Symmetry-Breaking Transitions in Equilibrium Shapes of Coherent Precipitates

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Stability of Microstructures (MM5290) Write-Up

Abstract

In this write-up, a brief overview of symmetry-breaking transitions as seen in cubic systems is presented. Most of the content is taken from the work of Sankarasubramanian et al. [1, 4].

1 Introduction

When studying the properties of crystalline materials, discussions on the symmetry exhibited by the material can give us useful information about what to expect from the material's properties. One of the fundamental postulates of crystal physics is the Neumann's Principle (given in Definition Box 1).

Definition Box 1: Neumann's Principle

The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal. [2]

The point group of the crystal is used to classify the material into various crystal classes (32 to be precise). Neumann's principle doesn't disallow the physical property to have a higher symmetry than the crystal, in fact, it merely states that the property must *include* the symmetry elements of the crystal. In the discussion that follows, Neumann's principle is used in arguments related to the elastic properties (given by the elastic stiffness tensor) of a material.

2 Why Symmetry-Breaking Transitions?

As noted earlier, symmetry plays a significant role in nearly all naturally occurring phenomena. Precipitation, or growth of a secondary phase particle inside a matrix, is no different. The shape of the precipitate (the morphology) is largely governed by the minimisation of the energy associated with the formation of the new precipitate. There are two major contributions to this energy:

1. Interface energy
   (arising due to the difference in the bonding environments at the interface and at the bulk)
2. Elastic energy
   (arising due to strains because of mismatch of lattice parameters and a need for coherence)

Both these contributions when individually considered in the minimisation may not lead to the same shape that minimises the energy. Also, the interface energy effects and the elastic energy effects scale differently with size (one goes as r^2 and the other as r^3). Hence, at low sizes, the interface energy plays a major role and as the size increases, the elastic energy plays the dominant role.

When we ignore the elastic effects at the interface, we obtain the morphology that is most preferred as dictated by the surface energy (which itself may be anisotropic). Such constructions are

called "Wulff constructions". However, when the matrix and precipitate have some degree of coherency, leading to elastic effects at the interface, the preferred equilibrium shape of the precipitate changes with the increasing average size of the precipitate.

In nearly all cases, some amount of symmetry is "broken" and a shape with lower symmetry is preferred. These transitions are termed "symmetry-breaking transitions". The IUPAC Gold Book definition for Symmetry-breaking transitions is given in Definition Box 2.

Definition Box 2: Symmetry-breaking transitions

Also called subgroup-supergroup transition, it's a transition in which the space-group symmetry of the lower symmetry phase is a subgroup of that of the higher symmetry phase. [3]

There are no analytical solutions to this minimisation problem, hence the need to resort to numerical techniques combined with some amount of optimisation principles. But these studies throw some light on symmetry-breaking transitions, which is of fundamental interest.

3 Analysing the 2-D Cubic System

Sharp-interface, diffuse-interface (phase field) and atomistic studies can show the evolution of the morphology. But, the point of focus here is to obtain the "equilibrium shape" of the precipitate. This can help in finding the influence of many factors like anisotropy and inhomogeneity on the morphology of the particles. A sharp interface approach is taken for this purpose.

3.1 The Model and Solution Techniques

An single 2-D particle (isolated precipitate) is assumed be coherently embedded in a 2-D matrix. Both the particle and the matrix possess cubic symmetry crystal structures. The interfacial energy is however assumed to be isotropic. The only stress present is due to the mismatch of lattice parameters between the particle and the matrix and the misfit strain tensor is given by ϵ^*. The particle size is non-dimensionalised as ρ and the radius for non-uniform shapes is defined as the radius of the circle R with the same area.

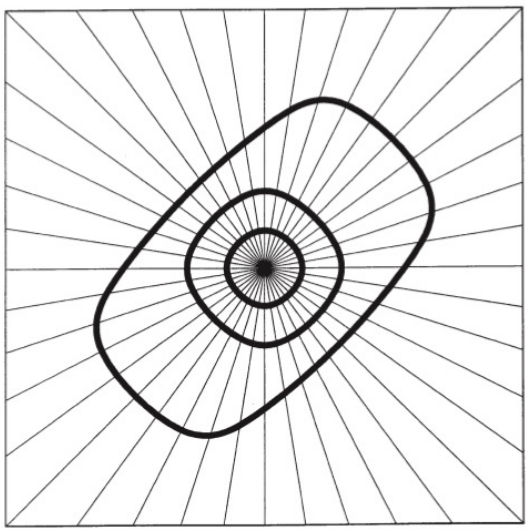

Figure 1: One of the symmetry-breaking transitions also showing the radial lines that were used to parameterise the shape. [4]

The shape of the precipitate is parameterised by the distance from a point inside the precipitate to many points on the interface. This ensures that the shape of the precipitate is not assumed to be a circle or a square to start with and instead results from the optimisation scheme. Figure 1 shows one example of this type of parameterisation.

