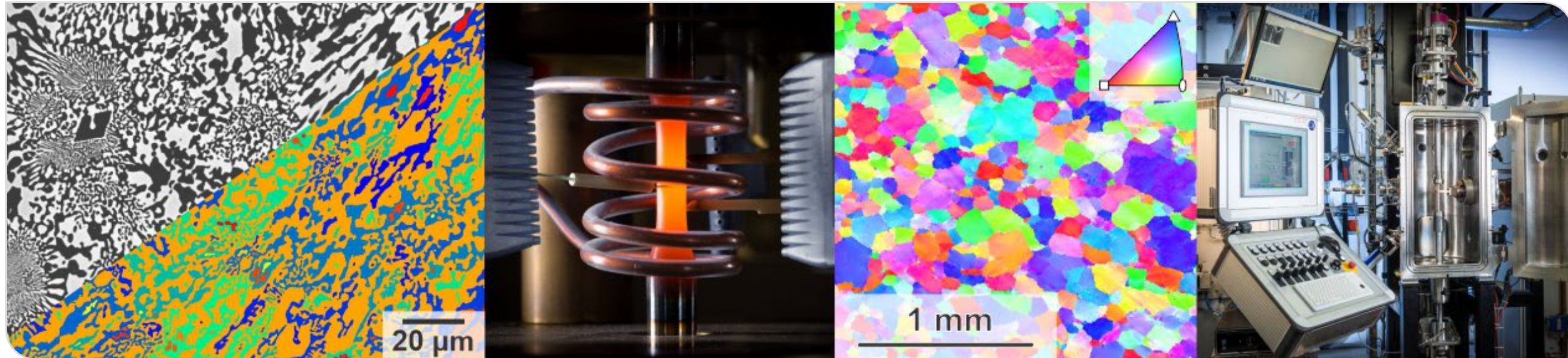


Phase Transformations in Materials

Lecture for “Mechanical Engineering” and “Materials Science and Engineering”
Dr.-Ing. Alexander Kauffmann (Bldg. 10.91, R. 375)
Dr. Sandipan Sen (Bldg. 10.91, R. 311)

