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# The effect of strain on the thermodynamics of the weakly first-order phase transition

M A Fradkin†

Laboratoire Léon Brillouin, CEA/CNRS, CE Saclay, Gif-sur-Yvette Cédex 91191, France

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**Abstract.** The thermodynamics of two-phase coherent equilibrium is analysed in the case of a phase transition without change of composition. The elastic contribution to the Gibbs free energy associated with a distortion of the matrix of the parent phase due to the transformation misfit strain is considered. The phase transition from the parent to the product phase is studied using Landau theory, with the transition volume change being coupled with the phenomenological order parameter. The minimization of the free energy with respect to the volume change and order parameter gives the dependence of the Gibbs energy on the volume fraction of the product phase. The transformation proceeds in a finite-temperature region with the equilibrium volume fraction depending on temperature rather than at a fixed temperature as would be expected from the Gibbs phase rule for the first-order transition.

## 1. Introduction

Spontaneous strain is known to play an important role in many cases of the phase transformations in solids [1, 2]. Due to the difference in crystalline structures and elastic properties of the parent and product phases the misfit strain is known to appear in a two-phase microstructure. Associated displacement fields in the inclusion and matrix tend to relax this misfit at the cost of an additional elastic energy [3]. The minimization of this elastic energy defines the shape and crystallographic orientation of the particles of the new phase [4]. The elastic effects change the phase diagram of heterophase systems qualitatively and the phase rule is no longer valid since it does not take into account the elastic interaction between the phases which coexist in a state of coherent equilibrium [5]. It has also been shown that the ‘chemical’ free energy alone cannot determine the equilibrium fractions of the phases with different compositions through the well-known double-tangent construction [6, 7] applied to the temperature–composition phase diagram.

For a single-component system the Gibbs rule implies that the two-phase equilibrium is possible only at a single temperature point. The same should be true for the phase transitions of fixed-composition compounds and of alloys with very slow diffusion kinetics which could be considered as systems with constant composition. In the present paper we show that elastic coherence strain in such a case results in a finite temperature interval of phase coexistence with equilibrium phase fractions depending on the temperature. We consider the first-order solid-state phase transition within the Landau theory and assume that the volume change can be analysed as a secondary order parameter. This leads to a self-consistent treatment of the coherence stresses which on the one hand are caused by

† On leave from: Institute of Crystallography, Russian Academy of Sciences, Moscow, 117333, Russia.

the transition and on the other hand play the role of an external pressure for this phase transition.

A standard approach [3] to elastic effects is to let the transformation proceed in an inclusion disconnected from the matrix, to allow the ‘zero-stress’ transformation strain tensor to appear, and then to bring the inclusion into elastic coherent contact with the surrounding matrix. The strain energy is then calculated using the disconnected inclusion as an elastic reference state for the product phase. Though the new phase is sometimes considered to have different elastic moduli, calculations are mostly being done within linear elasticity theory. However, a strain field in the matrix gives rise to an effective pressure felt by the inclusion. Hence, when the transformation is sensitive to an applied external pressure, the ‘zero-stress’ assumption is no longer valid, and a self-consistent treatment involving non-linear dependence of the free energy of the new phase on the stress level is necessary.

The simplest possible way of analysing the transition strain is to use the Landau theory of phase transitions [8, 9] taking into account the coupling of the phenomenological order parameter with the strain tensor components. This coupling appears naturally, e.g., in the case of a proper ferroelastic (martensitic) phase transition [10] where the elastic energy expansion contains terms of different degrees composed from the products of the shear and volumetric strain. Such a coupling has been recently considered for transitions in cubic crystals [11] and the effects of the hydrostatic and uniaxial pressure have been studied. In the present paper I consider the elastic interaction in a heterophase system for the model case of spherical inclusions of the product phase embedded into an isotropic elastic matrix of the parent phase. The quadratic coupling of the order parameter with the volume change that corresponds to a variety of systems (see e.g. [12]) is analysed.

