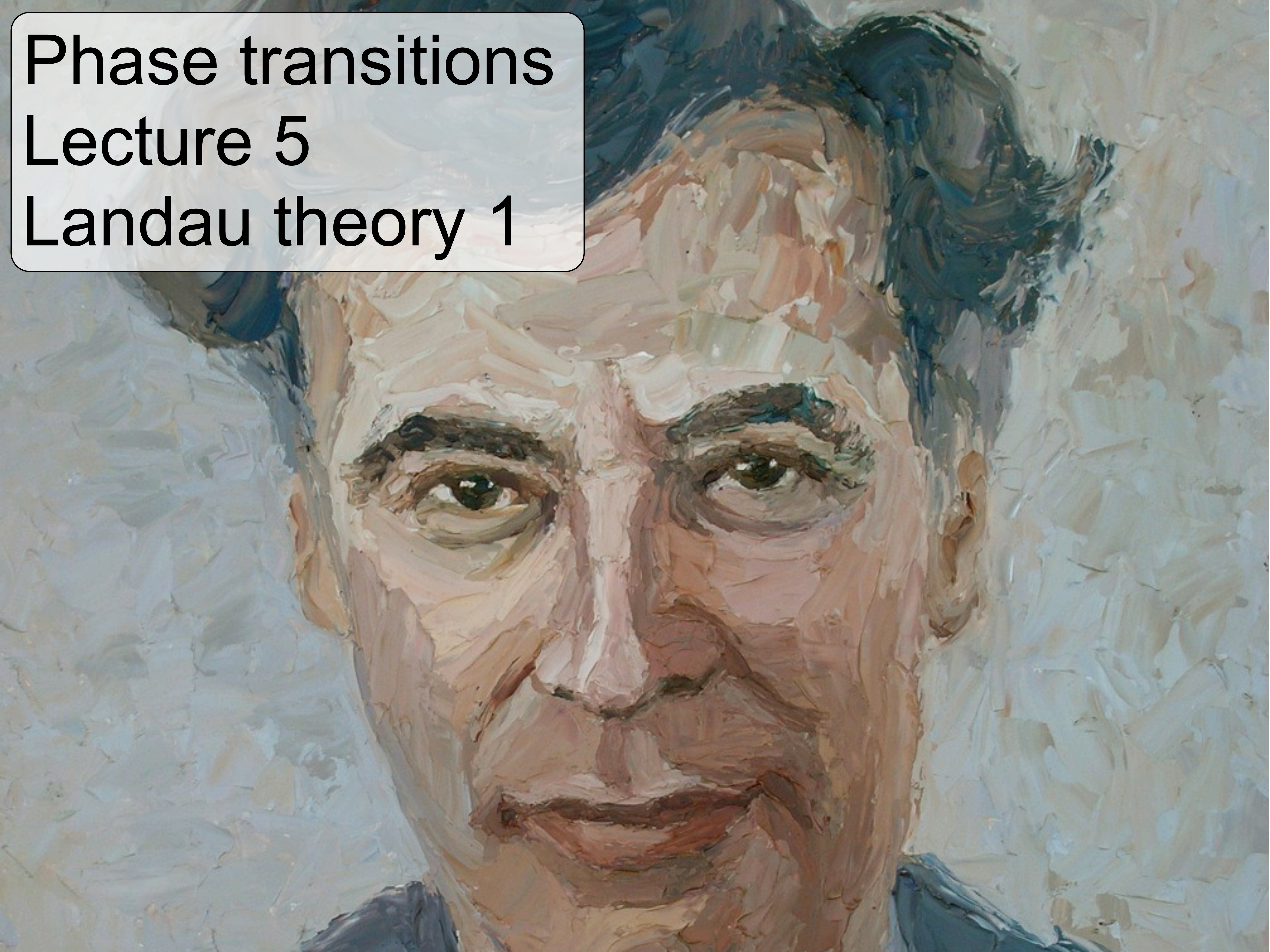
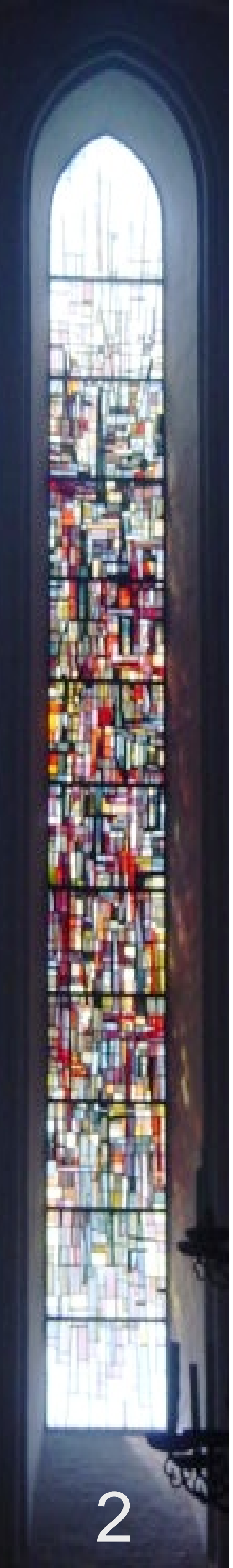
Phase transitions
Lecture 5
Landau theory 1





Learning outcomes

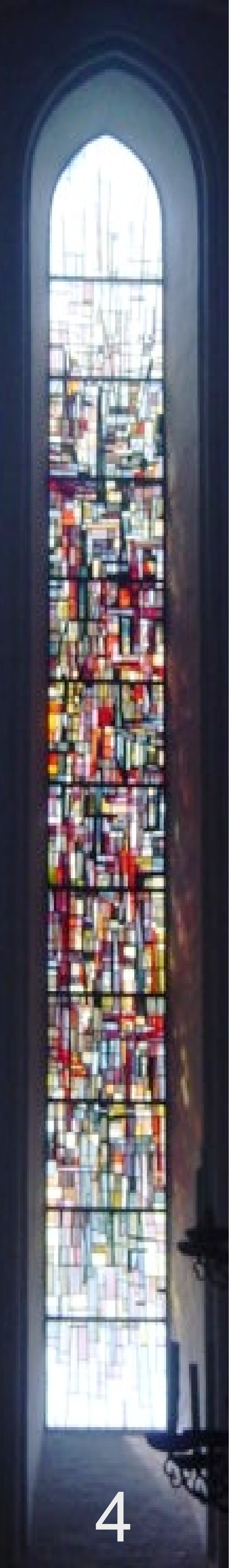
- Know how the order parameter can be incorporated into a thermodynamic theory of phase transitions
- Understand the general form of the free energy function and how it changes through the phase transition
- Derive equations for the temperature-dependence of the order parameter

Lev Landau

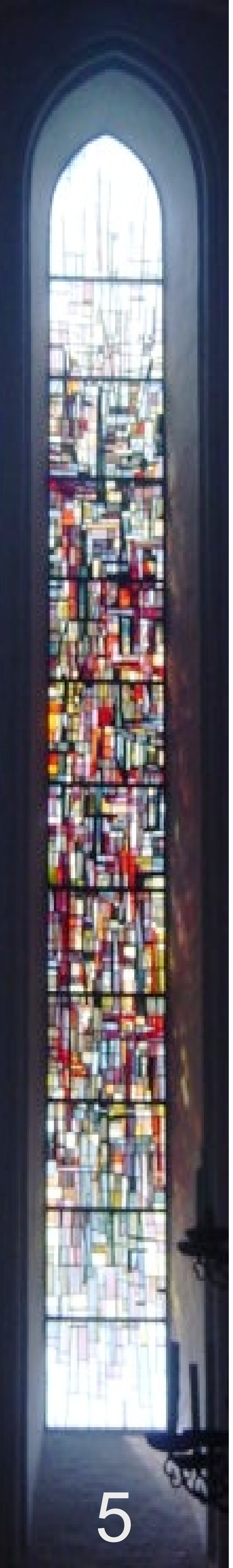
- 1908–1968
- Russian theoretician
- Nobel prize 1962
- First to identify the role of the order parameter and to develop a general theory of phase transitions