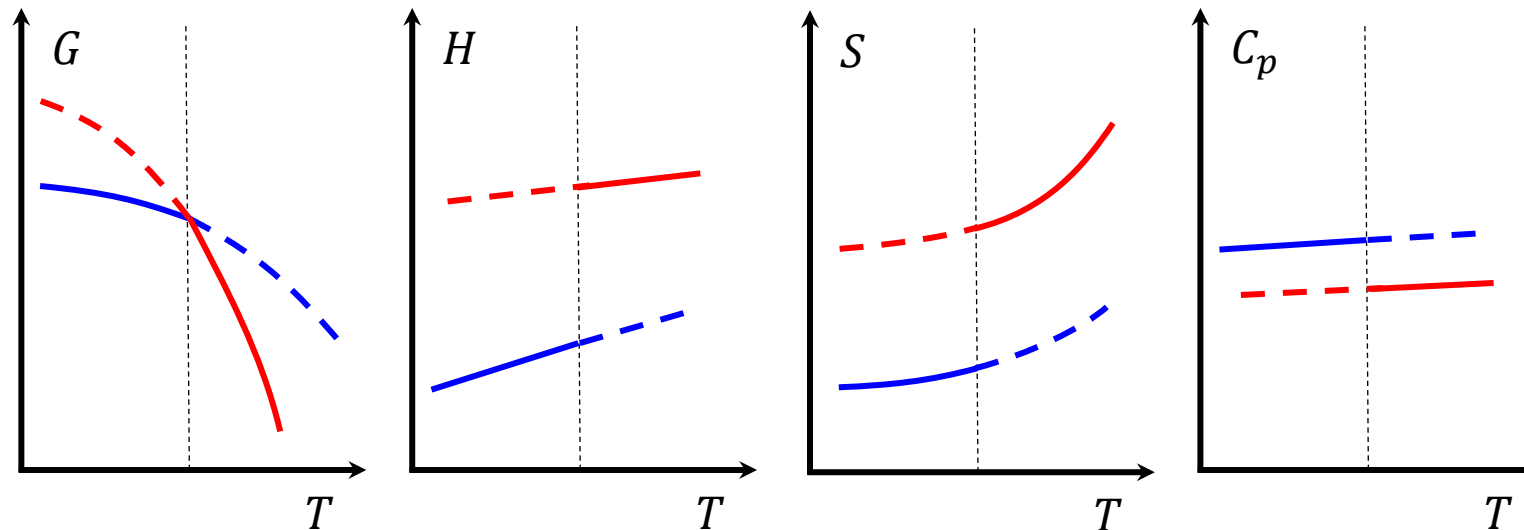
Version 23-12-15



- Continuous Phase Transformation
 - Discontinuous vs. Continuous
 - Concept of Series Expansion of G with Respect to the Order Parameter
 - 2nd Order Phase Transformation (Continuous)
 - 1st Order Phase Transformation (Discontinuous)
 - Examples

Discontinuous Phase Transformations

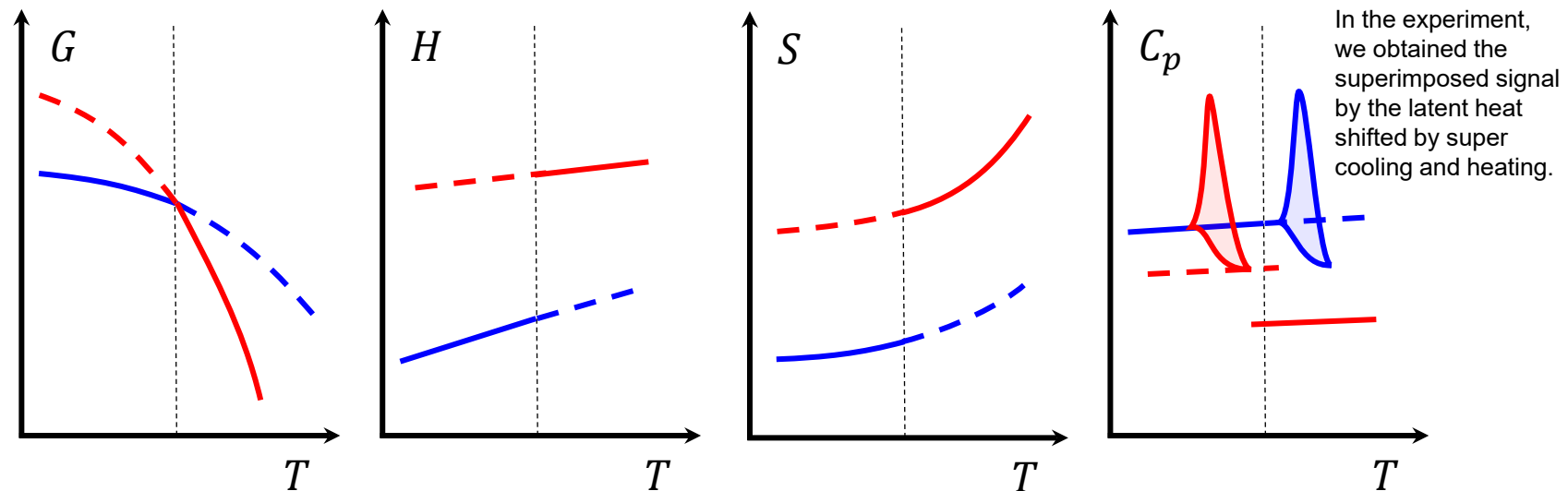
- So far, we mostly focused on discontinuous phase transformations. We have seen that they follow characteristics like this:



In the case of discontinuous phase transformations, there is a **latent heat** associated with the transformation, e.g. a **jump in enthalpy H** . Apart from this, the **order state** discontinuously changes, e.g. a **jump in entropy S** occurs. When materials properties are considered, there are discontinuous changes in density, lattice parameter, crystal structure, specific heat, etc.