The remainder of this paper is organized as follows. We begin with a linear elasticity analysis of the displacement field and the elastic energy associated with the volume change in an inclusion embedded into the isotropic matrix. Then the free-energy difference between the infinite bulk crystals of the parent and product phases is considered within Landau theory and the coupling of the phenomenological order parameter with the elastic strain is taken into account. The energy cost of the formation of a finite fraction of new phase as inclusions inside the bulk crystal of the parent phase is then considered. After minimization of this free energy with respect to a volumetric strain, the resulting expression that depends on the volume fraction of the new phase is analysed. Then the transformation kinetics including fluctuations is briefly discussed.

## 2. Elastic energy associated with a misfit strain

Let us start with the spherical inclusion in an isotropic matrix and consider the bulk crystal of the parent phase as a reference state for the calculation of the elastic energy. The radial displacement field  $u(r)$  appears due to the transformation misfit and it has the following form determined by the elastic equilibrium conditions [13]:

$$\mathbf{u}(r) = \begin{cases} a_1 r & \text{for } r \leq R \\ a_2 r + \frac{b_2}{r^2} & \text{for } R < r \leq R_0. \end{cases}$$

Here  $R$  is the inclusion radius and  $R_0 = R/\sqrt[3]{\nu}$  is the radius of the spherical domain of the parent phase attributed to the inclusion with  $\nu$  being the volume fraction of the new phase. This association of the matrix domains with the particles of a new phase is used in a similar way to analyse the precipitate coarsening [14]. Boundary conditions for this elastic

problem are determined by the system geometry. The first boundary condition states that the displacement field vanishes at  $R_0$ , and the continuity of the displacement field across the interface implies the second boundary condition. Hence, one can get

$$a_1 = \frac{\epsilon_0}{3} \quad a_2 = \frac{\epsilon_0}{3} \frac{\nu}{\nu - 1} \quad b_2 = \frac{\epsilon_0}{3} \frac{R^3}{1 - \nu}$$

where  $\epsilon_0 = \text{Tr}(\hat{\epsilon})$  is a volumetric strain inside the inclusion.

The elastic energy associated with the matrix strain and expressed per unit volume of the *new* phase is given by an expression

$$\Delta \mathcal{G}_{el}^{(m)} = \frac{K_0}{2} \epsilon_0^2 \frac{\nu + \gamma}{1 - \nu}$$

where  $\gamma = (4\mu_0)/(3K_0)$  is the renormalized ratio of elastic moduli of the parent phase. This energy corresponds to the stress that plays a role of the external pressure applied to the inclusion undergoing phase transition.

The pure elastic energy (per unit volume of the new phase) associated with volumetric strain inside the inclusion is

$$\Delta \mathcal{G}_{el}^{(i)} = \frac{K_0}{2} \epsilon_0^2.$$

The total elastic energy that has to be added to the difference in Gibbs energy between the phases is equal to

$$\Delta \mathcal{G}_{el}(\epsilon_0) = \Delta \mathcal{G}_{el}^{(i)} + \Delta \mathcal{G}_{el}^{(m)} = \frac{K_0}{2} \epsilon_0^2 \frac{1 + \gamma}{1 - \nu}. \quad (1)$$

This expression is valid for a sufficiently small  $\nu$  when the inclusions of the product phase are well separated and the overlapping of associated spherical domains of the parent phase can be neglected.

### 3. Landau theory

The difference in free energy between bulk crystals of the parent and product phases which are related by the symmetry-breaking phase transition can be expanded in the mean-field Landau theory [8] in powers of the ‘order parameter’  $\eta$ . The theory was initially developed for the second-order transition where  $\eta$  is continuous at the transition point; however, first-order transitions satisfying the symmetry conditions can be considered as well. We will briefly outline here the Landau theory of the first-order transition; more details can be found elsewhere [9].

