4.8 Quantum phase transitions

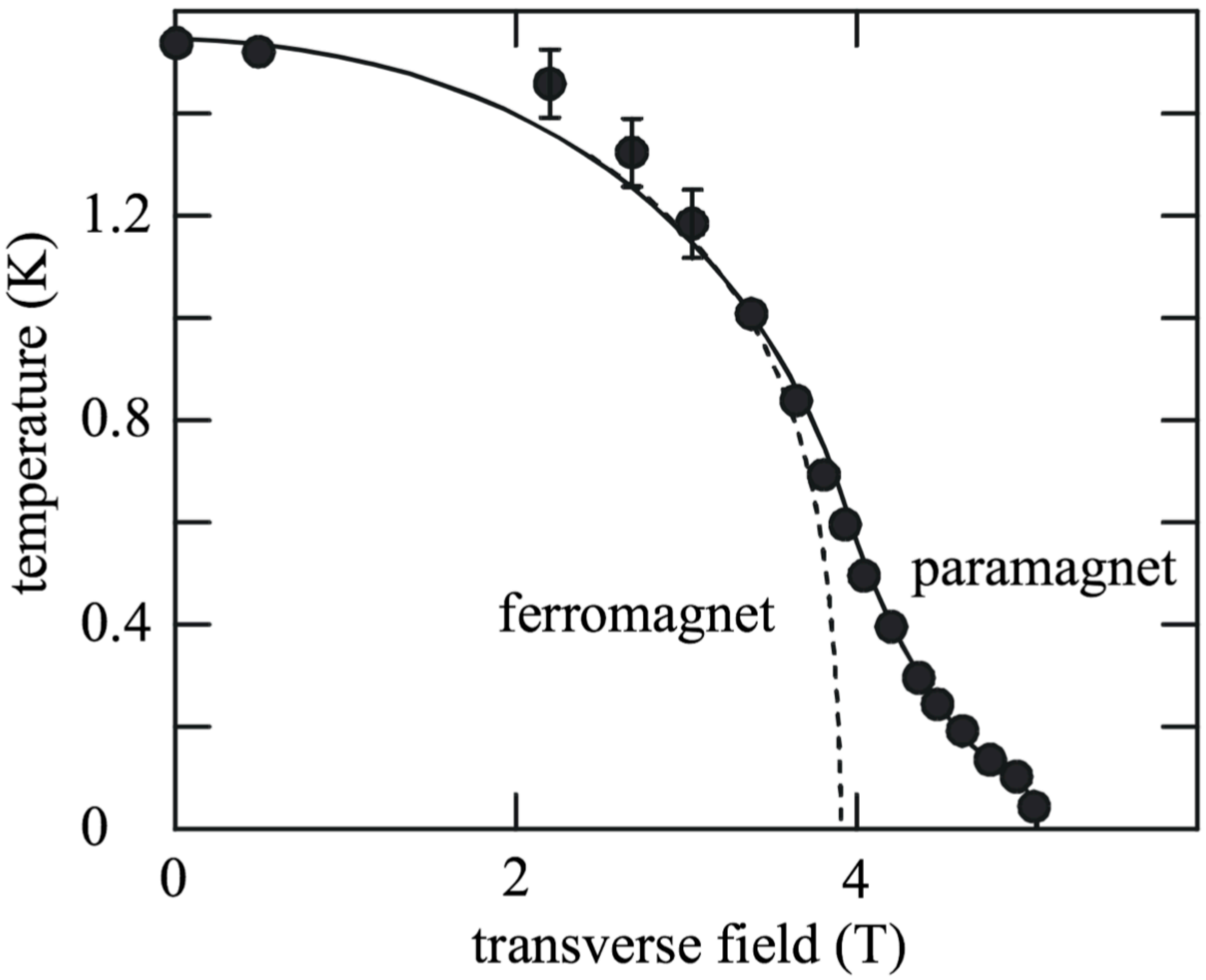
- "Regular" phase transition driven by *thermal fluctuations*
  - — These fluctuations diverge at the critical point
  - — Control the passage through the transition by varying the temperature
- "Quantum" phase transition driven by *quantum fluctuations*
  - — This is a transition at $T = 0$
  - — Pass through the transition by varying a *control parameter* (eg pressure, conc)
  - — Quantum fluctuations diverge at the Quantum Critical Point (2nd order)
    - — Transition between different ground states