Discontinuous Phase Transformations

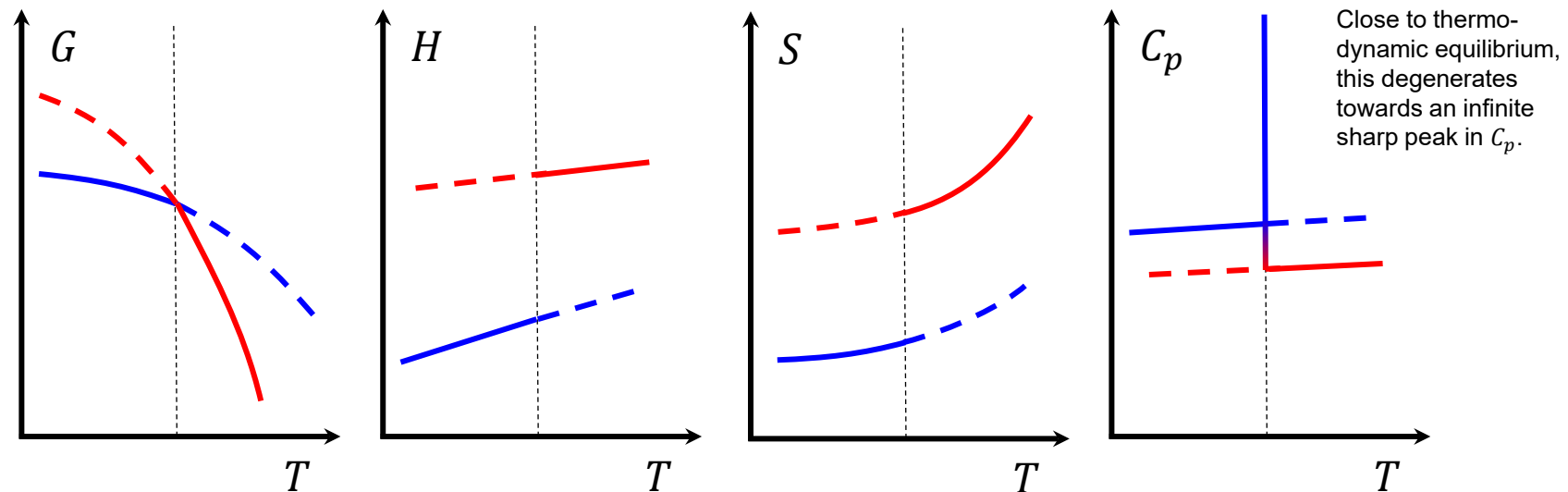
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Discontinuous Phase Transformations

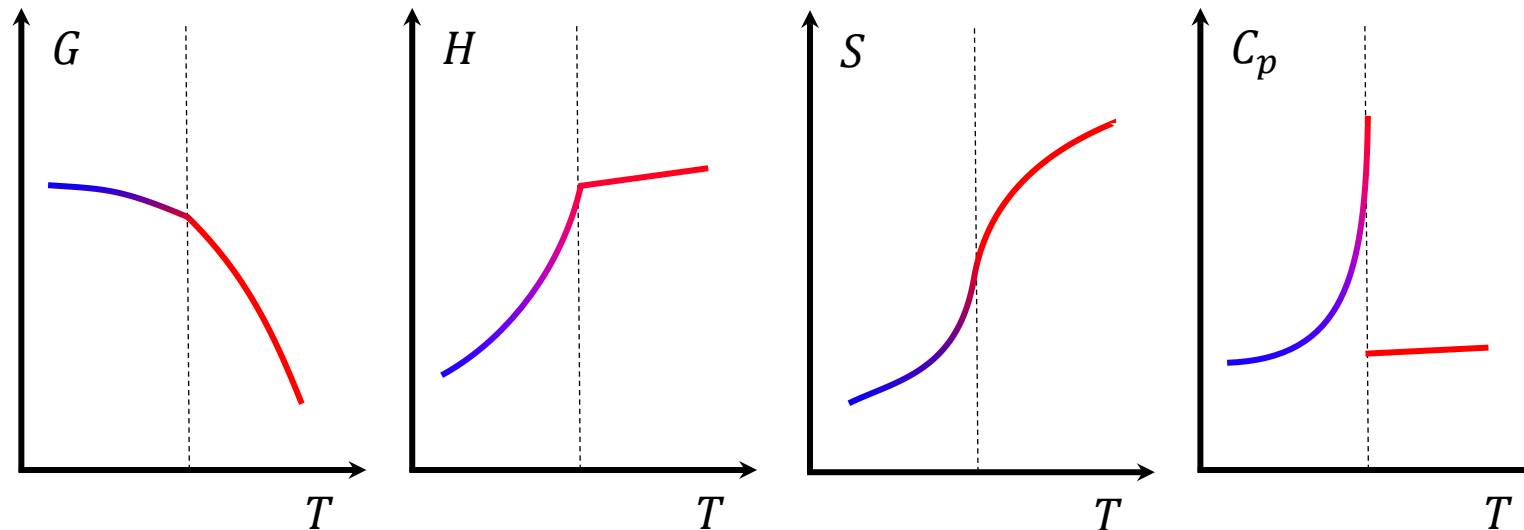
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Continuous Phase Transformations