#### 3.1. Ginzburg–Landau expansion of the free energy

If the symmetry groups of both the parent and product phases are known *a priori* then the we can choose one domain orientation and use the scalar order parameter. The Ginzburg–Landau expansion of the difference in free energy per unit of volume has the general form [8, 9]

$$\Delta \mathcal{G}_{GL}(T, \eta) = \frac{a}{2}(T - T_c)\eta^2 + \frac{B}{3}\eta^3 + \frac{C}{4}\eta^4 \quad (2)$$

where  $T_c$  is a critical temperature. It is assumed that only the second-degree coefficient depends on temperature, and the equilibrium value of  $\eta$  is determined by the minimization of  $\Delta \mathcal{G}$ . Stability requires the highest-order coefficient  $C$  to be positive and the third-degree term  $B \neq 0$  implies that the transition is of first order.

The Gibbs free energy (2) has two possible minima. One with  $\eta = 0$  corresponds to a high-temperature undistorted phase stable for  $T \geq T_c$ . Another minimum with

$$\eta = -\frac{B}{2C} \left( 1 + \left( \frac{T_0 - T}{T_0 - T_c} \right)^{1/2} \right) \quad (3)$$

corresponds to a low-symmetry distorted phase which exists for

$$T \leq T_0 = T_c + \frac{1}{4} \frac{B^2}{aC}.$$

The phase energies become equal at the temperature of the first-order transition

$$T_* = T_c + \frac{2}{9} \frac{B^2}{aC}$$

where the order parameter jumps from the  $\eta = 0$  to

$$\eta = -\frac{2}{3} \frac{B}{C} \quad (4)$$

overcoming the activation energy barrier

$$\Delta \mathcal{G}_b = \frac{1}{324} \frac{B^4}{C^3}.$$

### 3.2. The volume effect in the free-energy expansion

To analyse an associated strain effect, the coupling of  $\eta$  with the homogeneous strain tensor  $\hat{\epsilon}$  has to be considered and the Ginzburg–Landau expansion should include elastic terms (1). In the simplest case the symmetry allows the volumetric strain  $\epsilon_0 = \text{Tr}(\hat{\epsilon})$  to be coupled with  $\eta$  in the lowest order by the following term:

$$\Delta \mathcal{G}_{int}(\epsilon_0, \eta) = D_0 \epsilon_0 \eta^2. \quad (5)$$

Adding this term to the elastic energy (1) and finding the minimum of the resulting expression with respect to  $\epsilon_0$ , we obtain the dependence of the volumetric strain inside the inclusion on the phenomenological order parameter in the form

$$\epsilon_0(\eta) = -\frac{D_0}{K_0} \eta^2 \frac{1 - \nu}{1 + \gamma}. \quad (6)$$

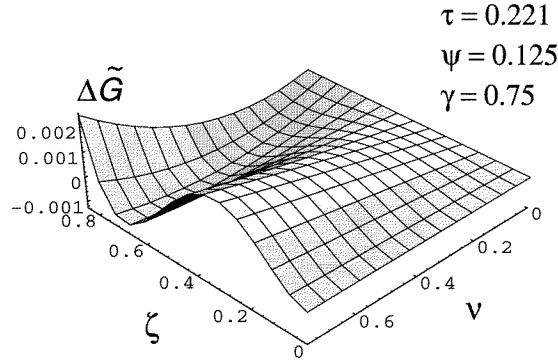
This leads to a renormalized Ginzburg–Landau expansion of  $\Delta \mathcal{G}$  in powers of  $\eta$  [11]:

$$\begin{aligned} \Delta \mathcal{G}(T, \eta) &= \Delta \mathcal{G}_{GL}(T, \eta) + \Delta \mathcal{G}_{el}(\epsilon_0(\eta)) + \Delta \mathcal{G}_{int}(\epsilon_0(\eta), \eta) \\ &= \frac{a}{2} (T - T_c) \eta^2 + \frac{B}{3} \eta^3 + \frac{C}{4} \eta^4 \left( 1 - \frac{2D_0^2}{K_0 C} \frac{1 - \nu}{1 + \gamma} \right). \end{aligned} \quad (7)$$