The equilibrium shape is assumed to be that which minimises the sum of elastic and interfacial energy given that the volume is constant. This shape cannot be obtained analytically, but can be obtained in multiple ways using iterative techniques. In this paper, the authors used finite element analysis (to get the energy values) as well as some optimisation techniques (to minimise the energy) to solve the problem.

3.2 The Different Regimes

3.2.1 Tetragonality Parameter

Given that the system is cubic, the tetragonality parameter is given by

$$t = \frac{\epsilon^*_{yy}}{\epsilon^*_{xx}}$$

Based on the value of t, we can classify all cubic 2-D systems into four types:

1. **Dilatational misfit**: $t = 1$.
2. **Non-Dilatational misfit**: $0 < t < 1$. The principal misfit components have the same sign
3. **Non-Dilatational misfit**: $-1 < t < 0$. The principal misfit components have opposite signs
4. **Pure shear**: $t = -1$

In cases 3 and 4, there's an invariant line, or a line along which there is no elastic stress because there's no misfit along this direction. Such an invariant line is only possible when two components can cancel each other (and therefore, must be of opposite signs), which can only happen when $t < 0$.

3.2.2 Zener anisotropy ratio

Because of Neumann's Principle (Definition Box 1), the elastic-stiffness tensors of both the particle and matrix must have cubic anisotropy, or they must be isotropic. The anisotropy is characterised by the Zener anisotropy ratio:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}$$

Here, C is the stiffness tensor. Using different values of A and defining average shear modulus and Poisson's ratio, we can get expressions for these stiffness tensor entries. The physical meaning for different values of A are:

1. **Isotropic**: $A = 1$.
2. $\langle 10 \rangle$ **is elastically soft and** $\langle 11 \rangle$ **is elastically hard** : $A > 1$.
3. $\langle 11 \rangle$ **is elastically soft and** $\langle 10 \rangle$ **is elastically hard**: $A < 1$.

3.2.3 Inhomogeneity Ratio

As discussed before, from Neumann's Principle (Definition Box 1), the elastic-stiffness tensors of both the particle and matrix must have cubic anisotropy, or they must be isotropic. But the values themselves can be different for the two phases. If the values are same, the system is **homogeneous**, and if they are different, the system is **inhomogeneous**. Though the inhomogeneity need not be

only in the shear moduli ($\bar{\mu}$), the inhomogeneity is parameterised easily if that is the case, by the inhomogeneity parameter.

$$\delta = \frac{\bar{\mu}_{\text{particle}}}{\bar{\mu}_{\text{matrix}}}$$

Physically if,

1. $\delta > 1$: Particle is harder.
2. $\delta < 1$: Particle is softer.

3.3 The Possible Symmetry-Breaking Transitions

There are four kinds of symmetry-breaking transitions that can happen in 2-D cubic systems. They are represented in Figure 2. In the first case, the infinite rotational symmetry of circle (**I**: isotropic) broken to a 2-fold symmetry of an ellipse (**O**: orthorhomic). In the second and third cases, the 4-fold symmetry of the square-like particles (**T**: tetragonal) is broken to the 2-fold symmetry of rectangle-like particles (**O**: orthorhombic). In the fourth case, the mirror-symmetry of the ellipse is broken (**O**: orthorhombic) is broken to give a S-shaped (**M**: monoclinic) particle.

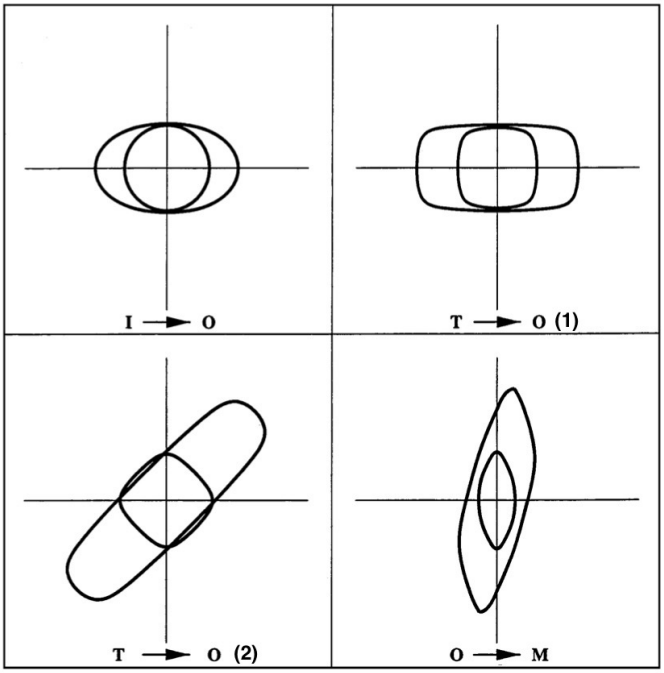

Figure 2: The four possible symmetry-breaking transitions. **I** stands for isotropic, **O** stands for orthorhombic, **T** stands for tetragonal, **M** stands for monoclinic. [4]