- In contrast, the characteristics of continuous transformations are like this:



In the case of continuous phase transformations, there are **no discontinuous changes of the thermodynamic potentials**, G , H or S . All of these functions are continuous, **only slopes are changing**. Hence, **higher order derivatives are discontinuous**. In the Ehrenfest nomenclature, the order of the phase transformation corresponds to the order of derivative that becomes discontinuous. The discontinuous phase transformations discussed in this lecture are of 1st order and the continuous are of 2nd order according to this nomenclature. When materials properties are considered, functional properties can change tremendously in the form of an anomaly at the critical temperature, for example susceptibility, coupling coefficients, etc.

Series Expansion of G

- In order to model the different situations, **Landau theory** proved successful.
- While **T and p are the natural variables of G** and can be controlled independently, the **equilibrium state** (minimum G) for a given pair of T and p might be **controlled by** a so-called **order parameter Q** . A series expansion might describe the situation close to a phase transformation:

$$G(T, p, Q) = G_0(T, p) + \frac{1}{2} A(T, p) Q^2 + \frac{1}{3} B(T, p) Q^3 + \frac{1}{4} C(T, p) Q^4 + \dots$$

- Depending on the order of the series and the coefficients, different phase transformations can be described on a phenomenological basis.

2nd Order Phase Transformation (Continuous)

- Ansatz: $G(T, Q) = G_0(T) + \frac{1}{2} A(T) Q^2 + \frac{1}{4} C(T) Q^4$
 $p = \text{const.}, B(T), D(T), E(T), \dots = 0$

- For a given T , minimization of G with respect to Q leads to the equilibrium state with Q_0 :

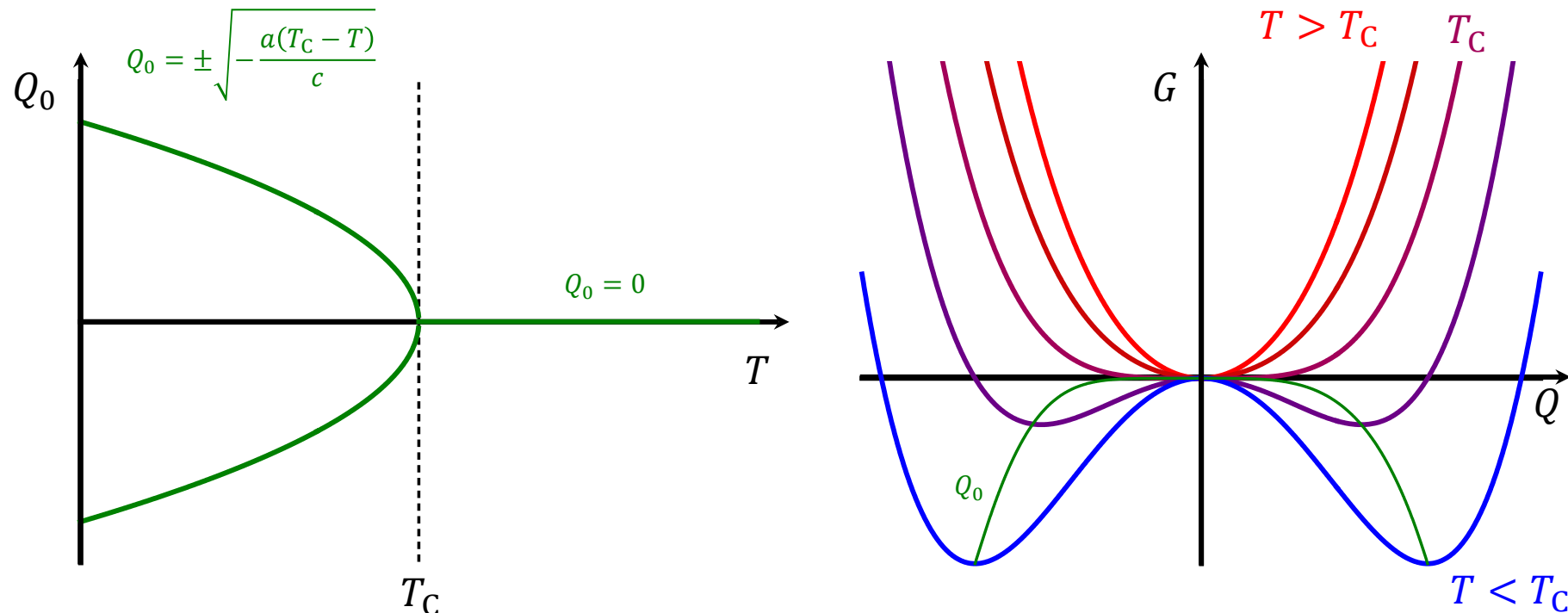
$$\frac{\partial G(T, Q)}{\partial Q} = Q(A(T) + C(T) Q^2) \text{ with } \left. \frac{\partial G(T, Q)}{\partial Q} \right|_{Q_0} = 0$$
$$\frac{\partial^2 G(T, Q)}{\partial Q^2} = A(T) + 3C(T) Q^2 \text{ with } \left. \frac{\partial^2 G(T, Q)}{\partial Q^2} \right|_{Q_0} > 0$$