4.8.2 Transverse Ising model

- At $B = 0$ have a conventional CP with a $T_c \sim 1.55\,\mathrm{K}$.
- At $T = 0$ have a QCP with a $B_c \sim 5\,\mathrm{T}$.
- This is an Ising system: $\mathscr{H}_\mathrm{I} \sim \sum S_z^i S_z^j$
- Control parameter is a *transverse* field B_x

$$\mathscr{H} = -2\hbar J \sum_{ij} S_z^i S_z^j - \gamma \hbar B_x \sum_i S_x^i$$

LiHoF$_4$



D. Bitko, T. Rosenbaum, and G. Aeppli, Physical Review Letters, vol. 77, pp. 940–943, 1996.

- At $B_x = 0$ have conventional Ising model
  — interaction favours parallel spins — ground state is a ferromagnet

- Application of transverse field induces transitions between $\uparrow$ and $\downarrow$ spins
  — because $[\mathscr{H}, S_z^i] \neq 0$. (Whereas $[\mathscr{H}_{\mathrm{I}}, S_z^i] = 0$.)

- So transverse field $\Longrightarrow$ fluctuations in M_z of the Ising ordered phase

- Sufficiently large B_x will kill M_z — will destroy the Ising ground state.

- So B_x will cause a transition to a different ground state.

- B_x is the control parameter.

- The ground state is changed by the control parameter.

