Dynamic Ginzburg-Landau Theory for the Liquid-Solid Phase Transition

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The anisotropy of the probability distribution function for the unit vector joining two nearest neighbour atoms is characterized by tensorial order parameters. For cubic symmetry, the most relevant tensor is of rank 4. Starting from an ansatz for the dependence of the (specific) internal energy, volume and entropy; the entropy production is calculated which is caused by a temporal change of the 4-th rank anisotropy tensor. A constitutive law which guarantees that the entropy production is positive leads to a nonlinear relaxation equation. It shows the features typical for a dynamic Ginzburg-Landau theory. The linearized version of the relaxation equation contains an effective relaxation time and a correlation length which exhibit a temperature dependence typical for a mean field theory. For a special case where the anisotropy tensor can be characterized by a scalar order parameter, the nonlinear relaxation equation is studied in some detail. Its stationary and spatially homogeneous solutions are zero and nonzero values for the order parameter depending on whether the temperature $T$ is larger or smaller than the transition temperature.

The unordered phase corresponds to a liquid state, the ordered phase to a simple or body centered cubic crystal. The phase transition is of 1st order. There exist also metastable states.

One of the most prominent features distinguishing a crystalline solid from a liquid is the fact that the nearest neighbours of an atom are found, with highest probability, in specific directions which are, in a single crystal, independent of the particular choice of a reference atom (long range order). Thus it seems appropriate to introduce a tensorial order parameter associated with this anisotropy and to develop a dynamic (Ginzburg)-Landau theory analogous to the theory for nonequilibrium phenomena in the isotropic and nematic phases of liquid crystals [1]. Short range angular correlations already exist in the liquid phase. This, e.g., is evident from an analysis of the three particle distribution function for molten salts as obtained from molecular dynamics calculations [2]. Thus the anisotropy tensor is expected to exhibit a pre-transitional behavior in the liquid phase. The program pursued here is in a certain sense complementary to theories [3] for the liquid-solid phase transition where the main attention is paid to the periodicity of the density.

This paper is organized as follows. In the first section, the tensorial order parameter is introduced and some of its properties are discussed. Of special interest is a case where the 4th rank anisotropy tensor can be characterized by a single scalar order parameter which, depending on its sign, describes simple and body centered cubic crystals. In the second section, the basic assumptions are stated which underly the present theory. In particular, a special ansatz is made for the dependence of the specific internal energy, volume and entropy on the anisotropy tensor. This allows the calculation of the entropy production associated with a irreversible change of that tensor.

In the third section, the relevant constitutive law which guarantees that the entropy production is positive is set up and thus a nonlinear relaxation equation is obtained for the anisotropy tensor. Some applications of the relaxation equation are considered in the two following sections. Firstly, the consequences of the linearized version of the relaxation equation are discussed. Secondly, the special case is considered where the tensor can be characterized a scalar order parameter. Depending on the temperature, the stationary and spatially homogeneous solutions of the nonlinear equation pertain to an unordered phase (liquid) and to an ordered phase with a nonzero value of the order parameter (cubic crystal). The phase transition is of first order.

Order Parameter

The tensor order parameter mentioned above can be introduced as follows. Let $u$ be a unit vector
pointing from an arbitrary atom (or molecule) of a solid or liquid to one of its nearest neighbours. The probability distribution function \( f(\mathbf{u}) \) for finding a nearest neighbour in the direction determined by \( \mathbf{u} \), in general, can be expanded with respect to spherical harmonics \( Y_l^m(\mathbf{u}) \) or, equivalently, with respect to the irreducible cartesian tensors \( a_{\mu \nu \kappa \lambda} \) constructed from the components of \( \mathbf{u} \). Apart from numerical factors depending on the normalization of the expansion tensors, the expansion coefficients are the averages of the expansion tensors. In a liquid in equilibrium, \( f(\mathbf{u}) \) is isotropic, i.e. all expansion tensors of rank \( l \geq 1 \) vanish. This is no longer true for a crystalline solid where \( f(\mathbf{u}) \) is anisotropic. As a specific example, a cubic crystal is considered here. For this symmetry, the lowest order nonvanishing expansion coefficient is the 4-rank tensor.