2nd Order Phase Transformation (Continuous)

- Ansatz: $G(T, Q) = G_0(T) + \frac{1}{2} A(T) Q^2 + \frac{1}{4} C(T) Q^4$
 $p = \text{const.}, B(T), D(T), E(T), \dots = 0$
- For a given T , minimization of G with respect to Q leads to the equilibrium state with Q_0 :
 - (1) $Q_0 = 0$ with $A > 0$
 - (2) $Q_0^2 = -\frac{A}{C}$ with $A < 0$ and $C > 0$
- In the simplest case, this might be achieved by
 $A(T) = a(T_C - T)$ and $C(T) = c > 0$.

2nd Order Phase Transformation (Continuous)

- In this simple case, there are two temperature ranges $T > T_C$ and $T < T_C$ observed. For the high temperature phase, minimum G for fixed T is achieved by $Q_0 = 0$. For the low temperature phase, non-zero Q_0 lead to a minimum in G . $Q_0 = 0$ is unstable for $T < T_C$!



2nd Order Phase Transformation (Continuous)

- Ansatz: $G(T, Q) = G_0(T) + \frac{1}{2} A(T) Q^2 + \frac{1}{4} C(T) Q^4$
 with $A(T) = a(T_C - T)$ and $C(T) = c > 0$:

$$Q_0 = \begin{cases} 0, & T > T_C \\ \pm \sqrt{-\frac{a(T_C - T)}{c}}, & T < T_C \end{cases}$$