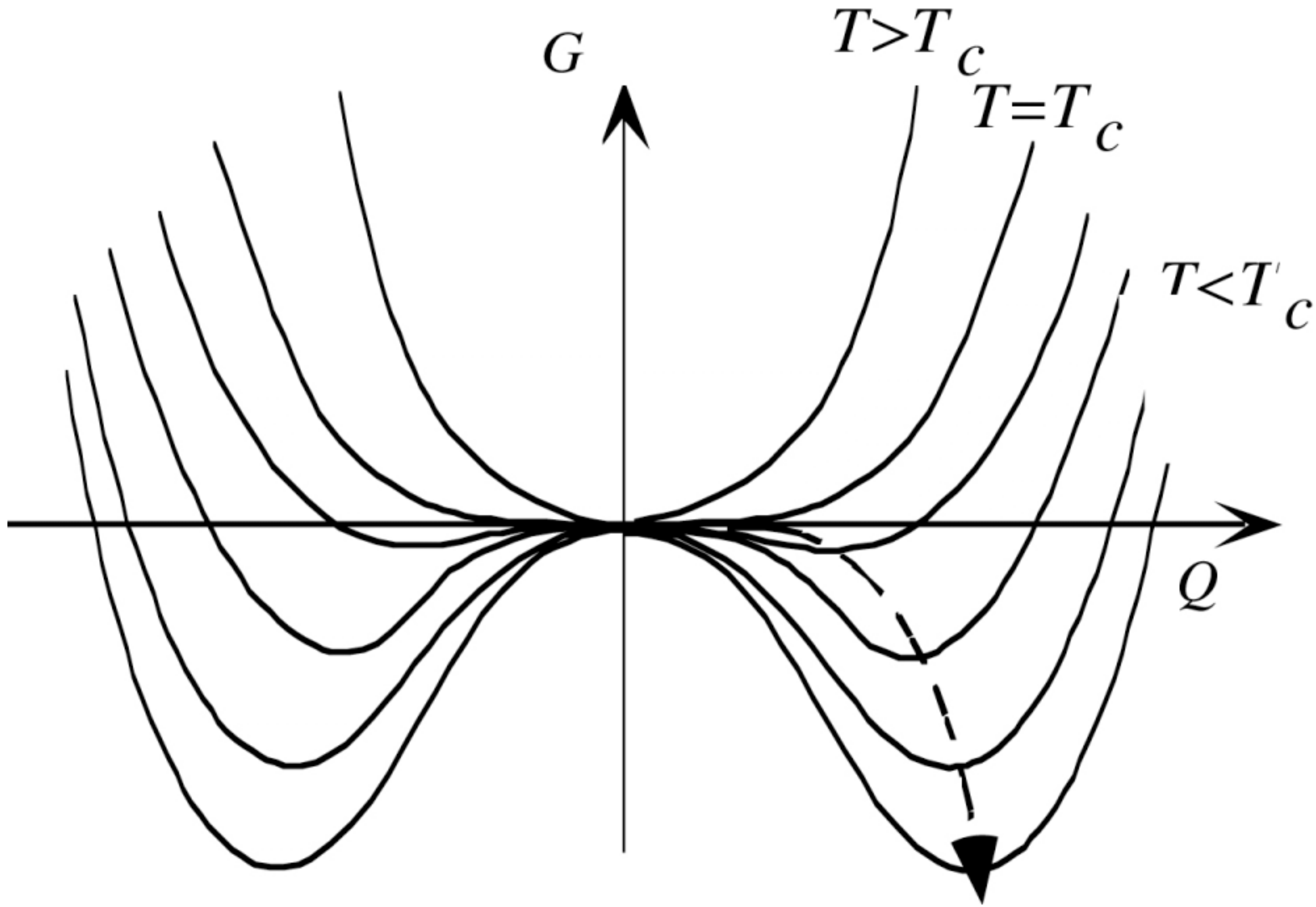
Role of free energy

- The minimum of the free energy defines the equilibrium state
- Free energy varies with temperature; assume that the minimum point also changes with temperature
- Assume we can write the free energy as a function of order parameter

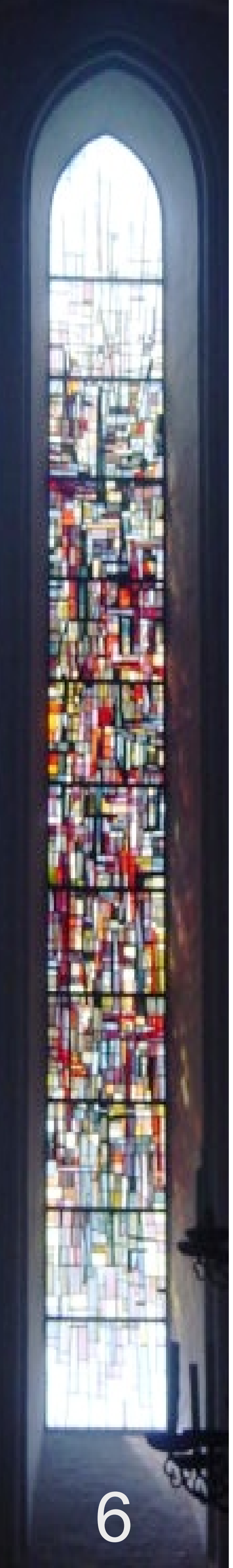


Free energy for a second-order phase transition





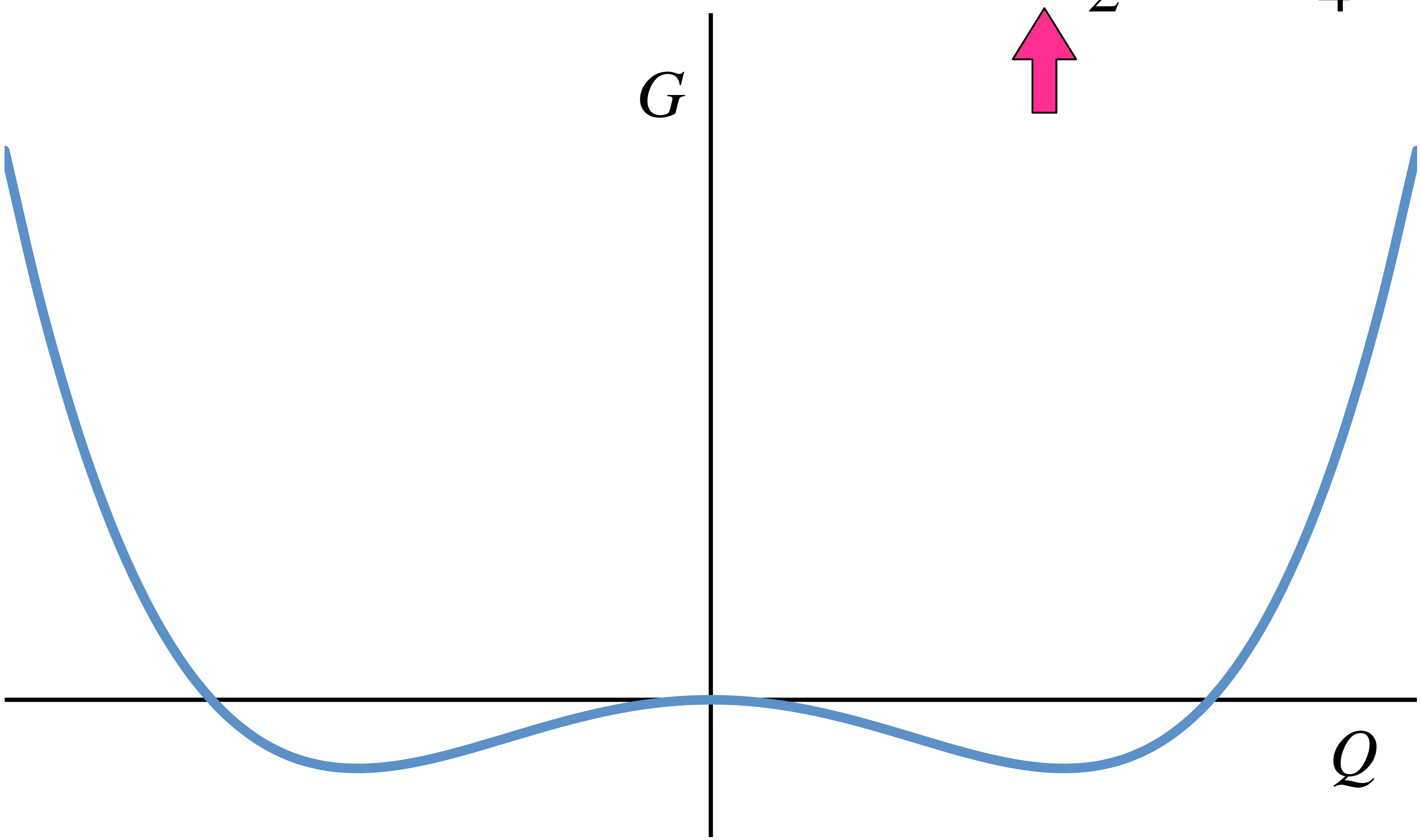
Form of the free energy

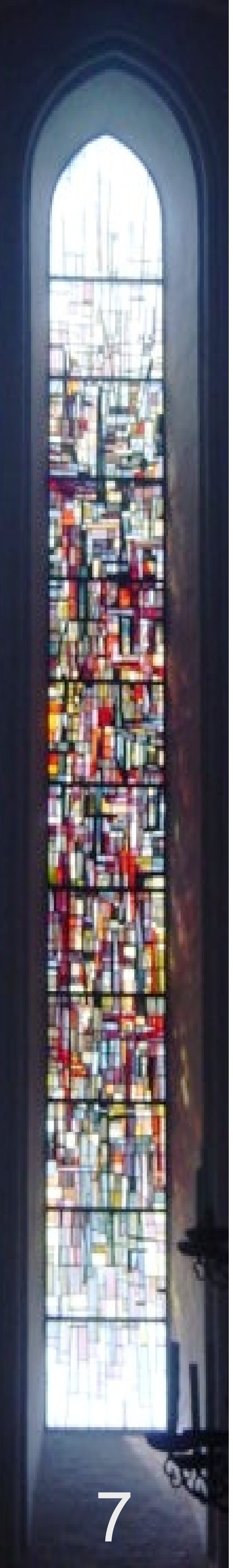


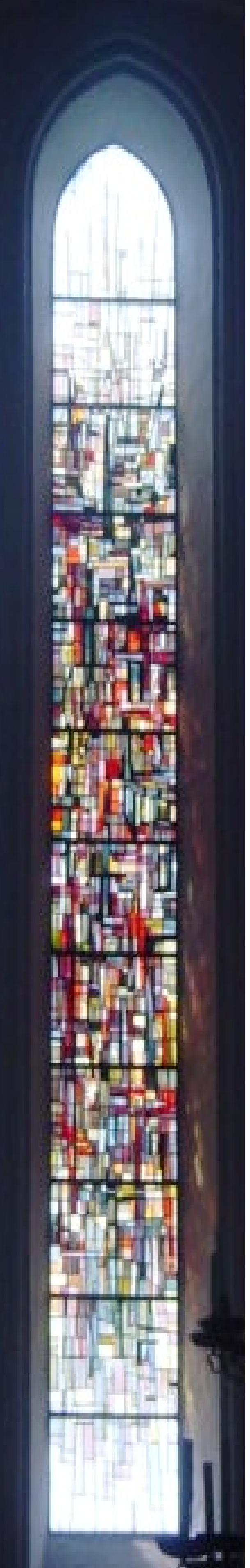
- Assume we can expand G as a power series in Q
- The condition $G(-Q) = G(Q)$ requires that the power series only has even powers of Q
- We will truncate the power series as soon as practically possible