\[
\alpha_{\mu \nu \kappa \lambda} = \zeta \langle a_{\mu \nu \kappa \lambda} \rangle. \tag{1}
\]

The bracket \( \langle \ldots \rangle \) refers to an average evaluated with \( f(\mathbf{u}) \), i.e.

\[
\langle \Psi \rangle = \int \Psi(\mathbf{u}) f(\mathbf{u}) d^2 u \quad \text{with} \quad \int f d^2 u = 1,
\]

for any function \( \Psi = \Psi(\mathbf{u}) \). The symbol \( \ldots \) indicates the irreducible (symmetric traceless) part of a tensor. In (1), \( \zeta \) is a numerical factor which can be chosen conveniently but need not to be specified now.

A special case of interest for the following applications is the 4-rank tensor with the symmetry of a cubic crystal, viz.

\[
\alpha_{\mu \nu \kappa \lambda} = \frac{5}{6} a \alpha_{\mu \nu \kappa \lambda}, \tag{2}
\]

with

\[
\alpha_{\mu \nu \kappa \lambda} = \epsilon_{\mu \nu \kappa \lambda} - \frac{1}{2} (\delta_{\mu \nu} \delta_{\kappa \lambda} + \delta_{\mu \kappa} \delta_{\nu \lambda} + \delta_{\mu \lambda} \delta_{\nu \kappa}),
\]

\[
\epsilon_{\mu \nu \kappa \lambda} = \sum_{i=1}^{3} \epsilon_{i \mu} \epsilon_{i \nu} \epsilon_{i \kappa} \epsilon_{i \lambda}. \tag{3}
\]

The \( \epsilon_i \) are three mutually perpendicular unit vectors. The scalar order parameter \( a \) is given by

\[
a = \frac{2}{5} \sqrt{\frac{5}{6}} \zeta \langle K \rangle,
\]

where

\[
K = \frac{5}{2} \left( u_1^4 + u_2^4 + u_3^4 - \frac{3}{5} \right), \tag{4}
\]

\[
= \frac{5}{2} \left[ \sin^4 \theta (\cos^4 q + \sin^4 q) + \cos^4 \theta - \frac{3}{5} \right].
\]

is a cubic harmonic [4, 5] of rank 4 with the normalization \( K(\theta, q) = 1 \) for \( \theta = 0 \); and \( \theta = \pi/2, q = 0 \) or \( \pi/2 \). In (5) \( u_i \) stands for \( \mathbf{u} \cdot e_i \) and \( \theta, q \) are the polar angles of \( \mathbf{u} \). The relation (4) with (5) follows from multiplication of Eq. (1) by \( \epsilon_{\mu \nu \kappa \lambda} \), use of (2) and of \( \epsilon_{\mu \nu \kappa \lambda} \epsilon_{\nu \kappa \lambda} = 6/5 \). In (2), the factor \( 5/6 \) has been inserted such that

\[
\alpha_{\mu \nu \kappa \lambda} a_{\mu \nu \kappa \lambda} = a^2. \tag{5}
\]

If the numerical factor \( \zeta \) introduced in (1) is put equal to \( 15/2 \), one has \( a = \langle K \rangle \). On the other hand, the choice \( \zeta = (9!!/4!)^{1/2} \) implies \( a = \langle K_4 \rangle \) where \( K_4 = \frac{1}{2} | J | 2 K \) is essentially the same cubic harmonic as \( K \) but now normalized according to [5] (4\( \pi \))\(^{-1} \int d^2 u K_r^2 = 1 \). With the help of these normalized quantities, the distribution function is, for this special symmetry, given by

\[
f = (4\pi)^{1/2} (1 + a K_4 + \cdots), \quad a = \langle K_4 \rangle, \tag{6}
\]

where the dots stand for terms associated with higher rank tensors which are disregarded here.

