplings. Let us first give a precise statement of the problem under investigation.

Consider a system described by an elastic free energy $F(\eta; X)$ in the undeformed reference state $X$. Let further $\tau_{ij} = \tau_{ij}(P)$ denote a ray in stress space parametrized by a quantity $P$, such that a parameter value $P$ corresponds to an applied stress $\tau_{ij}(P)$ defined in the corresponding reference state $\bar{X}[P]$, which is related to a Lagrangian strain $\eta = \eta(P)$ measured with respect to the undeformed reference system $X$. Usually $P$ will have the physical meaning of a hydrostatic stress $\tau_{ij}(P) = -P\delta_{ij}$, uniaxial stress $\tau_{ij}(P) = -P\delta_{ij}\delta_{jk}$ along the $z$-axis and so on. Let $G_0$ denote the space group of the crystal at $P = 0$. At $P \neq 0$, the symmetry of the crystal may depend on $P$, and we denote the corresponding space group by $\bar{G}[P]$. By definition of a HPPT, along the stress ray $\tau_{ij}(P)$, all these space groups will be isomorphic below/above a critical value $P = P_c$ of our pressure parameter, in the sense that $G := \bar{G}[P_1] \simeq \bar{G}[P_2]$ for $0 < P_1, P_2 < P_c$, while $G_1 := \bar{G}[P_3] \simeq \bar{G}[P_4]$ for $P_c < P_3, P_4$. In the following, we restrict our considerations to such HPPT’s, for which a group-subgroup relation

$$G_1 \subset G$$

holds. Landau theory then relates the symmetry breaking for $P > P_c$ to the appearance of nonzero equilibrium value $\bar{Q}$ for a trial (primary) order parameter $\bar{Q} = (Q_1, \ldots, Q_d)$ which transforms according to some $d$-dimensional irreducible representation $\hat{\rho}_P$ of the high symmetry space group $G$ [2]. Due to the coupling of strain and order parameter, which is the very reason for the occurrence of a HPPT, the relaxation of the additional internal degrees of freedom $\bar{Q}_I, \, \hat{Q} = 1, \ldots, d$ from zero to values $\bar{Q}_k \neq 0$ is compensated by the appearance of a spontaneous strain

$$\hat{\epsilon}_{ij} = \hat{\epsilon}_{ij}(P) := \frac{1}{2} \left( \sum_{k=1}^3 \hat{\alpha}_{ki} \hat{\alpha}_{kj} - \delta_{ij} \right)$$

measured with respect to the (fictitious) deformed state $\bar{X}_0[P]$ defined by the mathematical constraint $\bar{Q} \equiv 0$. For ferroelastic transitions [30], a certain combination of components of $\hat{\epsilon}_{ij}$ is identified with the primary order parameter itself, while for non-ferroelastic transitions it plays the role of a secondary order parameter [31]. The system’s physical (total) strain as observed with respect to the undeformed reference system $X$ is obtained as the nonlinear superposition

$$\hat{\eta}_{ij} := \epsilon_{ij} + \sum_{mn} \alpha_{mi} \hat{\epsilon}_{mn} \alpha_{nj}$$
of the spontaneous strain and the background strain

\[ e_{ij} := \frac{1}{2} \left( \sum_{k=1}^{3} \alpha_{ki} \alpha_{kj} - \delta_{ij} \right) \]  (26)

which is the strain accompanying the deformation \( \alpha \) which defines the reference state \( \hat{X}_0[P] \). In Ref. [17] we have shown for several minerals, how this reference state can be efficiently parametrized up to very high pressures.

Note that if the applied stress \( \tau_{ij}(P) \) is e.g. hydrostatic or chosen to act along certain high symmetry directions of the system, it is still possible to have \( G_0 = G \). However, in general the externally applied stress \( \tau_{ij}(P) \) will reduce the symmetry of the system such that \( G_1 \subset G \subset G_0 \). \( G \) is then characterized as the subgroup of all elements of \( G_0 \) that leave the infinitesimal strain \( \delta e_{ij} \) corresponding to an infinitesimal stress \( \tau_{ij}(\delta P) \) invariant.

The reader familiar with secondary order parameters will once more be reminded of the discussion given in Ref. [31].