## 4. Analysis of the total free energy

We have to consider a difference in Gibbs free energy between the two-phase configuration and the pure unstrained parent phase as the reference state of a system. Thus, the energy cost for the formation of the new phase (7) should be multiplied by its volume fraction  $\nu$ . Choosing the case of  $B < 0$  which implies a positive  $\eta$  in the product phase, we can finally write the expansion of the total free energy per unit *system* volume in the following form:

$$\Delta \tilde{\mathcal{G}} = \frac{C^3}{B^4} \Delta \mathcal{G} = \nu \left( \frac{\tau}{2} \zeta^2 - \frac{\zeta^3}{3} + \frac{\zeta^4}{4} \left( 1 - \frac{\psi(1 - \nu)}{1 + \gamma} \right) \right) \quad (8)$$



**Figure 1.** The dependence of  $\Delta\tilde{\mathcal{G}}$  on the order parameter  $\zeta$  and the volume fraction of the new phase  $\nu$ .

with

$$\eta = -\frac{B}{C}\zeta \quad \tau = \frac{aC}{B^2}(T - T_c) \quad \psi = \frac{2D_0^2}{K_0C}.$$

The dependence of  $\Delta\tilde{\mathcal{G}}$  on  $\zeta$  and  $\nu$  is shown in figure 1 for certain values of  $\tau$ ,  $\psi$  and  $\gamma$ .

The state of equilibrium is now determined by the minimum of this free energy with respect to both  $\zeta$  and  $\nu$ :

$$\frac{\partial\Delta\tilde{\mathcal{G}}}{\partial\zeta} = 0 \quad \text{and} \quad \frac{\partial\Delta\tilde{\mathcal{G}}}{\partial\nu} = 0 \quad (9a)$$

$$\frac{\partial^2\Delta\tilde{\mathcal{G}}}{\partial^2\zeta} + \frac{\partial^2\Delta\tilde{\mathcal{G}}}{\partial^2\nu} > 0 \quad (9b)$$

$$\frac{\partial^2\Delta\tilde{\mathcal{G}}}{\partial^2\zeta} \frac{\partial^2\Delta\tilde{\mathcal{G}}}{\partial^2\nu} - \left(\frac{\partial^2\Delta\tilde{\mathcal{G}}}{\partial\nu\partial\zeta}\right)^2 > 0. \quad (9c)$$

There is a trivial solution  $\zeta = 0$  of coupled equations (9a) which corresponds to the undistorted parent high-temperature phase. Since the fraction of second phase  $\nu$  is confined between 0 and 1, this pure high-symmetry state with  $\nu = 0$  corresponds to a free-energy minimum for

$$\tau > \tau_* = \frac{2}{9} \left( 1 + \frac{\psi}{1 + \gamma - \psi} \right) \quad (10)$$

even though it does not satisfy conditions (9a)–(9c).

For a two-phase configuration one can obtain the following expressions for the equilibrium  $\zeta$  and  $\nu$ :

$$\zeta = \frac{2}{3} \left( 1 + \frac{\psi}{1 + \gamma - \psi} \right) \quad (11a)$$

$$\nu = \frac{1 + \gamma - \psi}{2\psi} - \frac{9(1 + \gamma - \psi)^2\tau}{4(1 + \gamma)\psi}. \quad (11b)$$

The stability conditions (9b) and (9c) are satisfied for these  $\zeta$  and  $\nu$  in the temperature range  $\tau < \tau_*$ . In the  $\psi \rightarrow 0$  limit,  $\tau_*$  corresponds to the temperature of the first-order phase transition  $T_*$  in the absence of stresses. An important difference from the Landau theory description of the homogeneous first-order transition in section 3.1 consists of the fact that the distorted low-symmetry phase no longer corresponds to the free-energy minimum above