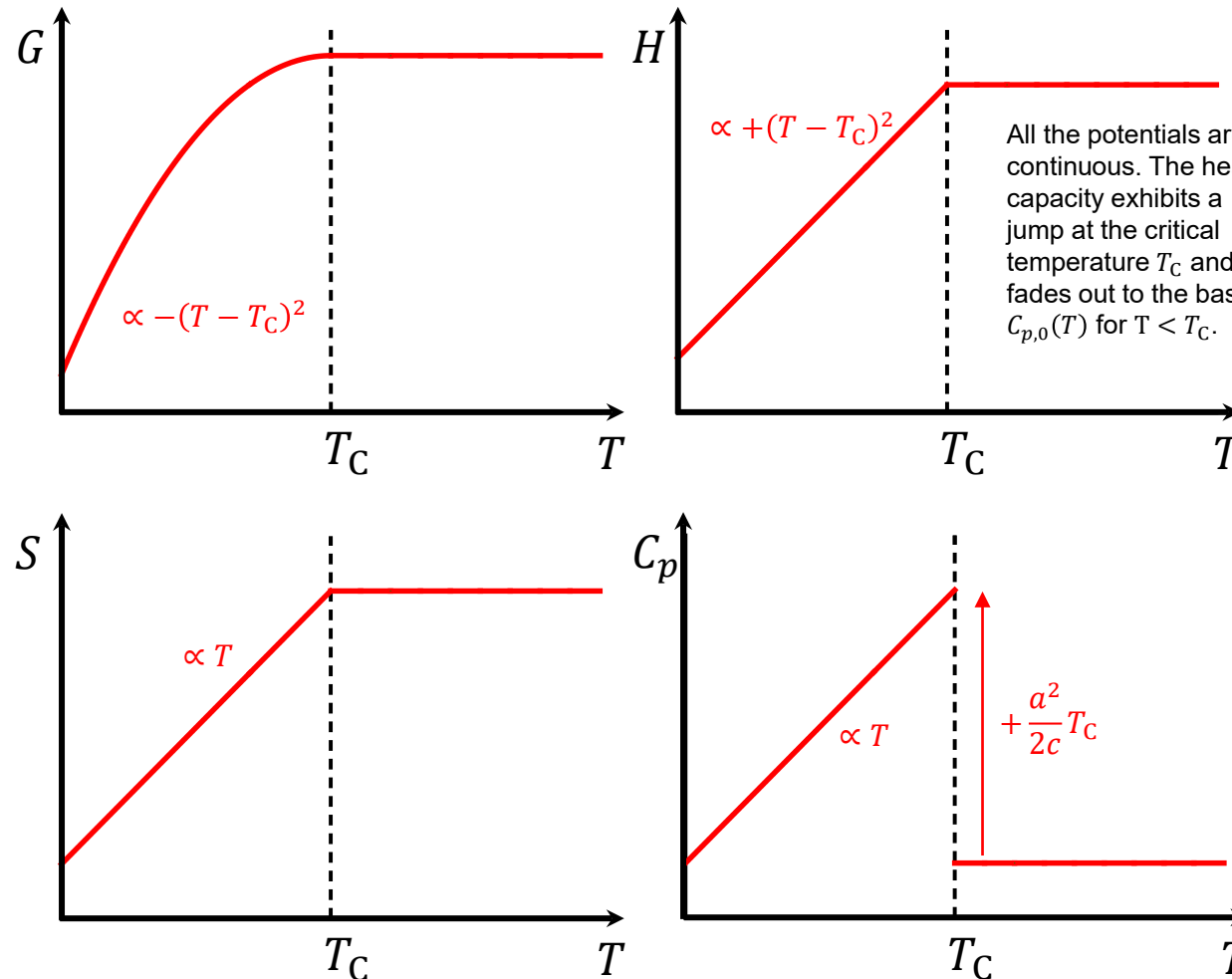
$$G = G(T, Q_0) = G_0(T) + \frac{a^2}{2c} (T - T_C)^2$$

$$S = -\frac{\partial G}{\partial T} \Big|_p = S_0(T) + \frac{a^2}{2c} (T - T_C)$$

$$C_p = T \frac{\partial S}{\partial T} \Big|_p = \begin{cases} C_{p,0}(T), & T > T_C \\ C_{p,0}(T) + \frac{a^2}{2c} T, & T < T_C \end{cases}$$

2nd Order Phase Transformation (Continuous)

Note that the non-linear base functions $G_0(T)$, $S_0(T)$, $H_0(T)$ and $C_{p,0}(T)$ can simply be added in order to obtain a more realistic behavior.



1st Order Phase Transformation (Discontinuous)

- Ansatz: $G(T, Q) = G_0(T) + \frac{1}{2} A(T) Q^2 + \frac{1}{4} C(T) Q^4 + \frac{1}{6} E(T) Q^6$,
 $p = \text{const.}, B(T), D(T), F(T), \dots = 0$

- For a given T , minimization of G with respect to Q leads to the equilibrium state with Q_0 :

$$\frac{\partial G(T, Q)}{\partial Q} = Q(A(T) + C(T) Q^2 + E(T) Q^4) \text{ with } \left. \frac{\partial G(T, Q)}{\partial Q} \right|_{Q_0} = 0$$
$$\frac{\partial^2 G(T, Q)}{\partial Q^2} = A(T) + 3C(T) Q^2 + 5E(T) Q^4 \text{ with } \left. \frac{\partial^2 G(T, Q)}{\partial Q^2} \right|_{Q_0} > 0$$

1st Order Phase Transformation (Discontinuous)