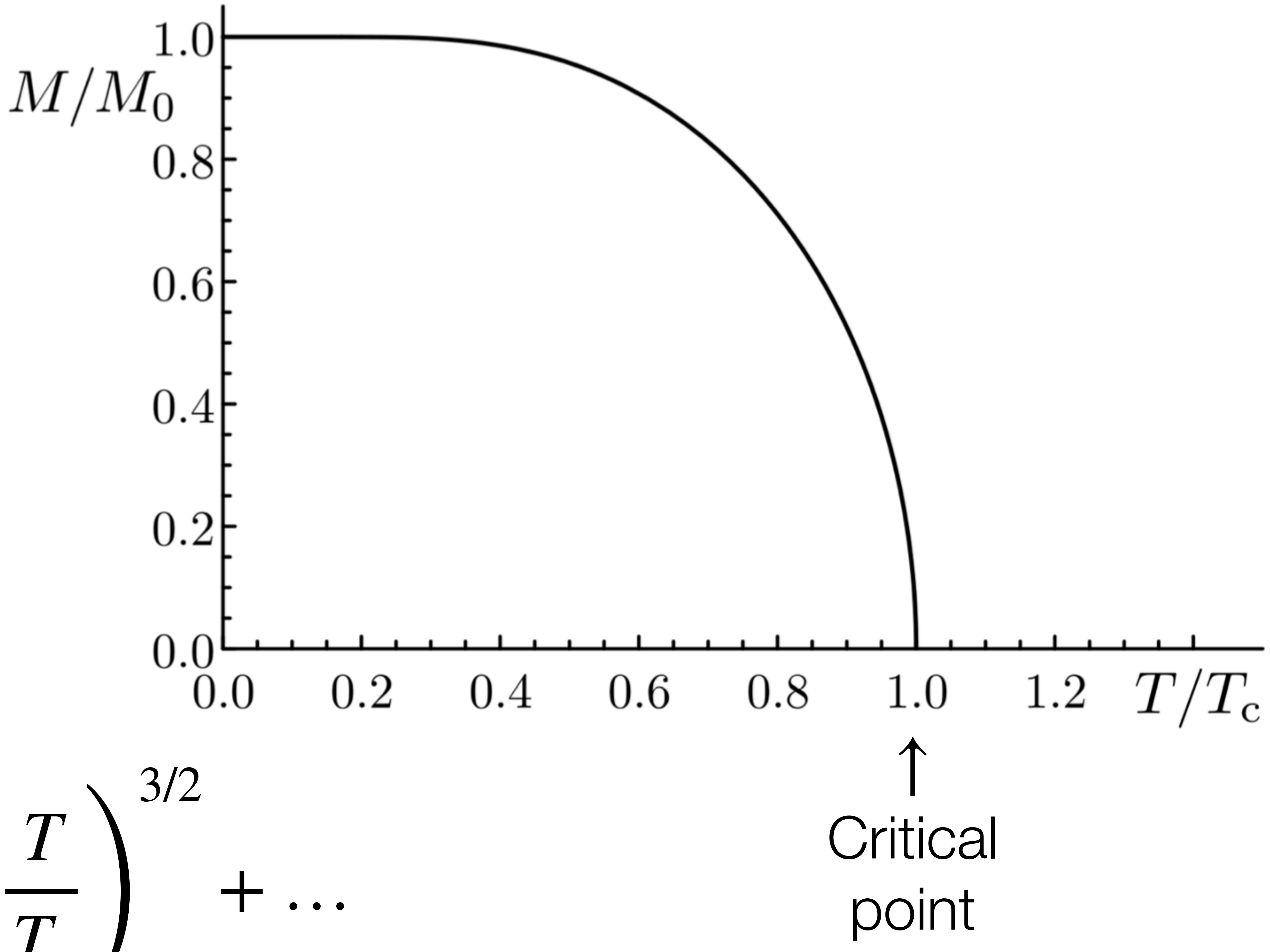
4.8.3. Recap of mean field Ising model

- Free spins $$\frac{M}{M_0} = \tanh\left(\frac{M_0 B}{NkT}\right) \qquad (\mathbf{M} \parallel \mathbf{B})$$
- Weiss local field $$\mathbf{b} = \lambda M_z \hat{\mathbf{z}} \qquad (\mathbf{b} \parallel \mathbf{z} : \text{comes from } S_z^i \langle S_z^j \rangle)$$
- Spontaneous magnetisation $$\frac{M_z}{M_0} = \tanh\left(\frac{M_z}{M_0}\frac{T_c}{T}\right) \text{ where } T_c = \frac{\lambda M_0^2}{Nk}$$
- "Solution": $$\frac{T}{T_c} = \frac{2M_z/M_0}{\ln(1 + M_z/M_0) - \ln(1 + M_z/M_0)}$$