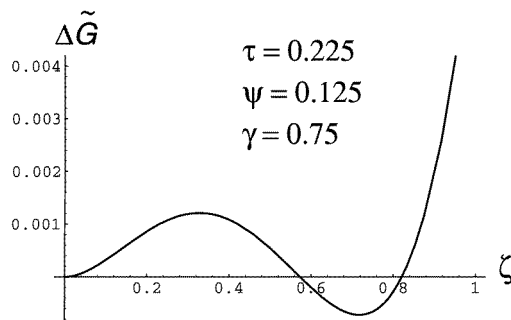
this temperature. It appears at  $\tau_*$  where  $\nu = 0$ , and its volume fraction increases linearly with the decrease of temperature according to (11b) up to  $\nu = 1$  at

$$\tau_1 = \frac{2(1+\gamma)(1+\gamma-3\psi)}{9(1+\gamma-\psi)^2}.$$

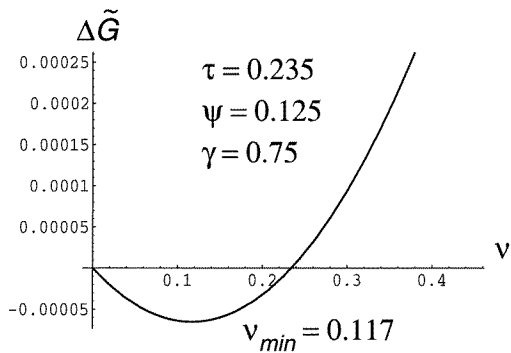
The width of two-phase temperature interval is

$$\Delta\tau = \frac{4\psi(1+\gamma)}{9(1+\gamma-\psi)^2}. \quad (12)$$

The equilibrium value of  $\zeta$ , equation (11a), does not depend on the dimensionless temperature  $\tau$ , and approaches the discontinuity of the homogeneous order parameter (4) for an equilibrium transition in the  $\psi \rightarrow 0$  limit. This is in a sharp contrast with the homogeneous transition where the order parameter undergoes continuous evolution in a low-symmetry phase [11].

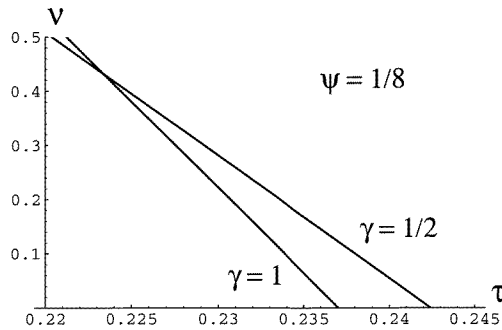


**Figure 2.** The free energy versus the phenomenological order parameter  $\zeta$ .



**Figure 3.** The dependence of  $\Delta\tilde{\mathcal{G}}$  on the volume fraction of the new phase  $\nu$ . The equilibrium value of  $\nu$  for these values of  $\tau$ ,  $\psi$  and  $\gamma$  is 0.117.

The energy dependence on  $\zeta$  is shown in figure 2 for  $\tau < \tau_*$ . It has a behaviour typical for the system described by Ginzburg–Landau free-energy expansion (2). There is an energy barrier separating the initial  $\zeta = 0$  state and the product phase that corresponds to a minimum of free energy for  $\zeta \neq 0$ . However, there is no barrier in the free-energy dependence on  $\nu$  shown in figure 3. This is a quite natural consequence of the fact that the free energy (8) is proportional to the phase fraction  $\nu$ . Since  $\Delta\mathcal{G}(T, \eta)$  given by (7) is negative for  $\tau < \tau_*$  the increase of  $\nu$  would reduce the total energy for small  $\nu$ s when the elastic contribution (1) is small as well.



**Figure 4.** The temperature dependence of the equilibrium volume fraction of the new phase  $\nu$  for two different values of the ratio of elastic moduli  $\gamma$ .