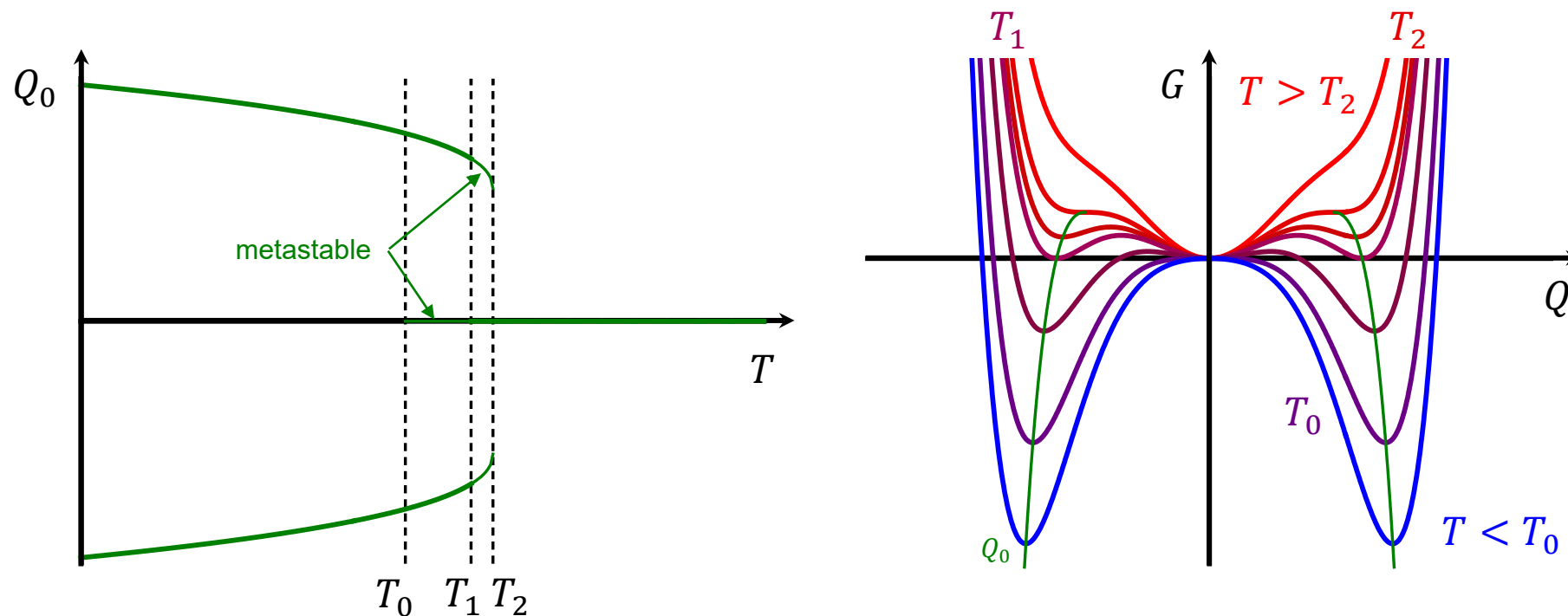
- Ansatz: $G(T, Q) = G_0(T) + \frac{1}{2} A(T) Q^2 + \frac{1}{4} C(T) Q^4 + \frac{1}{6} E(T) Q^6$
 with $A(T) = 2a(T_0 - T)$, $C(T) = -4c < 0$, $E(T) = 6e > 0$:

$$Q_0 = \begin{cases} 0, & T > T_2 = T_0 + \frac{c^2}{3ae} \\ \pm \sqrt{\frac{c}{3e} \left(1 + \sqrt{1 - \frac{3ae(T_0 - T)}{c}} \right)}, & T < T_1 = T_0 + \frac{c^2}{4ae} \end{cases}$$