Conventional Ising model

- Solution

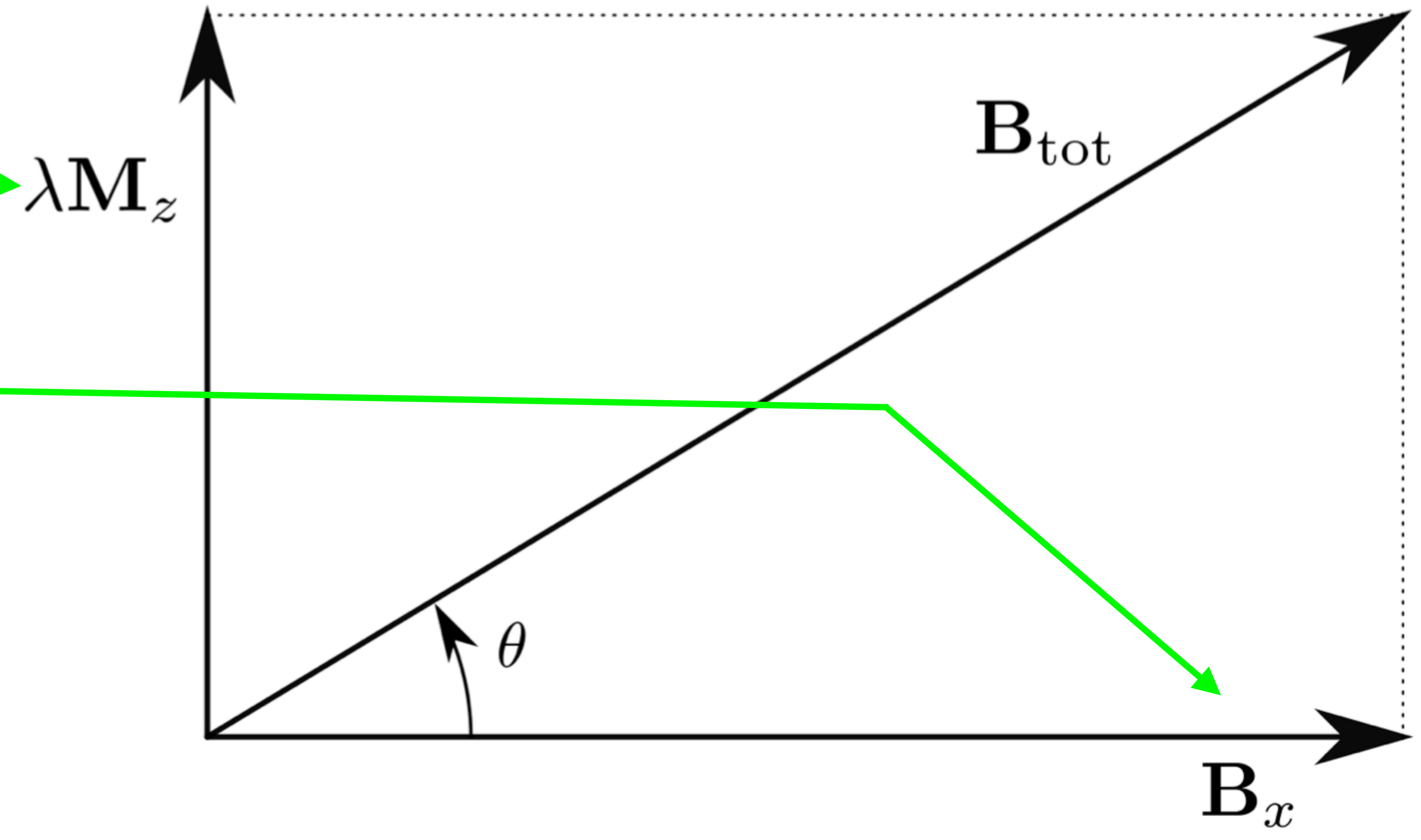
$$\frac{T}{T_{\rm c}} = \frac{2M_z/M_0}{\ln(1 + M_z/M_0) - \ln(1 + M_z/M_0)}$$



$$\frac{M_z}{M_0} = \sqrt{3}\left(1 - \frac{T}{T_{\rm c}}\right)^{1/2} + \frac{2}{5}\sqrt{3}\left(1 - \frac{T}{T_{\rm c}}\right)^{3/2} + \dots$$

4.8.4 Application of a transverse field

- Ising mean field: $\mathbf{b} = \lambda M_z \hat{\mathbf{z}}$
- Applied (transverse) field: $\mathbf{B} = B_x \hat{\mathbf{x}}$



- Total field: magnitude $$B_{\text{tot}} = \sqrt{B_x^2 + \lambda^2 M_z^2}$$

direction $$\sin\theta = \frac{\lambda M_z}{\sqrt{B_x^2 + \lambda^2 M_z^2}}$$

Mean field recipe says $M = M_0 \tanh\left(\frac{M_0 B_{\mathrm{tot}}}{NkT}\right)$

pointing *parallel* to the (total) field.

- We want the magnetisation pointing in the z direction: $M_z = M \sin\theta$

$$M_z = \frac{\lambda M_z}{\sqrt{B_x^2 + \lambda^2 M_z^2}} M_0 \tanh\left(\frac{M_0}{N}\frac{\sqrt{B_x^2 + \lambda^2 M_z^2}}{kT}\right)$$

$$M_z = \frac{\lambda M_z}{\sqrt{B_x^2 + \lambda^2 M_z^2}} M_0 \tanh\left(\frac{M_0}{N} \frac{\sqrt{B_x^2 + \lambda^2 M_z^2}}{kT}\right)$$