The situation can thus be summarized as follows: The system’s Landau free energy as seen from the reference state \( \hat{X}_0[P] \) is defined as a potential \( F(\hat{Q}, \epsilon; \hat{X}_0[P]) \) which is invariant under the action of the space group \( G \) acting (via its action on the state \( \hat{X}_0[P] \)) on the strain \( \epsilon \) and (via the representation \( \hat{\rho}_P \)) on the trial order parameter \( \hat{Q} \), and which fulfills the following requirements for \( i, j = 1, 2, 3, K = 1, \ldots d \):

\[ 0 \equiv \frac{1}{V[\hat{X}_0[P]]} \left. \frac{\partial F(\hat{Q}; \epsilon; \hat{X}_0[P])}{\partial \hat{Q}_K} \right|_{\hat{Q}=\hat{Q}} \]  (27a)

\[ \tau_{ij}(P) \equiv \left. \frac{1}{V[\hat{X}_0[P]]} \frac{\partial F(\hat{Q} \equiv 0, \epsilon; \hat{X}_0[P])}{\partial \epsilon_{ij}} \right|_{\epsilon=0} \]  (27b)

\[ \tau_{ij}(P) \equiv \sum_{mn} \tilde{\alpha}_{mi} \tilde{\alpha}_{nj} \frac{1}{J[\tilde{\alpha}]} \frac{1}{V[\hat{X}_0[P]]} \left. \frac{\partial F(\hat{Q}, \tilde{\epsilon}; \hat{X}_0[P])}{\partial \epsilon_{mn}} \right|_{\epsilon=0} \]  (27c)

- Equation (27a) is the equilibrium condition for the order parameter \( \hat{Q} \).
- Equation (27b) is the very definition of the reference state \( \hat{X}_0[P] \).
- Finally, Eqn. (27c) expresses the compensation of the appearance of a nonzero order parameter \( \hat{Q} \) by the spontaneous strain \( \epsilon \). Notice that the tensor

\[ \hat{T}_{ij}(P) := \frac{1}{V[\hat{X}_0[P]]} \left. \frac{\partial F(\hat{Q}, \epsilon; \hat{X}_0[P])}{\partial \epsilon_{mn}} \right|_{\epsilon=0} \]  (28)

identified in (27c) plays the role of the Piola-Kirchhoff stress corresponding to \( \tau_{ij}(P) \) in the reference state \( \hat{X}_0[P] \).

This completes the construction of Landau theory with respect to the “native” reference state \( \hat{X}_0[P] \). In Ref. [16] the equilibrium equations (III) were alternatively derived from imposing a stationarity condition on a free energy functional formulated with respect to the deformation state \( \hat{X}[P] \) of the fully deformed system. However, as this approach necessarily deals with inhomogeneous strains and will not be used in the following, we choose not discuss it further for now.
Without doubt, due to the apparent nonlinearities and the unknown nature of the potential $F$ the system of equations (III) is difficult to handle. Also they are formulated in the somewhat inconvenient reference state $\hat{X}_0[P]$, and there remains the task of finding the corresponding equations as seen from the laboratory state $X$, with respect to which the HPPT usually manifests itself in an anomaly of one or more components of the total strain $\eta$.

It also remains to clarify the relation between different reference states $\hat{X}_0[P]$ and choices of representations $\hat{\rho}_P$. In passing we note that, while admittedly being of a somewhat theoretical nature, the states $\hat{X}_0[P]$ are neither totally abstract nor irrelevant to experimentalists. In fact, for varying $P$, they define the base lines for the components of the total strain $\eta_{ij}(P)$ and the volume $V(P)$, from which the spontaneous strain components $\epsilon_{ij}(P)$ and the subsequent anomaly in the volume $V(P)$ can be derived. Moreover, they also play a certain role in the interpretation of computer simulation data, where one can deliberately inhibit relaxation of the crystal to its true equilibrium structure for values of $P$ well beyond $P_c$.

As was worked out above, a trial order parameter $\hat{Q} = \hat{Q}[P]$, which is defined with respect to $\hat{X}_0[P]$, is specified in a completely abstract way by its symmetry properties determined from the representation $\hat{\rho}_P$ and may not have any direct relation to elasticity. The physical value of the order parameter should thus obviously not depend on the particular choice of reference state for the elastic variables of the theory. However, in a number of cases $\hat{Q}$ is built from some expression involving the components of a tensor which itself is defined with respect to the reference state $\hat{X}_0[P]$. The transformation properties of $\hat{Q}$ under a change of elastic reference state therefore seem to be important, although they clearly remain unknown as long as a concrete physical realization of the order parameter is not known. This looks like a serious obstruction to formulating an abstract Landau theory of HPPT’s without making reference to a particular fixed deformation state. How can we overcome it?

Fortunately we can show that actually any kind of order parameter value can always be chosen to be specified independent of the choice of elastic reference state. The key is to observe that in the whole framework of our Landau theory, a choice of irreducible representation $\hat{\rho}_P$ made for a particular value of $P$ is only specified up to equivalence of such representations. The physics governed by the Landau free energy, on the other hand, certainly cannot depend on such choices made. Without loss of generality, we can thus utilize this freedom of choice to construct a family of “parallel transported” reference frames and representations, leading to an invariance of the order parameter components.