It follows from (6) with (4), that the next neighbours of an atom are found with highest probability at the six corners of octahedron or at the eight corners of a cube depending on whether the order parameter \( a \) is positive or negative. Thus \( a > 0 \) and \( a < 0 \) characterize a simple cubic solid and a body centered cubic crystal, respectively.

In the following, it is assumed that the 4-rank tensor \( a_{\mu \nu \kappa \lambda} \) is the only additional macroscopic variable that is needed to distinguish, under equilibrium conditions, a cubic solid from a liquid. This does not mean that higher rank tensors have to vanish but rather that they are determined ("slaved") by the 4th rank tensor. Of course, in a nonequilibrium situation, \( a_{\mu \nu \kappa \lambda} \) can also be nonzero in a liquid; but there it will relax towards zero rather than to a finite equilibrium value.

It seems worth mentioning that the 4th rank tensor \( a_{\mu \nu \kappa \lambda} \) plays a role analogous to that of the 2nd rank alignment tensor \([1, 6] a_{\mu \nu} \sim \langle u_\mu u_\nu \rangle \) in the theory of liquid crystals where \( \mathbf{u} \), however, is a unit vector parallel to the figure axis of a molecule. There an important special case is the uniaxial tensor \([1, 6] a_{\mu \nu} \sim S \langle n_\mu n_\nu \rangle \) with the spacefixed unit vector \( \mathbf{n} \) (director). The quantity analogous to \( a \) as given by (4) or \( \langle K \rangle \) is the order parameter of Maier and Saupe [6, 7], viz.

\[
S = \langle P_2 \rangle \quad \text{with} \quad P_2 = \frac{3}{2} | (\mathbf{n} \cdot \mathbf{u})^2 - \frac{1}{3} |.
\]


Basic Assumptions

Within the framework of irreversible thermodynamics, an expression for the entropy production caused by a nonequilibrium process is of crucial importance for the derivation of constitutive laws governing the transport- and relaxation phenomena. In order to obtain a (nonlinear) relaxation equation for the tensor $a_{\mu \nu \rho \lambda x}$, some modifications of the standard procedure have to be introduced which are stated next. It should be mentioned that the theory to be presented here largely parallels the corresponding treatment [1] of nonequilibrium phenomena in (nematic) liquid crystals.

Firstly, it is assumed that the (local) specific entropy $s$, the specific volume $q^{-1}$ ($q$ is the mass density), and the specific internal energy $u$ can be decomposed into parts $s_0$, $q_0^{-1}$, $u_0$, which are independent of the tensor $a$ and the corresponding terms $s_a$, $q_a^{-1}$, $u_a$ which depend on $a$ and vanish for $a \to 0$:

$$s = s_0 + s_a, \quad q^{-1} = q_0^{-1} + q_a^{-1},$$

$$u = u_0 + u_a.$$  \hfill (7)

Secondly, it is assumed that the Gibbs relation known from equilibrium thermodynamics still holds true in a nonequilibrium situation for the parts of the local thermodynamic functions which are independent of $a$, i.e.

$$d s_0 = T^{-1}(d u_0 + P d q_0^{-1})$$  \hfill (8)

where $T$ and $P$ are the (local) temperature and pressure, respectively. Notice that (8) is the standard assumption underlying the theory of irreversible thermodynamics [8]. Now, Eqs. (7), (8) yield (in the mass of a particle)

$$d s = T^{-1}(d u + P d q^{-1}) = \frac{k_B}{m} a_{\mu \rho \lambda \kappa x} d a_{\mu \nu \rho \lambda x}$$  \hfill (9)

with the "potential" $\Phi$ defined by

$$- \frac{k_B}{m} \Phi = s_a - T^{-1}(u_a + P q_a^{-1}).$$  \hfill (10)

The specific Gibbs free energy associated with the tensor $a$ is $g_a = (k_B T/m) \Phi$. Clearly, under equilibrium conditions where one has $\partial \Phi / \partial a_{\mu \nu \rho \lambda x} = 0$, the Gibbs relations (8) and (9) are equivalent.