- Reduced (dimensionless) variables

$$b_x = B_x/\lambda M_0, \quad m_z = M_z/M_0, \quad t = T/T_\mathrm{c}$$

- Then m_z satisfies the *implicit* equation

$$\sqrt{b_x^2 + m_z^2} = \tanh \frac{\sqrt{b_x^2 + m_z^2}}{t}$$

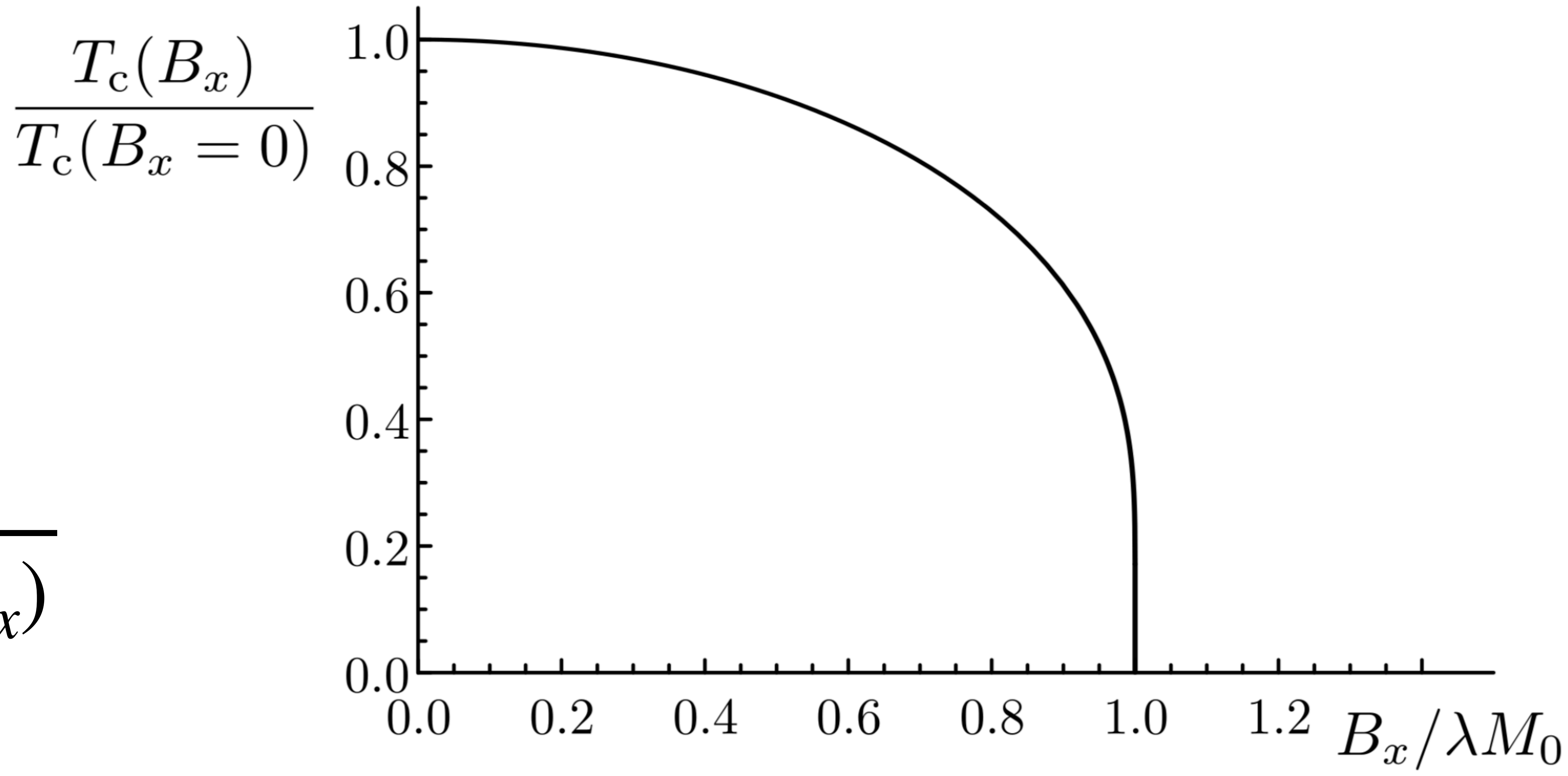
4.8.5 Transition temperature

$$\sqrt{b_x^2 + m_z^2} = \tanh \frac{\sqrt{b_x^2 + m_z^2}}{t}$$

- Transition occurs when $m_z \to 0$.
- Transition temperature will be a function of transverse field: $T_\mathrm{c} = T_\mathrm{c}(B_\mathrm{x})$

$$t_\mathrm{c}(b_x) = \frac{2b_x}{\ln(1+b_x) - \ln(1-b_x)}$$

$$\frac{T_\mathrm{c}\left(B_x\right)}{T_\mathrm{c}\left(B_x = 0\right)} = \frac{2B_x/\lambda M_0}{\ln(\lambda M_0 + B_x) - \ln(\lambda M_0 - B_x)}$$