Formally, a trial order parameter value $\hat{Q}[P]$ specified with respect to the reference state $\hat{X}_0[P]$ can be represented by an element $\hat{Q} = \sum_{l=1}^{d} \hat{Q}_l[P] w^l[P]$ of the abstract $d$-dimensional representation space $\hat{W}[P] \simeq \mathbb{R}^d$ with basis $\{w^1[P], \ldots, w^d[P]\}$. As one continuously changes the parameter $P$ labelling the reference frame from, say, $P_1$ to $P_2$, there should exist linear isomorphisms

$$R[P_1, P_2] : \hat{W}[P_1] \rightarrow \hat{W}[P_2]$$

(29)

inducing an equivalence of representations

$$\hat{\rho}_P(g) = R[P_1, P_2] \circ \hat{\rho}_P(g) \circ R^{-1}[P_1, P_2], \quad g \in G$$

(30)
By definition
\[ R[\hat{P}_1, \hat{P}_2] \hat{Q} \hat{P}_1] = \sum_{l=1}^{d} \hat{Q}_l [\hat{P}_1] R[\hat{P}_1, \hat{P}_2] \hat{v}^l [P_1] \] (31)

We now define new bases \{v^l[P], \ldots v^d[P]\} for the representation spaces \(\hat{W}[P]\) and new representations \(\rho_P\) by setting
\[ v^l[P] := R[0, P] \hat{v}^l [0] \] (32a)
\[ \rho_P (g) := R[0, P] \circ \hat{\rho}_0 \circ R^{-1}[0, P] \] (32b)

Then, since trivially
\[ \hat{Q} [P] = R[0, P] \hat{Q} [0] = \sum_{l=1}^{d} \hat{Q}_l [0] \hat{v}^l [P] \]
\[ \equiv \sum_{l=1}^{d} Q_l \hat{v}^l [P] \] (33)
the new order parameter components taken with respect to the bases \{v[P], \ldots v^d[P]\} will be identical in any reference frame \(\hat{W}[P]\). This completes the abstract justification for treating the order parameter as an invariant under changes \(\hat{X}_0[P_1] \rightarrow \hat{X}_0[P_2]\) of elastic reference states.

As a simple but illustrative example, consider a ferroelastic transition involving shear stress in an orthorhombic crystal with low pressure axes \(a, b\) and \(c\) at hydrostatic stress. We choose cartesian coordinates parallel to \(a, b\) and \(c\). In these coordinates the background deformation tensor \(\alpha\) is diagonal with components \(\alpha_{ik} = \alpha_{ii} \delta_{ik}\), which implies that the background strain \(e\) is also diagonal with components \(e_{ij} = \frac{1}{2}(\alpha_{ii}^2 - 1) \delta_{ij}\). Suppose now that the (scalar) order parameter at pressure \(P\) is given by the spontaneous strain component
\[ \hat{Q} [P] = \hat{\epsilon}_{12} \] (34)
measured with respect to its native reference state \(\hat{X}_0[P]\). Switching to the laboratory system, a possible order parameter would be represented by the difference \(\hat{Q}[0] = \eta_{12} - e_{12}\) of total and background strain, i.e.
\[ \hat{Q}[0] = \eta_{12} = \alpha_{11} \hat{\epsilon}_{12} \alpha_{22} \] (35)
by Eqn. (12) since \(e_{12} = 0\) (no shear deformation in the orthrhombic system). However, observe that since \(\alpha_{11}^2 = 2e_{11} + 1 = 1\) by assumption, \(\hat{Q}[P]\) can be trivially rewritten as
\[ \hat{Q}[P] = \frac{\hat{\epsilon}_{12}}{\alpha_{11} \alpha_{22}} = \frac{\hat{\epsilon}_{12}}{\sqrt{2e_{11} + 1} \sqrt{2e_{22} + 1}} \] (36)
Therefore, from classical elasticity theory [29], we deduce that actually \(\hat{Q}[P]\) represents the cosine
\[ \hat{Q}[P] = \cos \hat{\phi} \] (37)
of the distortion angle \(\phi\) between the axes \(\hat{a}, \hat{b}\) of the fully deformed crystal. It is easy to see that this interpretation of \(\hat{Q}\) is in fact invariant under the change of reference state
\( \hat{X}_0[P] \to X \): With respect to \( X \) we have

\[
\cos \phi = \frac{\eta_{12}}{\sqrt{2\eta_{11} + 1}} = \frac{\eta_{12}}{\alpha_{11}\alpha_{22}} = \hat{\epsilon}_{12} = \cos \hat{\phi}
\]  
(38)

In other words, the order parameter can be represented by the expression

\[
Q = \frac{\eta_{12}}{\alpha_{11}\alpha_{22}}
\]  
(39)

which in this sense is indeed invariant under a change of the elastic reference state. The accompanying transformation \( R[0, P] \) is obviously given by \( R[0, P] = \alpha_{11}\alpha_{22} \).