Low temperature

$$G = G_0 - \frac{1}{2}aQ^2 + \frac{1}{4}bQ^4$$

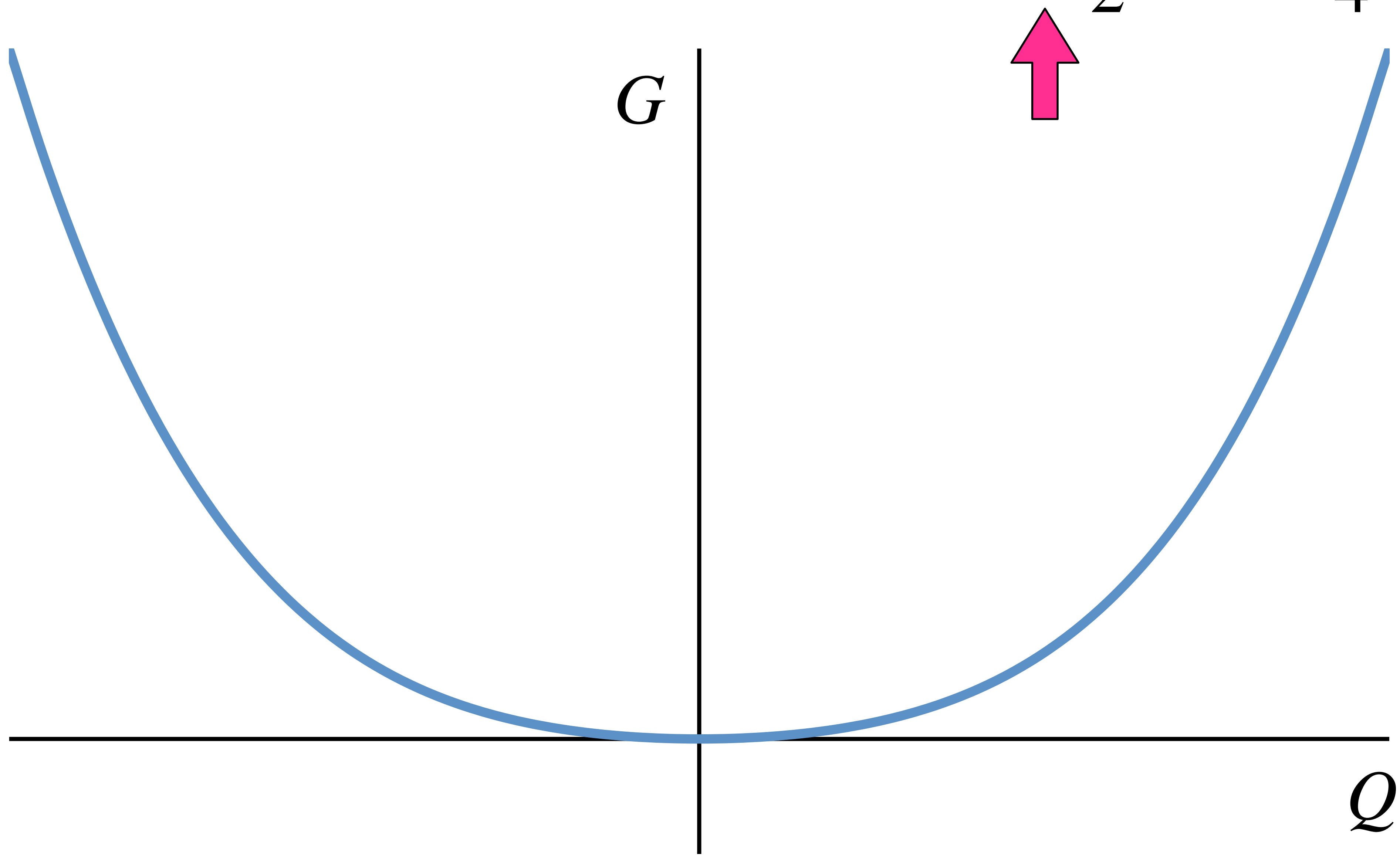






High temperature

$$G = G_0 + \frac{1}{2}aQ^2 + \frac{1}{4}bQ^4$$



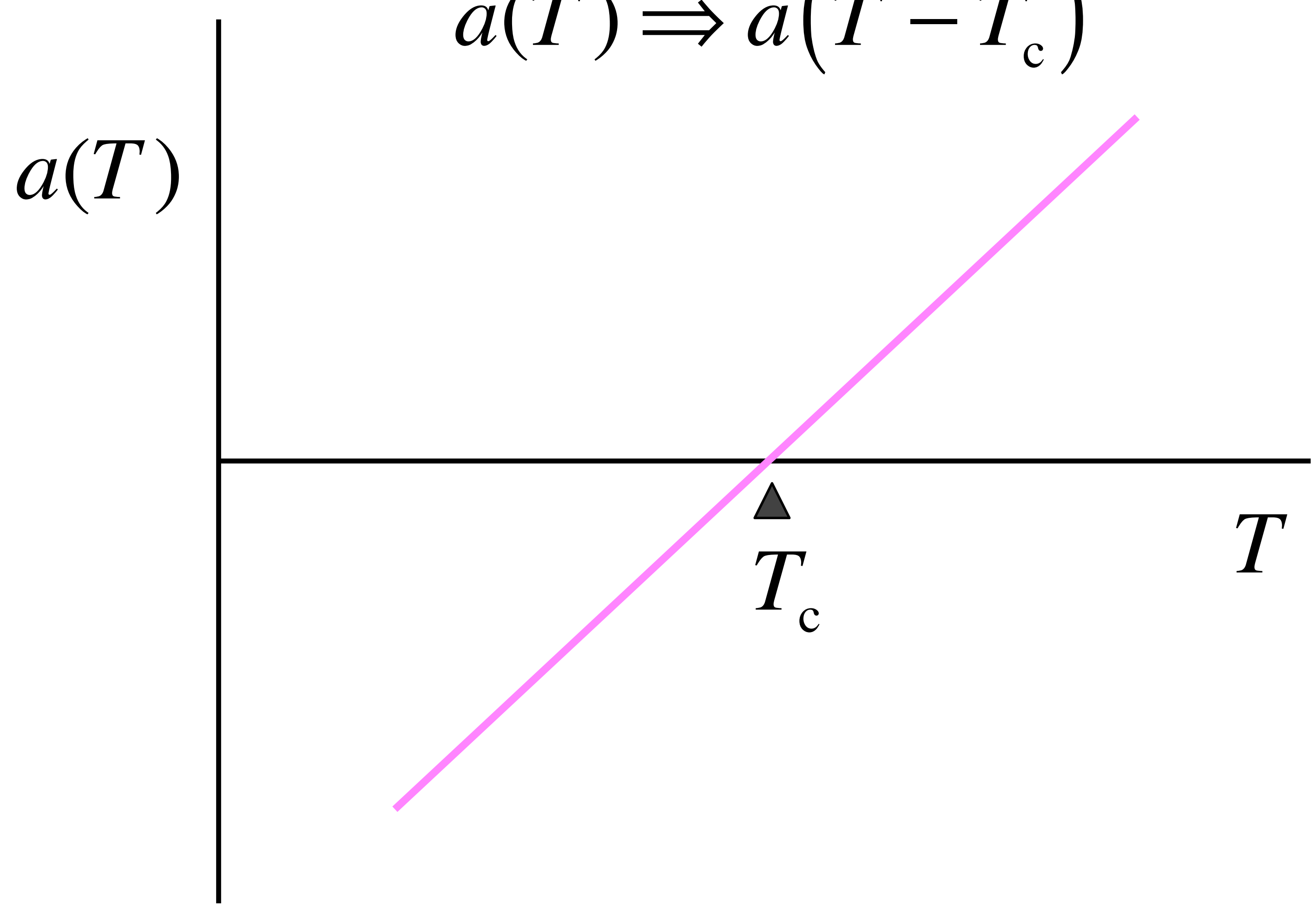
Guess the form of $a(T)$

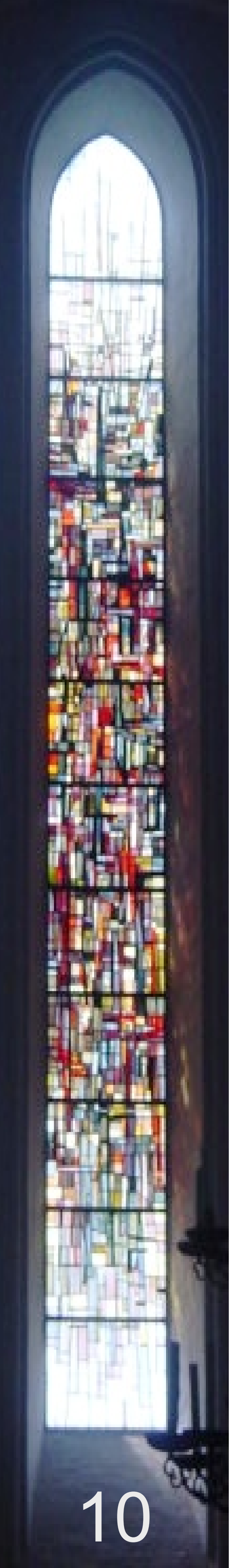
$$G = G_0 + \frac{1}{2}aQ^2 + \frac{1}{4}bQ^4$$