Next, a special ansatz is made for the thermodynamic functions $u_a$, $q_a^{-1}$, and $s_a$, viz.

$$u_a = - \frac{1}{2} \varepsilon a_{\mu \nu \rho \lambda \kappa x} a_{\mu \nu \rho \lambda \kappa x},$$  \hfill (11)

$$q_a^{-1} = - \frac{1}{2} \rho a_{\mu \nu \rho \lambda \kappa x} a_{\mu \nu \rho \lambda \kappa x}.$$  \hfill (12)

$$s_a = - \frac{k_B}{m} \left[ \frac{1}{2} A_0 a_{\mu \nu \rho \lambda x} a_{\mu \nu \rho \lambda x} - \frac{1}{30} B a_{\mu \nu \rho \lambda x} a_{\lambda \kappa \sigma \tau \rho \lambda x} a_{\sigma \tau \mu \nu x} \right. \right.$$  \hfill (13)

$$\left. + \frac{1}{4} C a_{\mu \nu \rho \lambda x} a_{\rho \lambda \kappa x} a_{\sigma \tau \mu \nu x}^2 \right].$$

In (11) and (12) $\varepsilon$ and $\rho$ are characteristic values for the specific energy and volume, respectively, associated with the anisotropy described by the tensor $a$; $\varepsilon > 0$ and $\rho > 0$ imply that the ordered state is energetically more favourable and that it has the smaller volume as compared with the unordered (liquid) phase. The quantities $\varepsilon$, $\rho$, as well as the dimensionless coefficients $A_0$, $B$, $C$ occurring in (13) can be expected to be weakly dependent functions of $T$ and $P$. The condition $s_a < 0$ (the ordered phase has a smaller entropy than the disordered one) requires $A_0 > 0$, $B > 0$, $(2/\rho) B^2 < A_0 C$; the coefficient $B$ may have either sign. In (13), the factor $\sqrt{3}$ has been inserted such that the third order term becomes simpler in the case where the cubic anisotropy is characterized by the scalar order parameter $a$.

The ansatz (11), (12), (13) is a power series expansion in the tensor $a$. In $s_a$, terms two orders higher than in $u_a$ and $q_a^{-1}$ have been included in order to obtain a Gibbs free energy or potential function $\Phi$ which obeys the thermodynamic stability conditions. The special ansatz made above can be looked upon as a "minimal" theory containing a minimal number of coefficients. In particular, there are three additional 4th order terms involving other scalars constructed from the tensor $a$ whose coefficients are put equal to zero for simplicity.

The ansatz (11), (12), (13) leads to a Landau type expression for the potential $\Phi$ viz.

$$\Phi = \Phi^L = \frac{1}{2} A(T, P) a_{\mu \nu \rho \lambda x} a_{\mu \nu \rho \lambda x}$$

$$\left. - \frac{1}{30} B a_{\mu \nu \rho \lambda x} a_{\lambda \kappa \sigma \tau \rho \lambda x} a_{\sigma \tau \mu \nu x} \right]$$

$$+ \frac{1}{4} C a_{\mu \nu \rho \lambda x} a_{\rho \lambda \kappa x} a_{\sigma \tau \mu \nu x}^2 \right].$$  \hfill (14)

with

$$A(T, P) = A_0 \left[ 1 - T^{-1} \frac{m}{A_0 k_B} (\varepsilon + P \rho) \right]$$

$$= A_0 \left[ 1 - \frac{T^*}{T} \right],$$  \hfill (15)

$$T^* = T^*(P) = \frac{m}{A_0 k_B} (\varepsilon + P \rho).$$

So far, the expression for $\Phi$ applies to a spatially homogeneous situation. For a spatially inhomo-
geneous system, gradient terms have to be included in $\Phi$. A minimal ansatz of Ginzburg-Landau type is made where

$$\Phi = \Phi^L + \frac{1}{2} \xi_0^2 (\nabla T) (\nabla T)$$

(16)

involves just one microscopic length scale $\xi_0$.