To summarize the discussion, the freedom of choosing equivalent representations for an abstractly defined order parameter \( Q \) has indeed liberates us from explicitly worrying about its transformation properties under a change of the background reference state. In the following we can therefore safely drop[32] the explicit reference \( \hat{Q}[P] \) of \( Q \) on the state \( \hat{X}_0[P] \) and assume it to be invariant with respect to such changes.

IV. Transformation to the Laboratory System

In applying Landau theory to a given phase transformation, the Landau potential is usually expanded into a power series of its variables, order by order consisting of combined invariants of order parameter and strain under the action of the high symmetry group \( G \). Thus, the potential \( F \) must necessarily be of the form

\[
F(Q, \tilde{\epsilon}; \hat{X}_0[P]) = V[\hat{X}_0[P]]\Phi(Q, \hat{X}_0[P])
\]

\[
+ V[\hat{X}_0[P]] \sum_{n=2}^{\infty} \sum_{k=1}^{n-1} \Psi_k^n(Q, \tilde{\epsilon}; \hat{X}_0[P]) + F_0(\tilde{\epsilon}; \hat{X}_0[P])
\]  
(40)

where \( \Phi(Q, \hat{X}_0[P]) \) denotes the pure order parameter part, \( F_0(\tilde{\epsilon}; \hat{X}_0[P]) = F(0, \tilde{\epsilon}; \hat{X}_0[P]) \) is the “bare” elastic contribution, and

\[
\Psi_k^n(Q, \tilde{\epsilon}; \hat{X}_0[P]) := \sum_{I_1, \ldots, I_{n-k}} \psi_{I_1, \ldots, I_{n-k}}(\hat{X}_0[P]) Q_{I_1} \cdots Q_{I_{n-k}} \tilde{\epsilon}_{I_1j_1} \cdots \tilde{\epsilon}_{I_kj_k}
\]  
(41)

represent the mixed invariants of total order \( n-k \) in order parameter and \( k \) in the spontaneous strain components. Without loss of generality, we can assume the coefficients \( \psi_{I_1, \ldots, I_{n-k}}(\hat{X}_0[P]) \) to be totally symmetric under permutations of the order parameter indices \( I_1, \ldots, I_{n-k} \), the exchange of strain indices \( (i_m, j_m) \) and the exchange of strain index pairs \( (i_m, j_m) \) and \( (i_n, j_n) \).

We now transform the quantities constituting our theory to the laboratory state \( X \) to make contact with the results of experimental measurements and get rid of the somewhat formal reference state \( \hat{X}_0[P] \). Physical invariance of the elastic Helmholtz free energy imposes the condition

\[
F(Q, \eta; X) = F(Q, \xi^+(\eta - e)\xi; \hat{X}_0[P])
\]  
(42)

For simplicity, and as this will be the only case of relevance below, let us neglect all mixed invariants \( \Psi_{n-k}^k \) of degree \( k > 1 \), such that the order parameter—strain coupling will be
entirely linear in the spontaneous strain. Then we can split the coupling terms (41) into well-separated background and total strain parts according to

\[ V[\hat{x}_0[P]]\psi_i^\alpha(Q, \eta; \hat{x}_0[P]) \]
\[ = V[X] (\psi_i^\alpha(Q, \eta; X) - \psi_i^\alpha(Q, e; X)) \] (43)

where for any strain \( \eta \)

\[ \psi_i^\alpha(Q, \eta; X) = \sum_{l_1 \cdots l_{n-1}, i} \psi_{i_1 \cdots i_{n-1}}^l[Q_{l_1} \cdots Q_{l_{n-1}}, \eta_{ij}] \] (44)

with coefficients

\[ \psi_{ij}^{l_1 \cdots l_{n-1}}[X] \equiv J(\alpha) \sum_{mn} \xi_{im} \psi_{mn}^{l_1 \cdots l_{n-1}}[\hat{x}_0[P]] \xi_{jn} \] (45)

Summarizing, we then obtain the transformed potential

\[ F(Q, \hat{\varepsilon}; X) = V[X]\Phi(Q; X) \]
\[ + V[X] \sum_{n=2}^{\infty} \psi_i^\alpha(Q, \eta; X) + F_0(\eta; X) \] (46)

as defined in the laboratory state \( X \), where

\[ \Phi(Q; X) \equiv J(\alpha)\Phi(Q; \hat{x}_0[P]) - \sum_{n=2}^{\infty} \psi_i^\alpha(Q, e; X) \] (47)

and \( F_0(\eta; X) \) denotes the “bare” elastic part of the Landau free energy with respect to the laboratory state \( X \). We can also trace back Eqs. (27a) and (27b) to \( X \). In \( X \), the equilibrium condition for the order parameter \( Q \) and the definition of the background strain \( e = e(P) \) are expressed as

\[ 0 \equiv \frac{1}{V[X]} \frac{\partial F(Q; \eta; X)}{\partial Q_l} \bigg |_{Q=\hat{Q}} \] (48a)
\[ \tau_{ij}(P) \equiv \sum_{mn} \frac{\alpha_{mi} \alpha_{nj}}{J(\alpha)} \frac{1}{V[X]} \frac{\partial F(Q; e; X)}{\partial \epsilon_{mn}} \] (48b)

The expression corresponding to Eqn. (27c) is rather complicated, but, as will be seen shortly, will not explicitly be needed in the following.