$$a > 0 \text{ for } T > T_c$$

$$a < 0 \text{ for } T < T_c$$

$$a(T) \Rightarrow a\left(T - T_c\right)$$



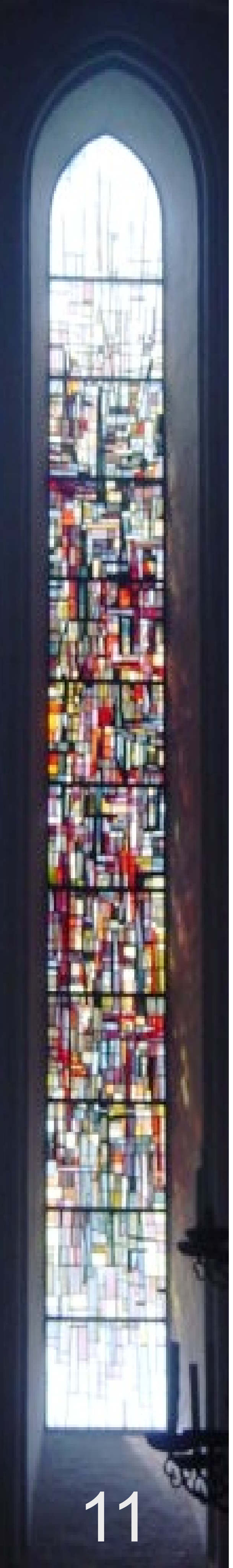


Free energy function

- Final function has the form:

$$G = G_0 + \frac{1}{2}a\left(T - T_c\right)Q^2 + \frac{1}{4}bQ^4$$

- Assume the values of the coefficients are independent of temperature



Extreme points

- Obtain the extreme point of $G(Q)$:

$$G = G_0 + \frac{1}{2}a\left(T - T_\text{c}\right)Q^2 + \frac{1}{4}bQ^4$$

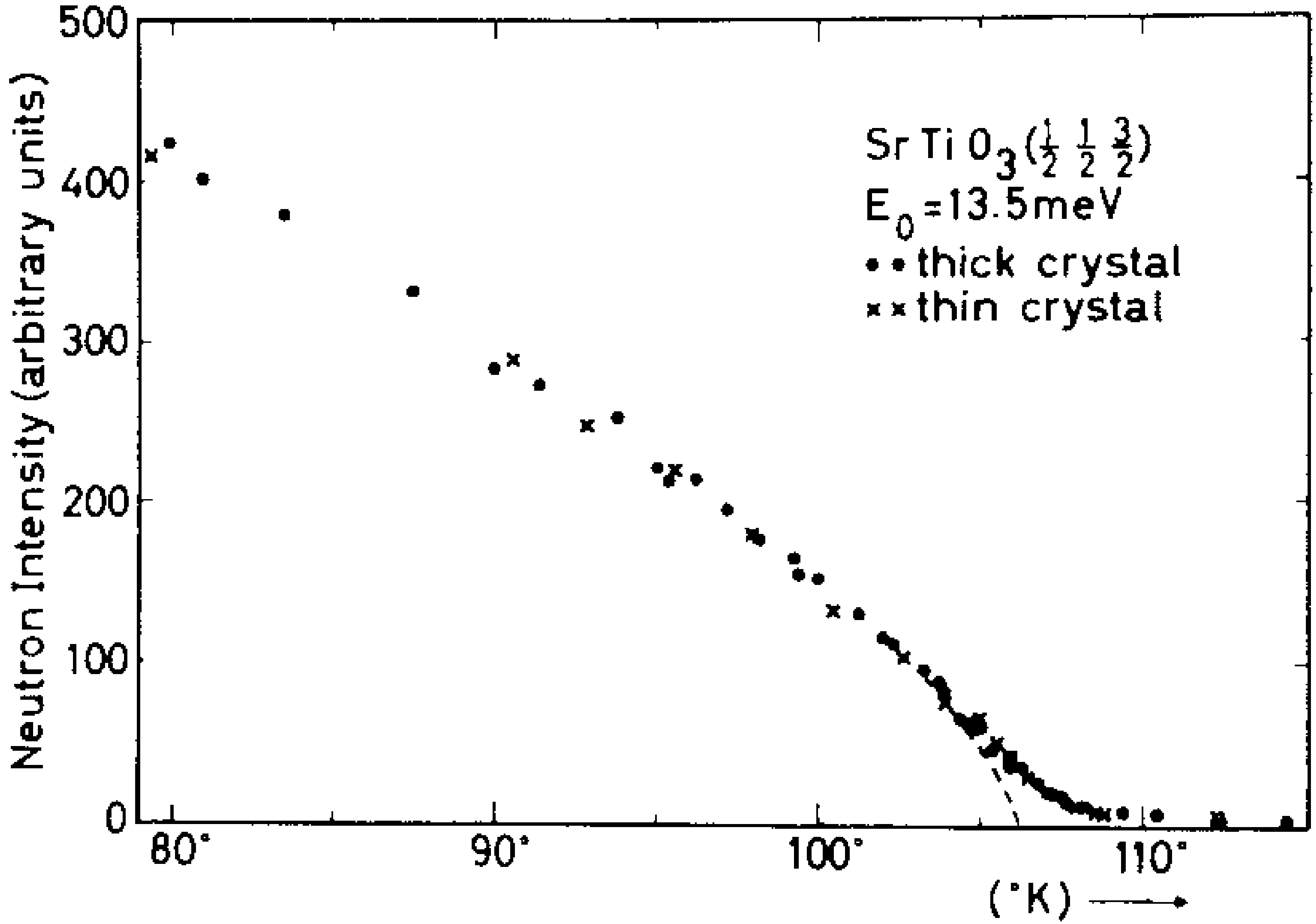
$$\frac{\partial G}{\partial Q} = a\left(T - T_\text{c}\right)Q + bQ^3 = 0$$

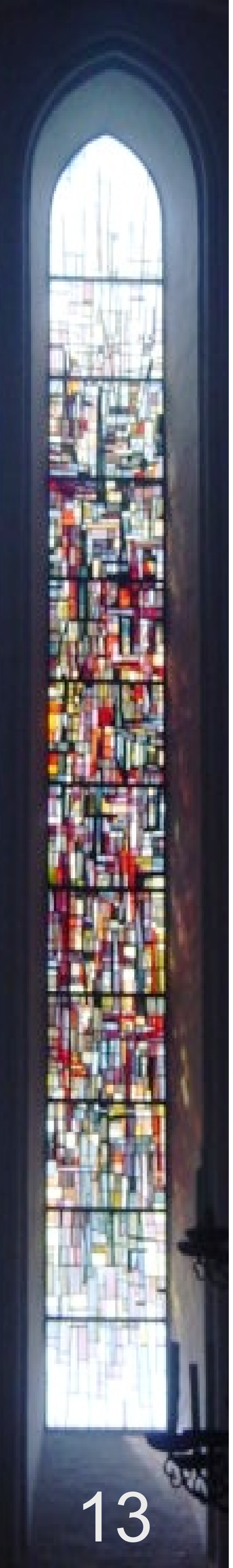
$$\Rightarrow bQ^3 = a\left(T_\text{c} - T\right)Q$$

- Two solutions:

1. $Q = 0$
2. $Q^2 = a\left(T_\text{c} - T\right)/b$

Example of $SrTiO_3$





Thermodynamic interpretation

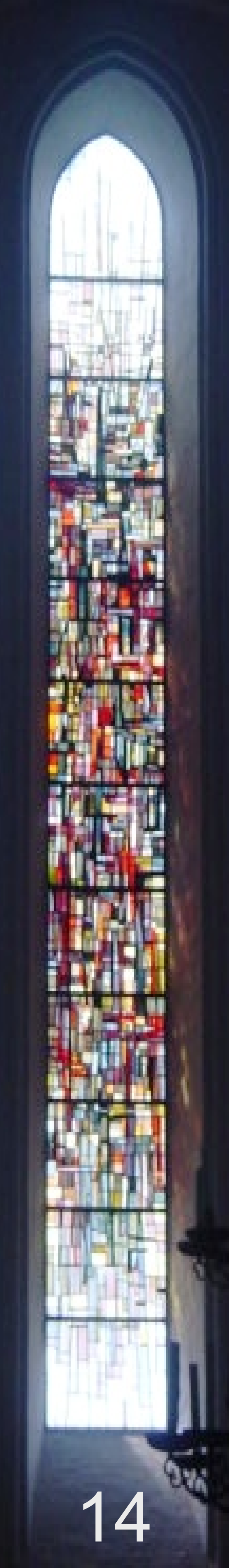
- Separate the free energy into enthalpy and entropy terms

$$G = G_0 + \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{4}bQ^4 = G_0 + \Delta H - T\Delta S$$

$$\Delta H = -\frac{1}{2}aT_cQ^2 + \frac{1}{4}bQ^4$$

$$-T\Delta S = \frac{1}{2}aTQ^2 \quad \Rightarrow \quad \Delta S = -\frac{1}{2}aQ^2$$