3.4 Summary of Transitions in the Different Regimes

Table 1 summarises not only the possible transitions, but also how the behaviour changes with the modulus mismatch (δ) and the elastic anisotropy (A). In nearly all the cases, the transitions happen only after a critical size (ρ_c) is reached and the value of this ρ_c depends on δ and A.

The presence or absence of the invariant line (possible when the tetragonality parameter is negative) plays a significant role in how the system behaviour changes with the inhomogeneity ratio and anisotropy.

1. If there is an invariant line, the particle can infinitely elongate itself in this direction, and there is no elastic energy as there is no misfit. The driving force for the transition doesn't

depend on whether the particle is elongated or equiaxed. Thus, as the inhomogeneity parameter increases, the driving force increases and the transition happens at a lower value of ρ, leading to a continuously increasing value of ρ_c^{-1}.

2. If there's no invariant line, the equiaxed shape is preferred compared to the elongated shape. Hence, there's no transition beyond a particular amount of inhomogeneity ($\rho_c^{-1} = 0$) as the cost saved is lost due to elastic-energy considerations of the elongated particles.

Table 1: Summary of the Symmetry-Breaking Transitions in all regimes. Adapted from [4].

<table>
<tr><td></td><td>$A = 1$
(I)</td><td>$A < 1$
(T)</td><td>$A > 1$
(T)</td></tr>
<tr><td>Case</td><td>I $\rightarrow$ O</td><td>T $\rightarrow$ O (1)</td><td>T $\rightarrow$ O (2)</td></tr>
<tr><td>$t = 1$</td><td colspan="3">As δ increases, ρ_c^{-1} reaches maxima and later goes to 0 at δ_c.</td></tr>
<tr><td>(I)</td><td colspan="3">δ_c increases, as $\left|\frac{A-1}{A+1}\right|$ increases.</td></tr>
<tr><td>Case</td><td rowspan="3">No Transition</td><td>O $\rightarrow$ M</td><td rowspan="3">No Transition</td></tr>
<tr><td>$0 < t < 1$</td><td>As δ increases, ρ_c^{-1} reaches maxima and later goes to 0 at δ_c.</td></tr>
<tr><td>(O)</td><td>δ_c increases, as $\left|\frac{A-1}{A+1}\right|$ increases.</td></tr>
<tr><td>Case</td><td>O $\rightarrow$ M</td><td>O $\rightarrow$ M</td><td>O $\rightarrow$ M</td></tr>
<tr><td>$-1 < t < 0$</td><td colspan="3">As δ increases, ρ_c^{-1} keeps increasing</td></tr>
<tr><td>(O)</td><td colspan="3">No δ_c</td></tr>
<tr><td>Case</td><td>T $\rightarrow$ O (2)</td><td>T $\rightarrow$ O (2)</td><td>T $\rightarrow$ O (2)</td></tr>
<tr><td>$t = -1$</td><td colspan="3">As δ increases, ρ_c^{-1} keeps increasing</td></tr>
<tr><td>(O)</td><td colspan="3">No δ_c</td></tr>
</table>

References

[1] C.S. Jog, R. Sankarasubramanian, and T.A. Abinandanan. "Symmetry-breaking transitions in equilibrium shapes of coherent precipitates". In: *Journal of the Mechanics and Physics of Solids* 48.11 (2000), pp. 2363 –2389. ISSN: 0022-5096. DOI: https://doi.org/10.1016/S0022-5096(00)00005-3. URL: http://www.sciencedirect.com/science/article/pii/S0022509600000053.

[2] J. F. Nye. *Physical Properties of Crystals*. Oxford University Press, 1985. ISBN: 9780198511656.

[3] International Union of Pure and Applied Chemistry. *IUPAC Compendium of Chemical Terminology – The Gold Book*. 2nd ed. 2009. URL: http://goldbook.iupac.org/.

[4] R. Sankarasubramanian, C. S. Jog, and T. A. Abinandanan. "Symmetry-breaking transitions in equilibrium shapes of coherent precipitates: Effect of elastic anisotropy and inhomogeneity". In: *Metallurgical and Materials Transactions A* 33.4 (2002), pp. 1083–1090. ISSN: 1543-1940. DOI: 10.1007/s11661-002-0210-6. URL: https://doi.org/10.1007/s11661-002-0210-6.