**Entropy Production, Relaxation Equation**

From (9) with the special ansatz (16), (14) one obtains

$$\sigma = - \frac{k_B}{m} \Phi_{\mu\nu\lambda\kappa} \frac{\partial a_{\mu\nu\lambda\kappa}}{\partial t}$$

(17)

for the entropy production $\sigma$ associated with the relaxation of the anisotropy tensor $a$. In (17), $\Phi_{\mu\nu\lambda\kappa}$ stands for

$$\Phi_{\mu\nu\lambda\kappa} = \Phi^L_{\mu\nu\lambda\kappa} - \xi_0^2 \Lambda a_{\mu\nu\lambda\kappa},$$

(18)

with

$$\Phi^L_{\mu\nu\lambda\kappa} = - i \Phi^L / \partial a_{\mu\nu\lambda\kappa},$$

for $\Phi^L$ see (14). The ansatz

$$\frac{\partial a_{\mu\nu\lambda\kappa}}{\partial t} = - \tau^{-1} \Phi_{\mu\nu\lambda\kappa},$$

(19)

with the positive relaxation time $\tau_a$ guarantees $\sigma > 0$. Notice that (19) is a nonlinear relaxation equation: explicitly, it reads

$$\frac{\partial a_{\mu\nu\lambda\kappa}}{\partial t} + \tau^{-1} [A a_{\mu\nu\lambda\kappa} - \xi_0^2 \Lambda a_{\mu\nu\lambda\kappa}] = 0,$$  

(20)

for $A$ see (15). Some applications of (20) are discussed next.

**Relaxation of the Anisotropy in the Disordered Phase**

For temperatures $T$ above the pseudo-critical temperature $T^*$ where $A$ vanishes and if the magnitude of the tensor $a$ is not too large, the relaxation equation (20) can be linearized. The resulting equation is

$$\frac{\partial a_{\mu\nu\lambda\kappa}}{\partial t} + \tau^{-1} [A a_{\mu\nu\lambda\kappa} - \xi_0^2 \Lambda a_{\mu\nu\lambda\kappa}] = 0.$$

(21)

It contains the relaxation time

$$\tau = \tau_a A^{-1} = \tau_a A_0^{-1}(1 - T^*/T)^{-1},$$

(22)

and the correlation length

$$\xi = \xi_0 A^{-1/2} = \xi_0 A_0^{-1/2}(1 - T^*/T)^{-1/2}. $$

(23)

which show a divergence for $T \to T^*$ that is typical for a mean field theory. The transition from the liquid to the solid phase however, occurs at a temperature $T$ which is higher than $T^*$.

The temperature dependence of $\tau$ and $\xi$ as given by (22) and (23) indicates that a partial ordering already takes place in the liquid phase. It should be possible to detect the pretransitional increase of the relaxation time $\tau$ in $\gamma-\gamma$ angular correlation experiments [9].