- Recall, expansion is around the high-temperature phase

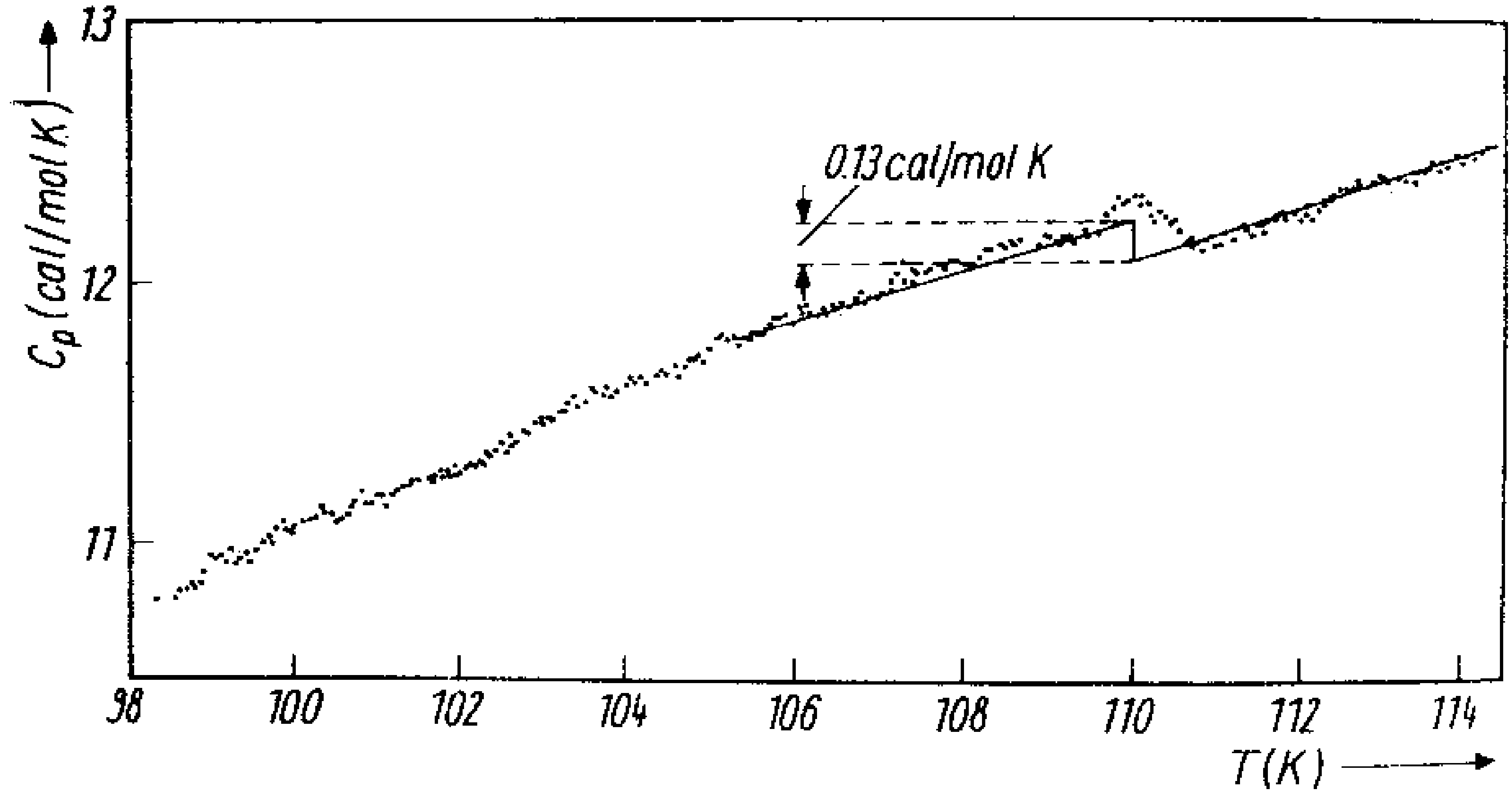


Heat capacity

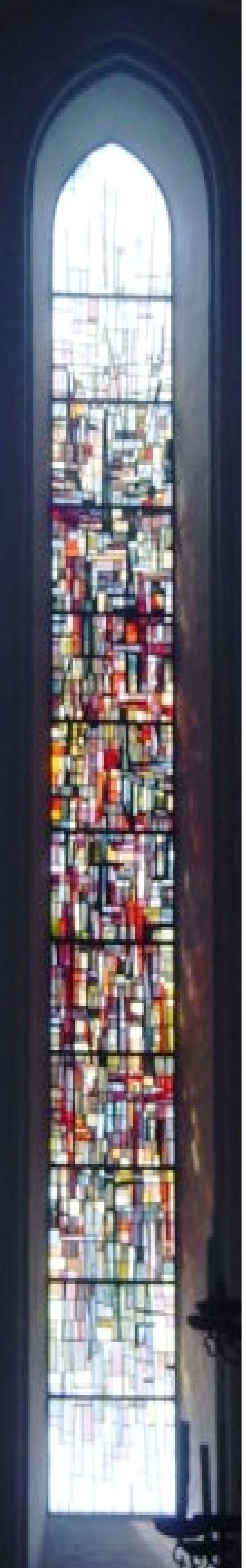
$$\Delta S = -\frac{1}{2} a Q^2 = -\frac{1}{2} a^2 \left(T_\mathrm{c} - T \right) / b$$

$$\Delta C = T \frac{\partial \Delta S}{\partial T} = \begin{cases} 0 & \text{for} \quad T > T_\mathrm{c} \\ \dfrac{a^2}{2b} T & \text{for} \quad T < T_\mathrm{c} \end{cases}$$