In the rest of this work we will assume \( F(Q, \eta; X) \) to be a polynomial in the variables \((Q_l, \eta_{ij})\) with constant coefficients in the reference state \( X \). Physically this corresponds to the assumption that the phase transition is driven by the elastic energy via the coupling coefficients of order parameter and strain and can be predicted from the knowledge of the potential with respect to the laboratory system, just like it would be the case in usual Landau theory. Mathematically, it amounts to specifying the potentials \( \Phi(Q; X) \) and \( F_0(\eta; X) \) as well as the coupling coefficients \( \psi_{ij}^{l_1 \cdots l_{n-1}}[X] \) as constant with respect to \( P \) in \( X \), while the pure order parameter potential per volume \( V[\hat{x}_0[P]] \)

\[ \Phi(Q; \hat{x}_0[P]) = \frac{1}{J(\alpha)} \left( \Phi(Q; X) + \sum_{n=2}^{\infty} \psi_i^\alpha(Q, e; X) \right) \] (49)
and the coupling terms $\Psi_i^L(Q, \hat{\varepsilon}; \hat{X}_0[P])$ with coefficients

$$
\psi^L_{ij,...,i_{n-1}}[\hat{X}_0[P]] = \frac{1}{J(\alpha)} \sum_{m,n} \psi^L_{mn...i_{n-1}}[X] \alpha_{im} \alpha_{jn} \tag{50}
$$

evaluated in the “moving” background state $\hat{X}_0[P]$ acquire an explicit $P$-dependence [33] via $\alpha = \alpha(P)$, $e = e(P)$, which can be computed once the bare elastic potential $F_0(e; X)$ is known [16, 17]. In principle, this completes the abstract construction of finite strain Landau theory.

V. The Approximation of Infinitesimal Spontaneous Strain

Reviewing our results so far, the bare elastic part $F_0(e; X)$ of the Landau potential definitely needs to be further specified for the formulae derived to be of any but purely theoretical value. Also, there are apparent strong nonlinearities severely complicating any attempt to explore the central relations (III). To make further progress in analytically developing a theory which is aimed towards practical use, further assumptions and approximations must be therefore introduced. In the present section we study the substantial simplifications of the theoretical formalism developed above for situations where the spontaneous strain $\hat{\varepsilon}$ is small enough to be treated as infinitesimal. In fact, this should be the case whenever the experimentally observed strain components exhibit continuous or at least not too large discontinuous anomalies, the corresponding possible jumps being considerably smaller than the background strain itself.

Mathematically, treating $\hat{\varepsilon}$ as infinitesimal yields the following simplifications:

$$
\hat{\alpha}_{mi}\hat{\alpha}_{nj}/J[\hat{\alpha}] \approx \delta_{mi}\delta_{nj}, \quad F_0(\hat{\varepsilon}; \hat{X}_0[P]) \approx V[\hat{X}_0[P]] \sum_{ij} \tau_{ij}(P)\hat{\varepsilon}_{ij} + \frac{V[\hat{X}_0[P]]}{2} \sum_{ijkl} C_{ijkl}[\hat{X}_0[P]]\hat{\varepsilon}_{ij}\hat{\varepsilon}_{kl} \tag{51}
$$

Here $C_{ijkl}[\hat{X}_0[P]]$ are the crystal’s elastic constants in the reference state $\hat{X}_0[P]$. Condition (27a), which determines the equilibrium order parameter $\bar{Q}$, becomes

$$
0 = \frac{\partial}{\partial \bar{Q}_K} \bigg|_{Q=\bar{Q}} \left[ \Phi(Q; \hat{X}_0[P]) + \sum_{n=2}^{\infty} \Psi_i^L(Q, \hat{\varepsilon}; \hat{X}_0[P]) \right] = \frac{\partial \Phi(\bar{Q}; \hat{X}_0[P])}{\partial \bar{Q}_K} + \sum_{ij} e_{ij} \sum_{n=2}^{\infty} (n-1) \left( \sum_{l_2...l_{n-1}} \psi_{ij}^{L_{l_2...l_{n-1}}}[\hat{X}_0[P]] \bar{Q}_{l_2}...\bar{Q}_{l_{n-1}} \right) \tag{52}
$$