**Cubic Symmetry, Phase Transition**

For temperatures $T$ close to $T^*$ and even more for $T < T^*$ where $A$ becomes negative, the nonlinear terms in the relaxation equation (20) cannot be disregarded. Notice, that in principle, (20) stands for 9 coupled nonlinear equations since a 4th rank irreducible tensor has $2^4 + 1$ independent components. Here, the special case of cubic symmetry is treated where the tensor $a_{\mu\nu\lambda\kappa}$ is assumed to be of the form (2) with constant directions for the symmetry axes, i.e. constant $e^i$, cf. (3). Then Eq. (20) reduces to a relaxation equation for the scalar order parameter $a$, viz.

$$\frac{\partial a}{\partial t} + \tau_a^{-1} [A a - B a^2 + C a^3 - \xi_0^2 \Lambda a] = 0.$$  

(24)

The stationary solutions ($\partial a / \partial t = 0$) for the spatially homogeneous case ($Ja = 0$) are determined by

$$\frac{\partial L(a)}{\partial a} = 0,$$

(25)

Due to the presence of the 3rd order term involving $B$ the phase transition to be inferred from (25) is of first order. Though most of the following results are well-known, it seems appropriate to state the main results here.

The stable stationary solutions of (24) are associated with the absolute minima of the Landau potential $\Phi^L(a)$. These are

$$a = 0 \quad \text{for} \quad T > T_s$$

and

$$a = \frac{1}{2} B C^{-1} (1 + \frac{1}{2} A C B^{-2})$$

(26)

for $T < T_s,$

where the (mean field) transition temperature from the disordered (liquid) to the ordered (solid) phase is determined by

$$A(T_s) = \frac{2}{9} \frac{B^2}{C}.$$  

(27)
This implies
\[ T_s = T^* \left( 1 - \frac{2}{9} B^2 A_0^{-1} C^{-1} \right)^{-1} > T^*. \] (28)

Notice that \( T^* \) depends on the pressure \( P \), cf. (15). Thus if the characteristic quantities \( \varepsilon \) and \( \nu_2 \), as well as \( A_0, B, C \) are practically independent of \( P \), the relative change of the transition temperature is given by
\[ T_s^{-1} \frac{dT_s}{dP} = (T^*)^{-1} \frac{dT^*}{dP} = (A_0 k_B T^*)^{-1} m v_a. \] (29)

At the transition temperature, the order parameter “jumps” from zero to the finite value
\[ a_s = \frac{2 B}{3 C}; \] (30)
for \( T = T^* \) where \( A \) vanishes, it assumes the value
\[ a^* = B/C. \] (31)

The order parameter as given by (26) or (30), (31) has the same sign as \( B \). Notice, however, that this is due to the insertion of a minus sign in front of the term involving \( B \) in (13) and (14).

The difference \( \delta q^{-1} \) between the specific volume in the liquid and solid phases at \( T_s \), is, according to (12) and (5)
\[ \delta q^{-1} = \frac{1}{2} v_a a_s^2. \] (32)

Similarly, the specific latent heat is
\[ \delta h = \delta u + P \delta q^{-1} = T_s \delta s \]
\[ = \frac{1}{2} A_0 (k_B T^*/m) a_s^2. \] (33)

Relations (29), (32), (33) are consistent with the Clausius-Clapeyron equation
\[ \partial T_s / \partial P = T_s \delta q^{-1} / \delta h. \]

Since \( T^* \sim T_s \), cf. (28), Eq. (33) is in accord with Richards’ law which states \( \delta h \sim T_s \). For comparison with experimental data, one can even go a step further and assume that the order parameter practically corresponds to full ordering at \( T_s \). For a body centered cubic crystal this means
\[ \langle K \rangle \approx -\frac{2}{3} \quad \text{and} \quad a_s \approx -\frac{1}{3} \sqrt{2} 1, \]
if the same normalization factor \( \zeta \) is used as in (6). With \( A_0 \approx 1 \) which is suggested by analogous considerations in connection with liquid crystals [1], this leads to
\[ 2m \delta h / k_B T_s \leq 7/3 \approx 2.33. \]

This crude estimate agrees surprisingly well with the experimental values [10] of 1.7 (Na, K, Rb, Cs); 2.0 (Cu, Ag, Pb) and 2.3 (Au) observed for the same quantity of several body centered cubic crystals.