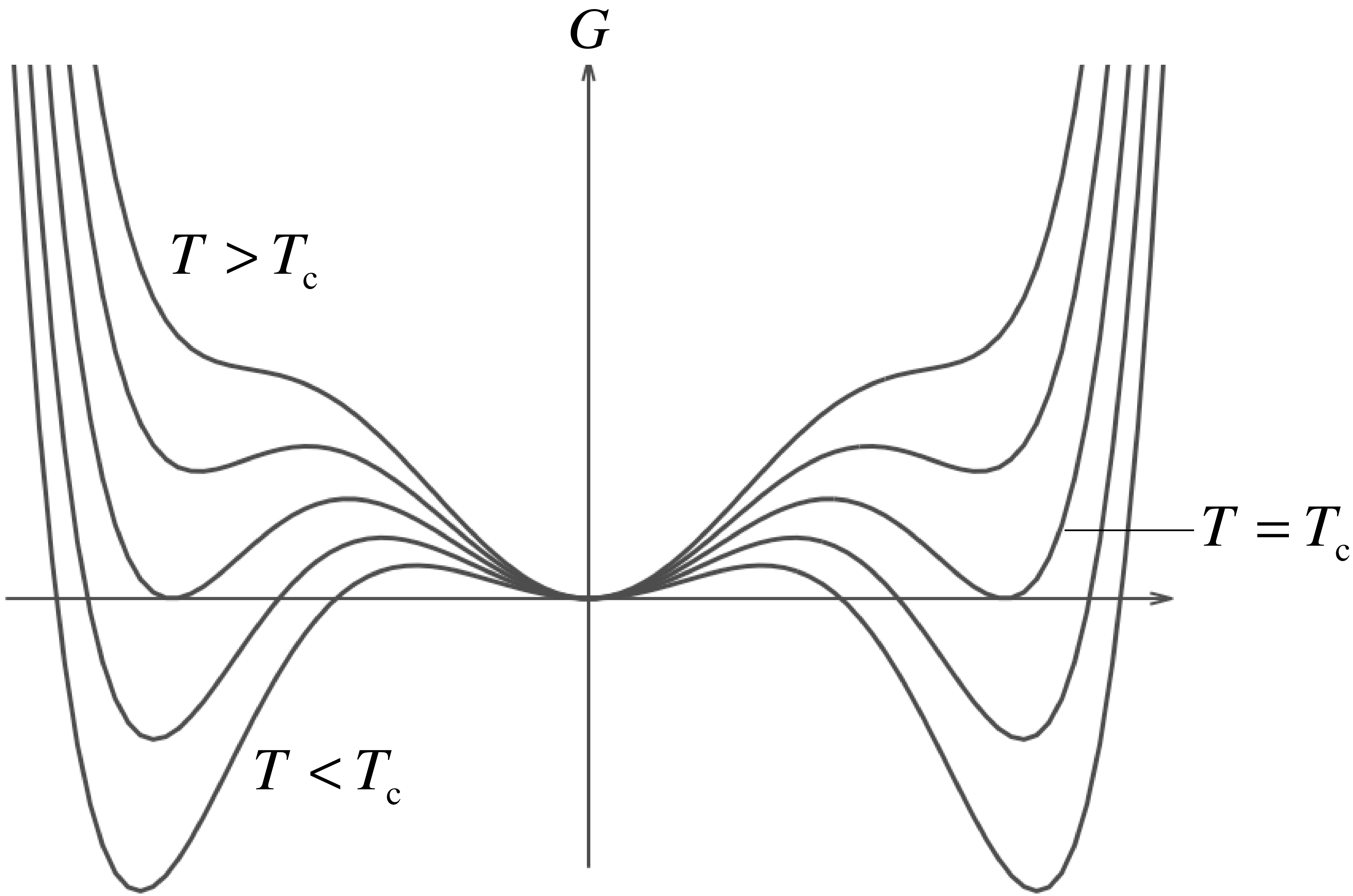
Example of $SrTiO_3$

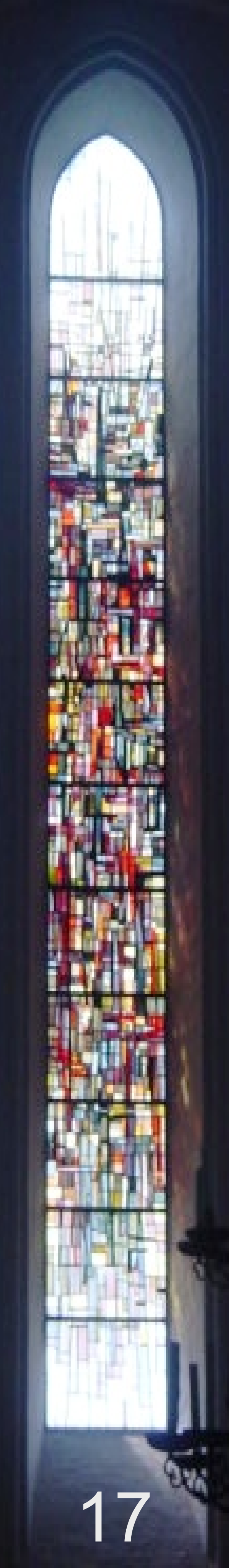


- Small step in heat capacity at the phase transition – hard to measure



Free energy for a first-order phase transition



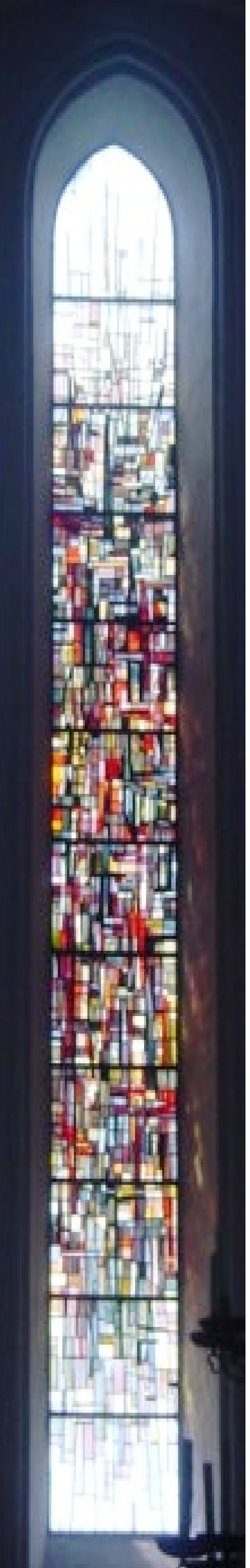


Free energy function

- Needs to be extended to sixth order with negative quartic term

$$G = G_0 + \frac{1}{2}a\left(T - T_0\right)Q^2 - \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6$$

- T_0 is <u>not</u> the transition temperature

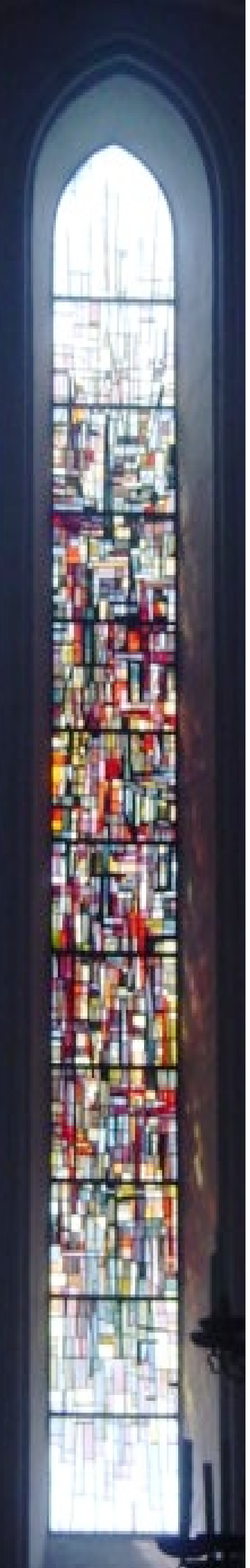


Extreme points

$$G = G_0 + \frac{1}{2}a\left(T - T_0\right)Q^2 - \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6$$

$$\frac{\partial G}{\partial Q} = a\left(T - T_0\right)Q - bQ^3 + cQ^5 = 0$$

$$\Rightarrow Q = 0 \quad \text{or} \quad Q^2 = \frac{b \pm \sqrt{b^2 - 4ac\left(T - T_0\right)}}{2c}$$



Computing T_c

- At $T = T_c$ we have

$$G - G_0 = \frac{1}{2}a\left(T_c - T_0\right)Q^2 - \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6 = 0$$

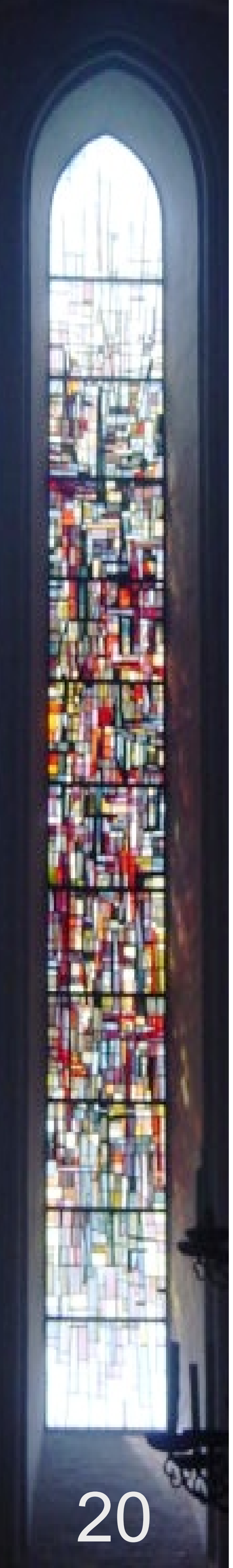
$$\Rightarrow a\left(T_c - T_0\right) - \frac{1}{2}bQ^2 + \frac{1}{3}cQ^4 = 0$$

$$\frac{\partial G}{\partial Q} = a\left(T_c - T_0\right)Q - bQ^3 + cQ^5 = 0$$

$$\Rightarrow a\left(T_c - T_0\right) - bQ^2 + cQ^4 = 0$$

- The jump in the order parameter is

$$\Delta Q^2 = \frac{3b}{4c}$$

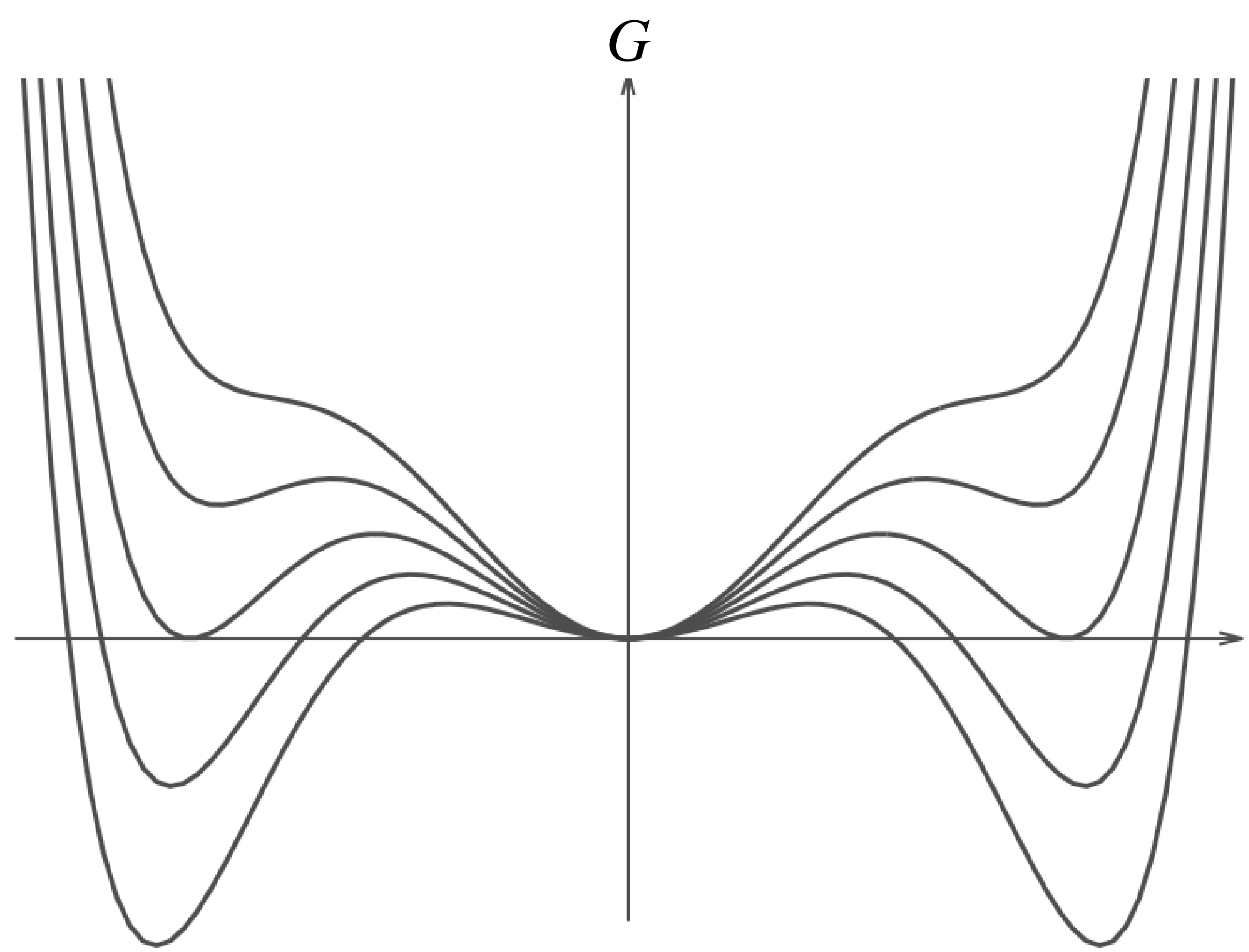


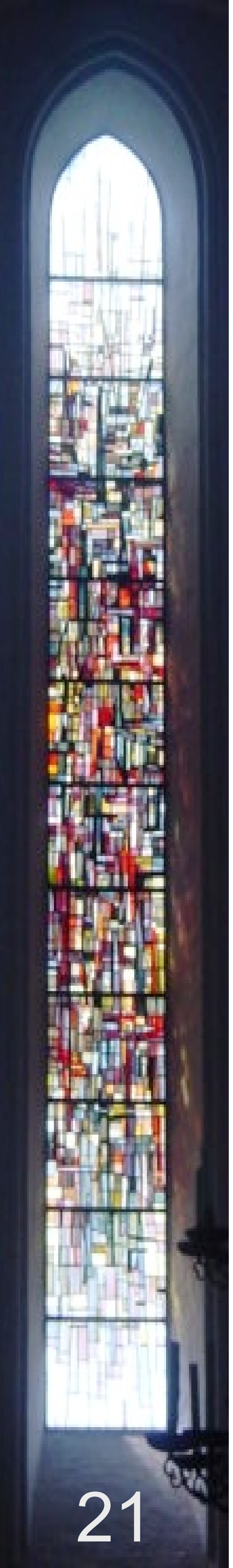
Computing T_c

$$a(T_c - T_0) - bQ^2 + cQ^4 = 0$$

$$\Rightarrow a(T_c - T_0) - b\frac{3b}{4c} + c\left(\frac{3b}{4c}\right)^2 = 0$$