(27b) yields the trivial relation $\tau_{ij}(P) = \tau_{ij}$, and the defining Equation (27a) for the spontaneous strain $\hat{\varepsilon}$ in $\hat{X}_0[P]$ simplifies to

$$
0 = \sum_{n=2}^{\infty} \sum_{l_2...l_{n-1}} \psi_{ij}^{L_{l_2...l_{n-1}}}[\hat{X}_0[P]] \bar{Q}_{l_2}...\bar{Q}_{l_{n-1}} + \sum_{kl} C_{ijkl}[\hat{X}_0[P]]\hat{\varepsilon}_{kl} \tag{53}
$$

in which the stress $\tau_{ij}(P)$ appears only implicitly through the dependence of the elastic constants on $P$. Eqn. (53) can be readily solved, which yields the spontaneous strain $\hat{\varepsilon}$ as a
function of the equilibrium order parameter $\hat{Q}$:

$$\hat{c}_{ij} = - \sum_{n=2}^{\infty} \sum_{l_1 \ldots l_{n-1}} \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}} \sum_{kl} C_{ijkl}^{-1} [\hat{X}_0[P]] \psi_{kl}^{l_1 \ldots l_{n-1}} [\hat{X}_0[P]]$$  \hfill (54)

Elimination of $\hat{c}$ from (52) by (54) then gives the equations

$$0 = \frac{\partial (\Phi(\hat{Q}; \hat{X}_0[P]))}{\partial \hat{Q}_K} - \Delta \Phi^K (\hat{Q}; \hat{X}_0[P]), \quad K = 1, \ldots d$$  \hfill (55)

in which we isolate a $Q$–dependent $d$-dimensional vector field

$$\Delta \Phi^K (\hat{Q}; \hat{X}_0[P]) = \sum_{m,n=2}^{\infty} (n-1) \sum_{l_1 \ldots l_{n-1}} \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}} \Delta \Phi^{l_1 \ldots l_{n-1}} [\hat{X}_0[P]] \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}}$$  \hfill (56)

with coefficients

$$\Delta \Phi^{l_1 \ldots l_{n-1}} [\hat{X}_0[P]] := \sum_{ijkl} \psi_i^{l_1 \ldots l_{n-1}} [\hat{X}_0[P]] C_{ijkl}^{-1} [\hat{X}_0[P]] \psi_{kl}^{l_1 \ldots l_{n-1}} [\hat{X}_0[P]]$$  \hfill (57)

From the symmetry properties of these coefficients it follows that

$$\frac{\partial \Delta \Phi^K (\hat{Q}; \hat{X}_0[P])}{\partial \hat{Q}_L} = \frac{\partial \Delta \Phi^L (\hat{Q}; \hat{X}_0[P])}{\partial \hat{Q}_K}, \quad K, L = 1, \ldots d$$  \hfill (58)

With the aid of Poincare’s Lemma, a potential $\Delta \Phi(\hat{Q}; \hat{X}_0[P])$ solving the $d$ equations

$$\frac{\partial (\Delta \Phi(\hat{Q}; \hat{X}_0[P]))}{\partial \hat{Q}_K} = \Delta \Phi^K (\hat{Q}; \hat{X}_0[P]), \quad K = 1, \ldots d$$  \hfill (59)

is therefore readily computed as

$$\Delta \Phi(\hat{Q}; \hat{X}_0[P]) = \int_0^1 dt \sum_K \hat{Q}_K \sum_{m,n=2}^{\infty} (n-1) \left( \int_0^1 dt t^{n+m-3} \right)$$

$$\times \sum_{l_1 \ldots l_{n-1}} \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}} \Delta \Phi^{l_1 \ldots l_{n-1}} [\hat{X}_0[P]] \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}}$$

$$= \sum_{n=1}^{\infty} \sum_{m=2}^{\infty} (n-1) \sum_{l_1 \ldots l_{n-1}} \Delta \Phi^{l_1 \ldots l_{n-1}} [\hat{X}_0[P]]$$

$$\times \frac{1}{n+m-2} \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}} \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}}$$  \hfill (60)

The equilibrium value $\hat{Q}$ of the order parameter $Q$ is thus obtained from the condition

$$0 = \frac{\partial (\Phi_K(\hat{Q}; \hat{X}_0[P]))}{\partial \hat{Q}_K}, \quad K = 1, \ldots d$$  \hfill (61)
imposed on a renormalized order parameter potential in the reference state \( \hat{X}_0[P] \)

\[
\Phi_R(\hat{Q}; \hat{X}_0[P]) := \Phi(\hat{Q}; \hat{X}_0[P]) - \Delta \Phi(\hat{Q}; \hat{X}_0[P])
\]  

(62)

It remains to find the corresponding expression in the laboratory system \( X \). For this purpose one calculates coefficients replacing those of (57) in the laboratory state \( X \) by applying the transformation formula (50) on (57), i.e.