$$a, c, e > 0$$

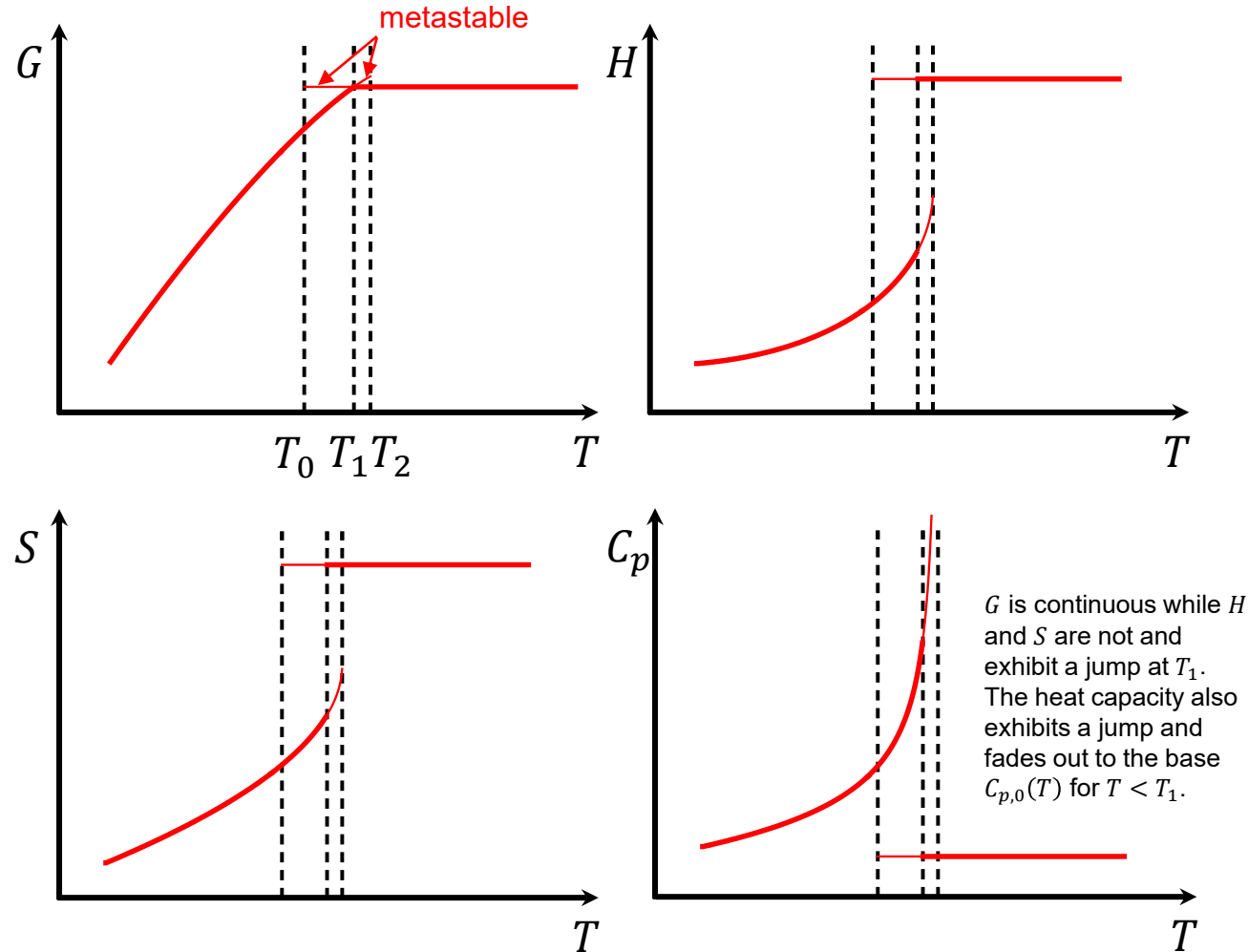
1st Order Phase Transformation (Discontinuous)

- For $T > T_2$, only $Q_0 = 0$ is stable. For $T_1 < T < T_2$, the non-zero Q_0 become metastable, $Q_0 = 0$ is stable. For $T_0 < T < T_1$, the non-zero Q_0 are stable while the zero Q_0 is metastable. For $T < T_0$, the zero Q_0 is unstable and only the non-zero Q_0 situation exist as stable states.



1st Order Phase Transformation (Discontinuous)

Note that the non-linear base functions $G_0(T)$, $S_0(T)$, $H_0(T)$ and $C_{p,0}(T)$ can simply be added in order to obtain a more realistic behavior.



Application to Various Phenomena

- The challenge in experiment is to identify the proper order parameter. In general, the order parameter is a tensor. The coefficients of the series expansion can be obtained by experimental observation of the properties close to the phase transformation.
- Examples for the powerful application are

Phenomenon	Order Parameter	Type
Gaseous – Liquid, Liquid – Solid, allotropic Solid – Solid	Density, Lattice Parameter	1 st order
Ferro/ferri/antiferromagnetic – Paramagnetic	Magnetic moment, Magnetization	usually 2 nd order
Ferroelectric – Dielectric (Landau-Devonshire theory)	Polarization	1 st and 2 nd order
Superconductive transition (Ginzburg-Landau theory)	Cooper Pair Density	usually 2 nd order
etc.		

- By application of the additional thermodynamic variables from Ch. 1a, also the impact of external fields on the order parameter can be described. Further, microscopic interpretation of the order parameter can lead to proper estimates of the coefficients.