$$T_c = T_0 + \frac{3b^2}{16ac}$$

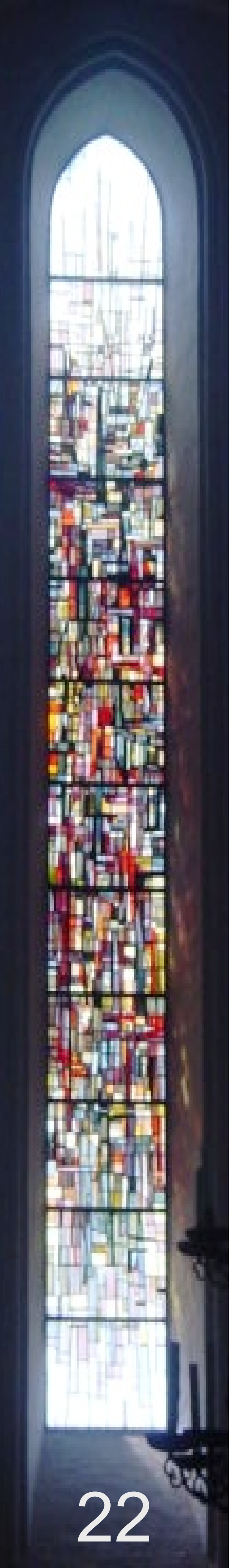




Latent heat at T_c

$$\Delta H = -\frac{1}{2}aT_0Q^2 - \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6$$
$$= -\frac{3abT_\mathrm{c}}{8c} = -\frac{aT_\mathrm{c}}{2}\Delta Q^2$$

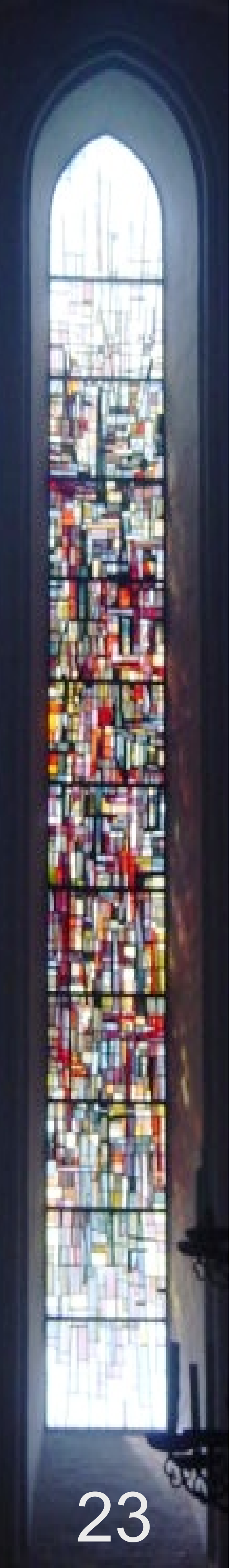
The existence of a latent heat at a first-order phase transition is often said to be the defining feature of a first-order phase transition



Ehrenfest categorisation

Idea is to categorise a phase transition by the first differential that is not zero

- First order: $$\left.\frac{\partial G}{\partial T}\right|_{T=T_\mathrm{c}} \neq 0 \Rightarrow \Delta S, \Delta H \neq 0$$
- Second order: $$\left.\frac{\partial^2 G}{\partial T^2}\right|_{T=T_\mathrm{c}} \neq 0 \Rightarrow \Delta C \neq 0$$
- Third order: $$\left.\frac{\partial^3 G}{\partial T^3}\right|_{T=T_\mathrm{c}} \neq 0$$



Tricritical phase transitions

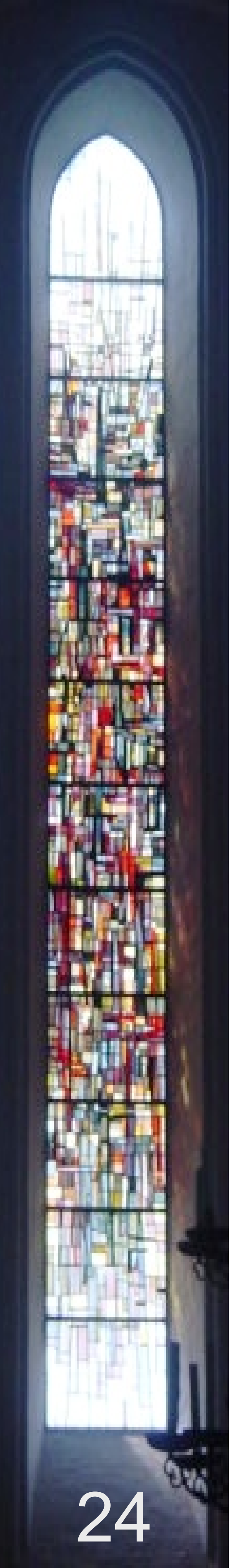
$$G = G_0 + \frac{1}{2}a\left(T - T_0\right)Q^2 + \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6$$

$b > 0$: Second-order

$b < 0$: First-order

$b \sim 0$: Tricritical

$$G = G_0 + \frac{1}{2}a\left(T - T_0\right)Q^2 + \frac{1}{6}cQ^6$$



Order parameter

- Order parameter

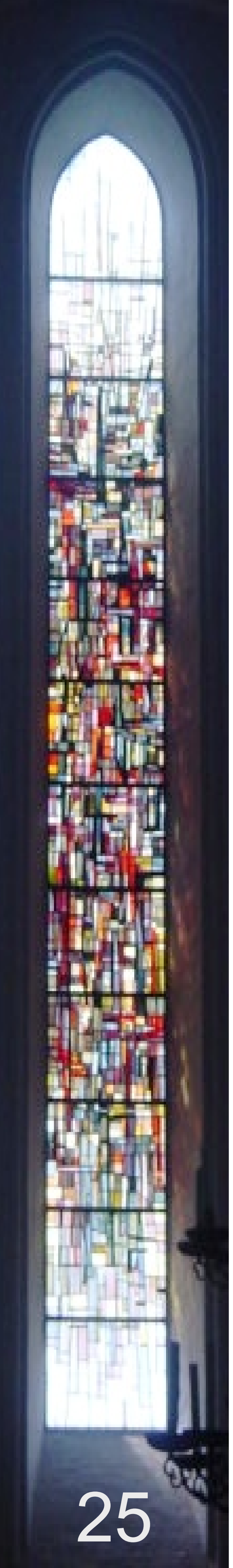
$$G = G_0 + \frac{1}{2}a\left(T - T_c\right)Q^2 + \frac{1}{6}cQ^6$$

$$\frac{\partial G}{\partial Q} = a\left(T - T_c\right)Q + cQ^5 = 0$$

$$\Rightarrow \quad Q = \left(\frac{a}{c}\left(T_c - T\right)\right)^{1/4}$$

- Entropy

$$\Delta S = -\frac{1}{2}aQ^2 = -\frac{1}{2}\left(\frac{a^3}{c}\left(T_c - T\right)\right)^{1/2}$$

