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3.21 Kinetics of Materials—Spring 2006

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Lecture 21: General Features of Phase Transformations.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapter 17.

Key Concepts

- Phase transformations occur in systems at points where free energy functions or their derivatives with respect to intensive variables exhibit singularities. Sometimes transformations are characterized by denoting them as "first-order," "second-order," etc. according to the level of derivative of free energy that first shows a discontinuity. Thus, melting of a single-component crystalline substance would be first-order because it would be accompanied by discontinuous changes in volume and entropy.

- Phase transformations can also be categorized as being either "continuous" or "discontinuous." Continuous phase transformations occur in systems that are thermodynamically *unstable*, such that the transformation can occur without surmounting any activation-energy barrier. Continuous transformations occur uniformly throughout a transforming system. Discontinuous transformations occur from systems that are thermodynamically *metastable*, such that the transformation begins a discrete nucleation sites and evolves by outward growth of the nuclei of the new phase.

- The state of a thermodynamic system can be specified by defining *order parameters* such as concentration and magnetization. *Conserved order parameters* specify conserved quantities such as composition variables. *Nonconserved order parameters* specify quantities such as degree of antiferromagnetic order that are not conserved.

- The two important categories of continuous transformations in materials are: *spinodal decomposition*, in which an unstable, nearly homogeneous solution phase-separates into two phases with the same structure but different compositions; and *continuous ordering* in which an unstable homogeneous solution phase transforms into a closely-related structure of lower symmetry.

- Models for continuous transformation kinetics can be developed by deriving appropriate equations for the evolution of the order parameters. The *Cahn–Hilliard equation* describes the evolution of conserved variables. The *Allen–Cahn* equation describes the evolution of nonconserved variables.

- Because spinodal decomposition and continuous ordering develop gradually from infinitesimal fluctuations (remember, the initial homogeneous state is unstable), *diffuse interfaces* develop in the early stages of the transformations.

- A key aspect of the theories of continuous transformation is the *free energy of an inhomogeneous system* expressed as the free energy *functional* in *KoM* Eq. 18.13 in terms of the spatial dependence of the order parameter ξ:

$$f(\xi, \nabla\xi) = f^{\text{hom}}(\xi) + K|\nabla\xi|^2 \tag{1}$$

Related Exercises in *Kinetics of Materials*

None in Chapter 17!