Metastable states determined by a relative but not absolute minimum are the disordered phase \( (a = 0) \) in the temperature interval \( T^* < T < T_s \) and the ordered phase where \( a \) is given by (26) for \( T_s < T < T_s^* \) with
\[ T_s^* = T^* (1 - \frac{1}{2} B^2 A_0^{-1} C^{-1})^{-1}. \] (34)

Furthermore, for \( T < T^* \), a metastable state exists where the order parameter \( a \) is given by an expression similar to (26), but with a negative square root, i.e.
\[ a = \frac{1}{2} BC^{-1} (1 - \sqrt{1 - 4 ABCB^{-2}}). \] (35)

In terms of the scaled order parameter \( \alpha \) defined by
\[ \alpha = a_s \alpha = \frac{2 B}{3 C} \alpha, \] (36)
the Landau potential can be written as
\[ \Phi^L(\alpha) = \frac{1}{2} a_s^4 C \Phi^L(\alpha) \]
with
\[ \Phi^L(\alpha) = \frac{1}{2} \theta \alpha^2 - \alpha^3 + \frac{1}{2} \alpha^4. \] (37)

Here \( \theta \) is a scaled temperature variable given by
\[ \theta = \frac{2 AC}{9 B^2} \left( 1 - \frac{T^*}{T} \right) \left( 1 - \frac{T^*}{T_s} \right)^{-1}. \]
\[ = \frac{T - T^*}{T_s - T^*} \frac{T_s}{T}. \] (38)

Notice that the coefficients of the 3rd and 4th order terms in (37) are universal. The values of \( \alpha \) with \( \alpha = 0 \) where \( \Phi^L(\alpha) \) assumes a minimum are given by
\[ \alpha(\theta) = \frac{2}{3} (1 + \sqrt{1 - \frac{1}{3} \theta}). \] (39)

In this section, the main point was to demonstrate that the stationary and spatially homogeneous solutions of (24) correspond to a liquid or to a crystalline phase if the temperature \( T \) is larger or smaller than the transition temperature. For an analysis of the full nonlinear relaxation equation, it is advantageous to use the scaled variables. More specifically, Eq. (24) is equivalent to
\[ \partial \alpha / \partial t + \tau_s^{-1} [\partial \alpha - 3 \alpha^2 + 2 \alpha^3 - \xi_s^2 \Delta \alpha] = 0. \] (40)

In (40), the relaxation time \( \tau_s \) and the correlation length \( \xi_s \) are given by (22), and (23), respectively,
with \( T = T_s \). The methods used e.g. in Ref. [11] for a magnetic phase transition in an external field can be adapted to study further consequences of Equation (40). In such an analysis which, however, is not performed here, one has to take into account that the temperature \( T \) and consequently the quantity \( \vartheta \) occurring in (40) are also functions of \( t \) and \( r \) unless the heat conductivity is extremely large such that the relaxation of the order parameter is practically isothermal.

**Concluding Remarks**

In this article, a dynamic Ginzburg-Landau theory has been presented for the relaxation of a tensorial order parameter which is of relevance for the liquid-solid phase transition. In particular, an anisotropy tensor of rank 4 was considered which, for a special case, can be characterized by a scalar order parameter describing simple and body centered cubic crystals. The generalization of the present approach to other order parameters associated with different symmetries should be straightforward.

The phenomenological coefficients such as \( A_0, B, C \) (cf. Eq. (13)) which are related to equilibrium properties can be evaluated with the methods of statistical mechanics (e.g. see Ref. [1] where the similar problem has been treated for liquid crystals). A mean field calculation analogous to the Maier-Saupe theory [7] can also be made. Furthermore, it should be feasible to use a Fokker-Planck equation approach similar to Ref. [12] to derive a nonlinear relaxation equation of the form (20) with specific coefficients \( A_0, B, C \) and where the relaxation time \( \tau_2 \) is related to (semi-)microscopic quantities.