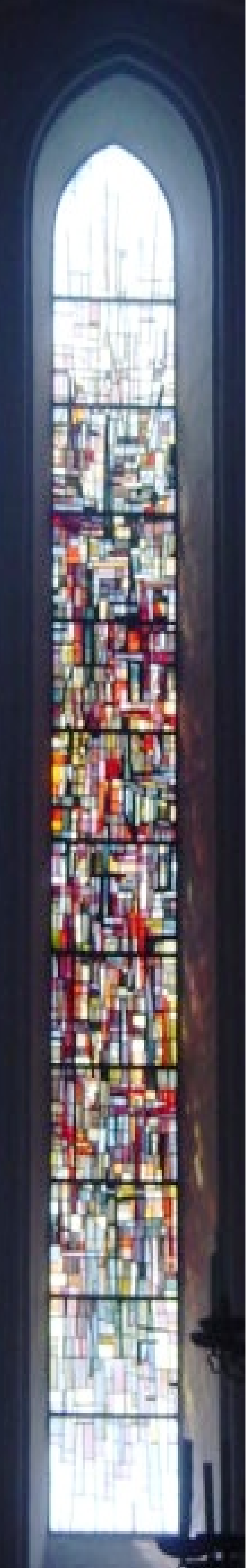


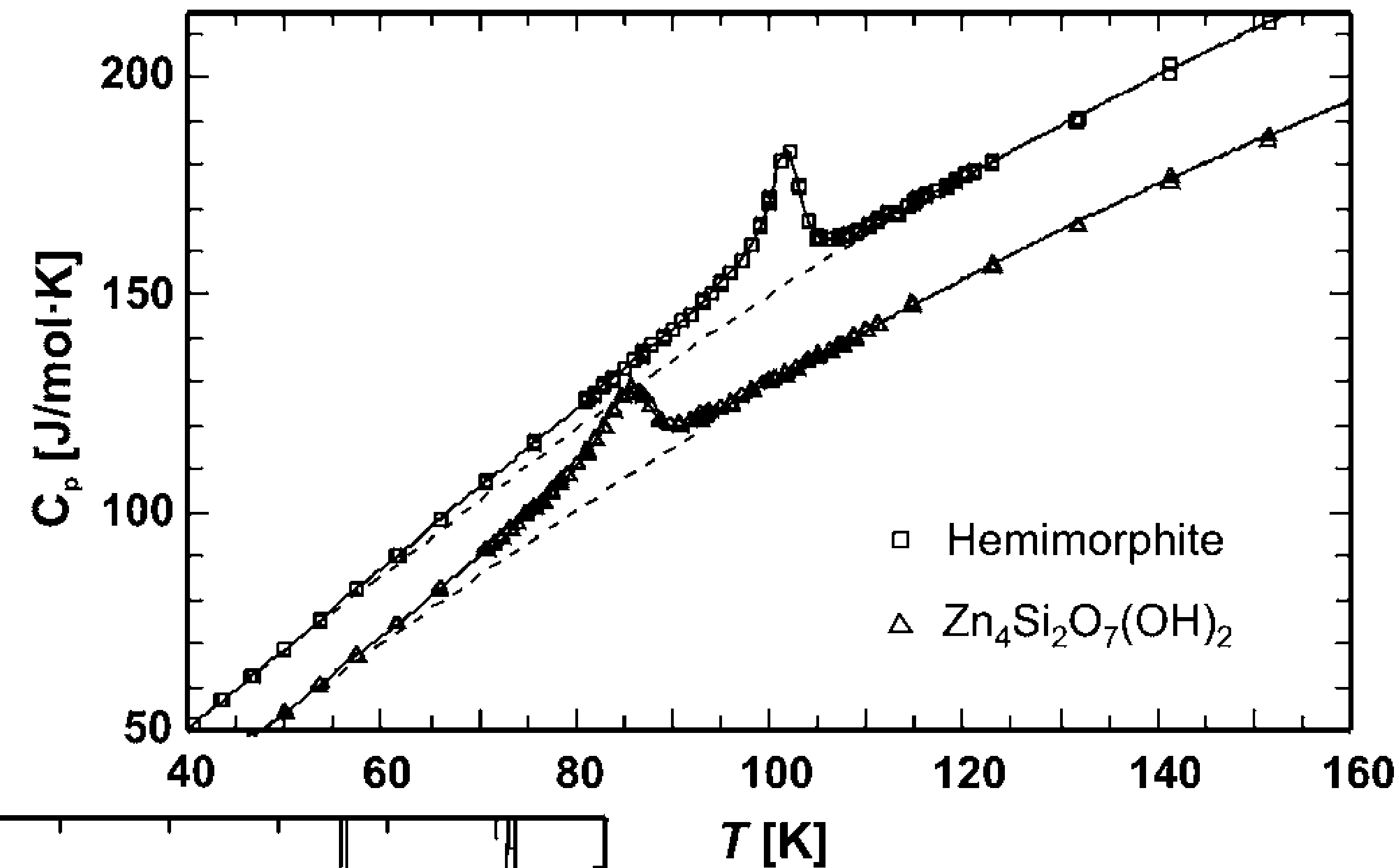
Heat capacity

$$\Delta S = -\frac{1}{2} a Q^2 = -\frac{1}{2}\left(\frac{a^3}{c}\left(T_\mathrm{c} - T\right)\right)^{1/2}$$

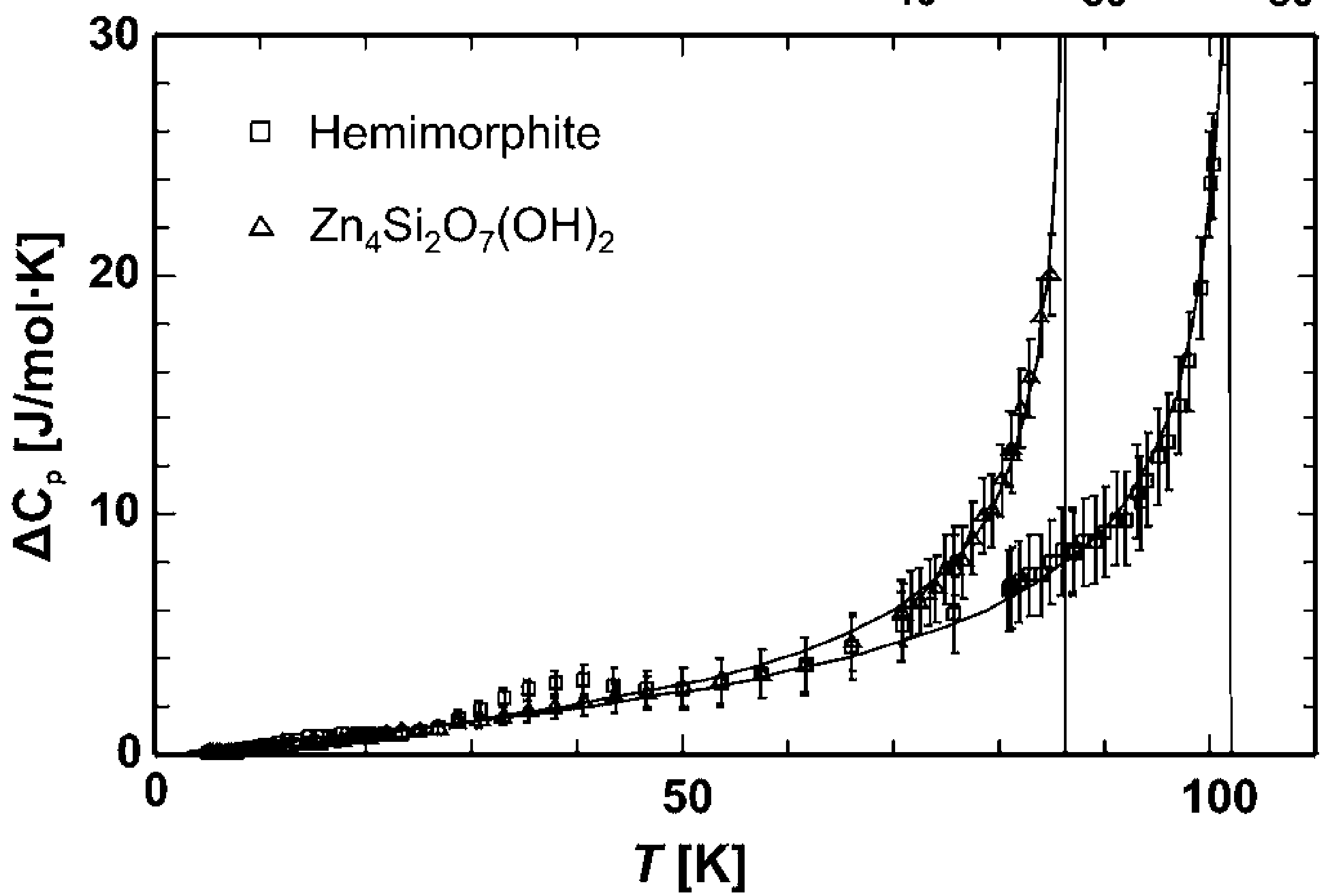
$$\Delta C = T\frac{\partial \Delta S}{\partial T} = \frac{1}{4}\sqrt{\frac{a^3}{c}} T\left(T_\mathrm{c} - T\right)^{-1/2}$$

Example

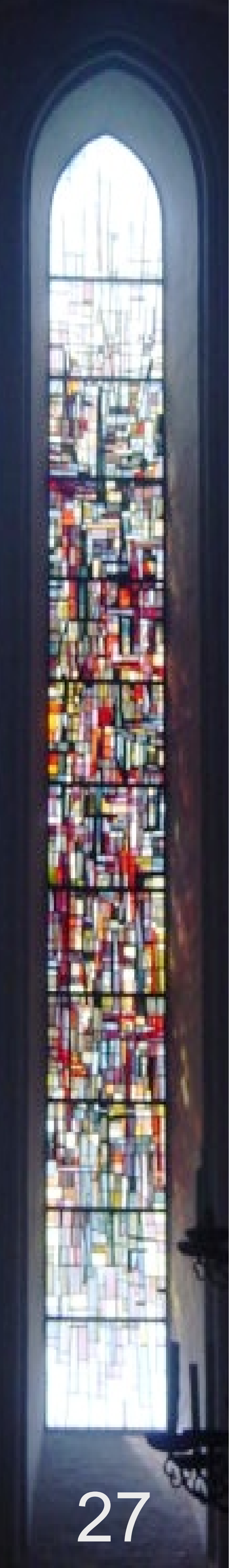




C_p [J/mol·K]
200
150
100
50
40
60
80
100
120
140
160
T [K]
Hemimorphite
$Zn_4Si_2O_7(OH)_2$



ΔC_p [J/mol·K]
30
20
10
0
0
50
100
T [K]
Hemimorphite
$Zn_4Si_2O_7(OH)_2$



Summary

- Described a free energy function that describes first and second-order phase transitions
- Seen how minimisation of the free energy leads to temperature-dependence of the order parameter
- Computed properties such as heat capacity associated with the phase transition