\[
\Delta \Phi_{j_1 \ldots j_{m-1}}[X] := \frac{1}{f(\alpha)} \sum_{ijkl} \sum_{rost} \psi_{l_1 \ldots l_{n-1}}[X] \alpha_{ir} \alpha_{jl} C_{ijkl}^{-1}[\hat{X}_0[P]] \alpha_{ks} \alpha_{lt} \psi_{st}^{j_1 \ldots j_{m-1}}[X]
\]

\[
= \sum_{rost} \psi_{l_1 \ldots l_{n-1}}[X] T_{rost}[X][P] \psi_{st}^{j_1 \ldots j_{m-1}}[X]
\]

(63)

where we define the compliance-like tensor

\[
T_{rost}[X][P] := \frac{1}{f(\alpha)} \sum_{ijkl} \alpha_{ir} \alpha_{jl} C_{ijkl}^{-1}[\hat{X}_0[P]] \alpha_{ks} \alpha_{lt}
\]

(64)

for later convenience. We thus obtain

\[
\Delta \Phi(\hat{Q}; \hat{X}_0[P]) = \frac{1}{f(\alpha)} \Delta \Phi(\hat{Q}; X)
\]

(65)

where we identify

\[
\Delta \Phi(\hat{Q}; X) \equiv \sum_{n=1}^{\infty} \sum_{m=2}^{n-1} (n - 1) \sum_{j_1 \ldots j_{m-1}} \Delta \Phi^{l_1 \ldots l_{n-1}}[X]
\]

\[
\times \frac{1}{n + m - 2} \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}} \hat{Q}_{J_{j_1}} \ldots \hat{Q}_{J_{j_{m-1}}}
\]

(66)

with the coefficients \( \Delta \Phi^{l_1 \ldots l_{n-1}}[X] \) defined by Eqn. (63), (64). Combining Eqs. (49), (62), and (65), we arrive at

\[
\Phi_R(\hat{Q}; \hat{X}_0[P]) = \frac{1}{f(\alpha)} \left( \Phi(\hat{Q}; X) + \sum_{n=2}^{\infty} \Psi^n(Q, e; X) - \Delta \Phi(\hat{Q}; X) \right)
\]

(67)

from which we read off the desired renormalized order parameter potential in the laboratory state \( X \)

\[
\Phi_R(\hat{Q}; X) := \Phi(\hat{Q}; X) + \sum_{n=2}^{\infty} \Psi^n(Q, e; X) - \Delta \Phi(\hat{Q}; X)
\]

(68)

Finally, we derive an expression for the total strain \( \eta \) measured in \( X \). By Eqs. (13), (50), (54) and (64) we have

\[
\eta_{ij} = e_{ij} = \frac{1}{f(\alpha)} \sum_{n=2}^{\infty} \sum_{J_{j_1} \ldots J_{j_{n-1}}} \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}} \sum_{kllrost} \alpha_{ir} \alpha_{jl} C_{ijkl}^{-1}[\hat{X}_0[P]] \alpha_{ks} \alpha_{lt} \psi_{st}^{J_{j_1} \ldots J_{j_{m-1}}}[X]
\]

\[
= e_{ij} - \sum_{n=2}^{\infty} \sum_{J_{j_1} \ldots J_{j_{n-1}}} \hat{Q}_{l_1} \ldots \hat{Q}_{l_{n-1}} \sum_{kllrost} T_{ijkl}[X][P] \psi_{st}^{J_{j_1} \ldots J_{j_{m-1}}}[X]
\]

(69)
A. Example

We close this section gathering the formulas relevant to studying the interesting practical example of a HPPT induced by hydrostatic stress $\tau_{ij}(P) \equiv -P \delta_{ij}(P)$ and driven by $d = 1$-dimensional irreducible representation $\rho$ of $G$ (i.e. scalar order parameter $Q$), the corresponding Landau potential being of the form

$$\Phi(Q; \hat{X}_0[P]) = V[\hat{X}_0[P]] \times$$
$$\times \left( \frac{A[\hat{X}_0[P]]}{2} Q^2 + \frac{B[\hat{X}_0[P]]}{4} Q^4 + \frac{C[\hat{X}_0[P]]}{6} Q^6 \right)$$

(70)

and the only nonzero order parameter-strain coupling term

$$\Psi_1(Q, \tilde{\epsilon}; \hat{X}_0[P]) := Q^2 \sum_{ij} \psi_i[\hat{X}_0[P]] \delta_{ij} \tilde{\epsilon}_{ij}$$

(71)

being quadratic in $Q$ and linear in the strain. As hydrostatic pressure does not change the space group symmetry $G$ for $P < P_c$ by definition of $P_c$, the laboratory expressions are therefore of a structure similar to the above. Regarding them as fundamental, we write

$$\Psi_1(Q, \eta; X) = Q^2 \sum_i \psi_i \eta_{ii}$$

(72)

with $\psi_i = \psi_i[X] = J(\alpha) \xi_{ii} \psi_i[\hat{X}_0[P]]$ (see Eq. (44)) for the coupling term. According to formula (63), the only coefficient $\Delta \Phi_{1111}[X] = \Delta \Phi[X]$ is

$$\Delta \Phi[X] = \sum_{kl} \psi_k T_{kkll} [X][P] \psi_l$$

(73)