## 5. Discussion

The classical phase rule allows the equilibrium coexistence of parent and product phases of the same composition only at the fixed temperature  $T_*$ . However, the phase rule is based on the assumption that there is no *long-range* interaction, e.g. elastic, between the phases. The finite equilibrium volume fraction of the second phase  $\nu$  that corresponds to the minimal  $\Delta\tilde{G}$  in the present model appears in some temperature interval below  $\tau_*$ . It depends linearly on the dimensionless temperature  $\tau$  according to equation (11b) which is illustrated in figure 4. The width of the two-phase temperature interval (12) is proportional to the dimensionless coupling parameter  $\psi$  and vanishes when  $\psi \rightarrow 0$ . Thus, elastic interaction between product and parent phases is a reason for this deviation from the phase rule.

The orientational ordering transition in solid fullerene  $C_{60}$  is described by the Landau theory with quadratic coupling (5) of the orientational order parameter with volumetric strain [12], and, thus, the present model can undergo experimental checking in this case. The finite temperature interval of an equilibrium coexistence of low- and high-temperature phases was indeed found in a diffraction study of  $C_{60}$  [15]. The same symmetry breaking and, hence, the same form of coupling appears in the first-order chemical ordering transition in the intermetallic compounds with  $Cu_3Au$ -type structure ( $L1_2$ ) [16].

The order parameter of the low-symmetry phase continuously evolves with temperature in the Landau theory of phase transitions [8, 9]. In sharp contrast with this result, the distortion of the low-symmetry phase which is proportional to the order parameter  $\zeta$  does not depend on the temperature in our model according to (11a). Thus, a proper account of the elastic strain associated with the first-order transition implies the fixed structure of the product phase, with a particular value of the distortion being determined by the coefficients of the renormalized Ginzburg–Landau expansion of the free energy. Such a situation arises for the FCC–BCC martensitic transition in pure Fe and some alloys, and could not be adequately described by classical Landau theory (see [11] and references therein for further details).

Our model apparently corresponds to the ‘athermal’ kind of martensitic transformation in which the transformation begins at some starting temperature  $M_s$ , but the parent phase still exists until the temperature goes down to  $M_f$ , a martensite finishing point. No annealing can change an equilibrium phase fraction at fixed temperature, and the system has to be cooled down further to achieve the increase in  $\nu$ , i.e. for the transformation to proceed. The finishing point  $M_f$  corresponds to  $\nu = 1$ , and the present model cannot be used in this region because the inclusions of the new phase are thought to be well separated.

The martensite spontaneous strain, e.g. Bain strain, playing the role of the order parameter for Landau theory is a shear [10], and the spherical shape of the new phase



inclusion in our model implies that the transformation strain does not have shear components. However, in many cases of martensitic phase transformations, microstructure with multiple domains appears which has a lower elastic misfit energy [4]. After averaging over the ensemble of twinned domains of different orientations composing the inclusion, the shear components disappear and only volumetric misfit strain remains. Thus, our model might be relevant for at least some cases of martensitic transformations.

The present model does not involve the interface energy, which is important at small  $\nu$ . It leads to the absence of a critical volume fraction that would correspond to a critical nucleus in a classical nucleation theory [1]. The energy of the elastic coherent interface can be estimated through the gradient terms in the elastic energy expansion for proper ferroelastic (martensitic) phase transitions [10]. However, this interface energy is small in comparison with the elastic energy associated with long-range accommodation strain and can be neglected for finite volume fraction  $\nu$ . The experiments show that martensitic transitions are characterized by easy nucleation and very small values of the possible supercooling. So, classical nucleation theory is believed to be inapplicable in this case.

It is known that the order parameter fluctuations do not play a significant role for the phase transitions associated with strain [17]. However, there is a possibility of inhomogeneous distribution of the inclusion radius and, accordingly, of the volume fraction  $\nu$  of the product phase. In order to take this effect into account one has to consider a free-energy functional involving non-local effects at least in a lowest-order gradient approximation. Such an approach is obviously beyond the scope of our simplified model.

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