We introduce the abbreviations $V_0 := V[X], T_{ijkl}(P) := T_{ijkl}[X][P]$, and write (cf. Eqn. (47)) $A := A[X] = J(\alpha) A[\hat{X}_0[P]], \ldots$. Then for the renormalized Landau potential (68) in the laboratory system we obtain

$$\Phi_R(Q; X)/V_0 = \frac{A}{2} Q^2 + \frac{B}{4} Q^4 + \frac{C}{6} Q^6$$
$$+ Q^2 \sum_i \psi_i e_{ii} - \frac{1}{4} \left[ 2 \sum_{kl} \psi_k T_{kkll} [P] \psi_l \right] Q^4$$

(74)

We can still rewrite this as

$$\Phi_R(Q; X) = V_0 \left( \frac{A_R}{2} Q^2 + \frac{B_R}{4} Q^4 + \frac{C}{6} Q^6 \right)$$

(75)

with renormalized coefficients

$$A_R = A_R(P) := A + 2 \sum_k \psi_i e_{kk}(P)$$

(76a)

$$B_R = B_R(P) := B - 2 \sum_{kl} \psi_k T_{kkll}(P) \psi_l$$

(76b)
We thus observe that the \( P \)-dependence of the equilibrium order parameter \( \bar{Q} = \bar{Q}(P) \) calculated from minimization of (75) is the result of the quadratic and cubic coefficients of the renormalized order parameter potential becoming \( P \)-dependent. Finally, the total strain is computed as

\[
\eta_{ij}(P) = e_{ij}(P) - \bar{Q}^2(P) \sum_k T_{ijkl}(P) \psi_k
\]

(77)

For small pressures \( P \), \( A_R(P) \) will be linearly \( P \)-dependent, while the \( P \)-dependence of \( B_R(P) \) can be neglected, and \( T_{ijkl}(P) \) reduces to the ordinary compliance tensor \( S^0_{ijkl} = C^0_{ijkl} \) at \( P = 0 \). Thus the familiar structure of Landau theory coupled to infinitesimal strains as found e. g. in Ref. [34] is reproduced.

VI. Summary and Discussion

Suppose that

- the group-theoretic invariants up to the desired order constituting the pure order parameter potential \( \Phi(Q; \hat{X}_0[P]) \) and the coupling terms \( \Psi^I(Q, \hat{\epsilon}; \hat{X}_0[P]) \) have been determined from the analysis of the irreducible representation \( \rho \) of \( G \),
- the background deformation matrix \( \alpha \) (and consequently the background strain \( e = e(P) \)) induced by the stress \( \tau(P) \) and
- the elastic constants \( C_{ijkl}[\hat{X}_0[P]] \) at stress \( \tau(P) \) are known. This problem has been extensively studied in Ref. [17]

Then we can calculate the tensor \( T_{ijkl}[X][P] \) as well as the structure of \( \Phi(Q; X) \) and of the coupling terms \( \Psi^I(Q, e; X) \) in the laboratory state \( X \). Taking the functions \( \Phi(Q; X) \) and \( \Psi^I(Q, e; X) \) as the basic input of our theory, the renormalized order parameter potential \( \Phi_R(Q; X) \) is derived, from which we determine the equilibrium order parameter \( \bar{Q} \). Finally, the total strain \( \eta \) observed in \( X \) is computed from Eqn. (69).

In applying the theory to a concrete high pressure phase transition, the potential \( \Phi(Q; X) \) will, as always in Landau theory, expanded into a polynomial in the order parameter components \( Q_I \), whose coefficients, together with the coupling coefficients \( \psi^{I_1...I_n}(Q, \hat{\epsilon}; \hat{X}_0[P]) \) are treated as fit parameters.

We expect, that with our present theory one will be able to describe numerous high pressure phase transitions of minerals or synthetic crystals similar as has been successfully done using Landau-Ginzburg theory for temperature induced phase transitions.

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References


28. In a sloppy way, this is sometimes formulated by saying that “the deformed body has coordinates $\hat{X}$”. And in fact, the (generally curvilinear) coordinate system defined by the tangents to the images of the undeformed coordinate system lines under the applied deformation is the one used to formulate the Eulerian version of the theory.


32. This should not lead to confusion with the fact that the equilibrium order parameter $\bar{Q} = \bar{Q}(P)$ does depend on $P$, this $P$-dependence being the result of the requirement of minimizing the Landau potential at $P$, but not due to a particular choice of reference state.

33. In principle, dependence of the order parameter on temperature could also be introduced in a standard way by making the quadratic order parameter coefficients a linear function of $T$.