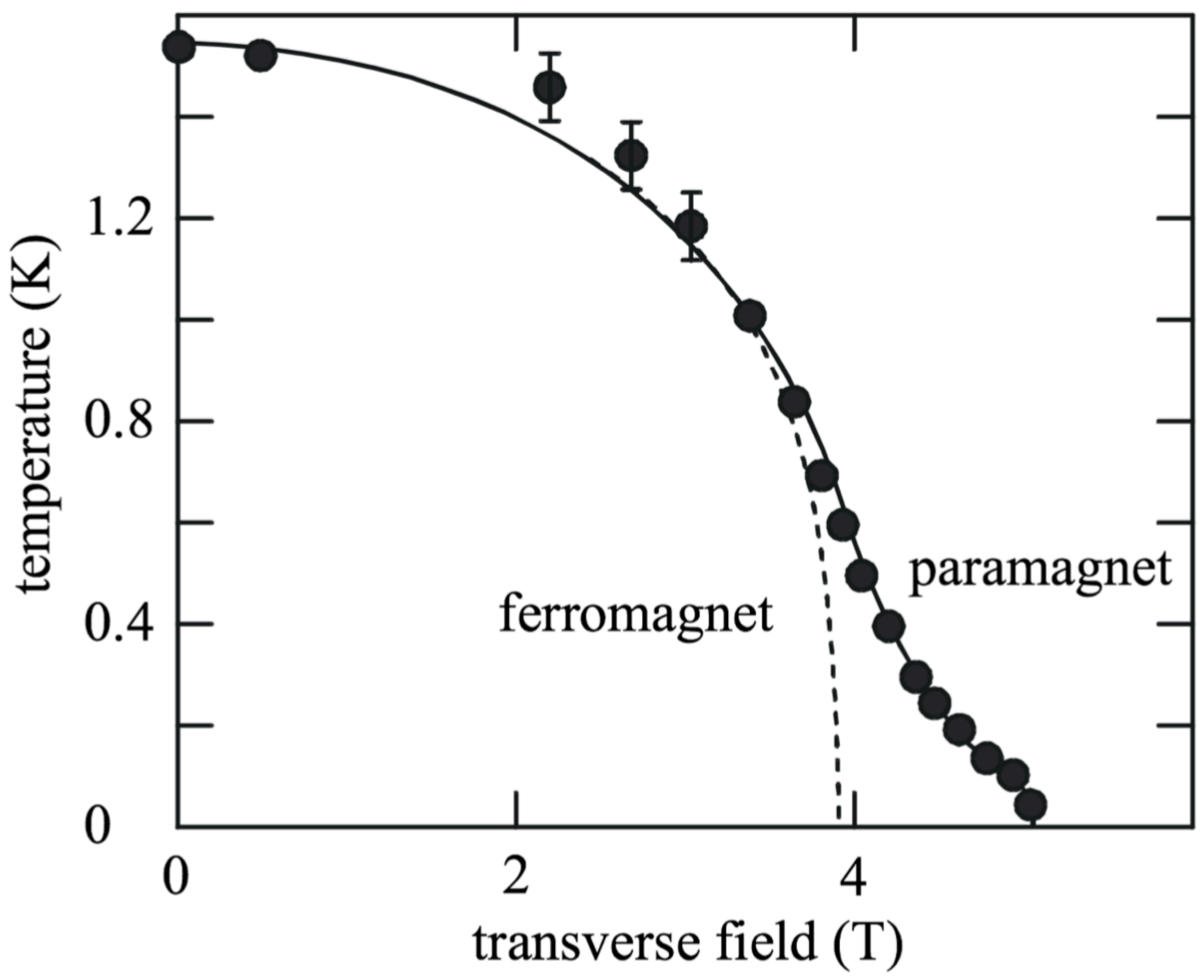


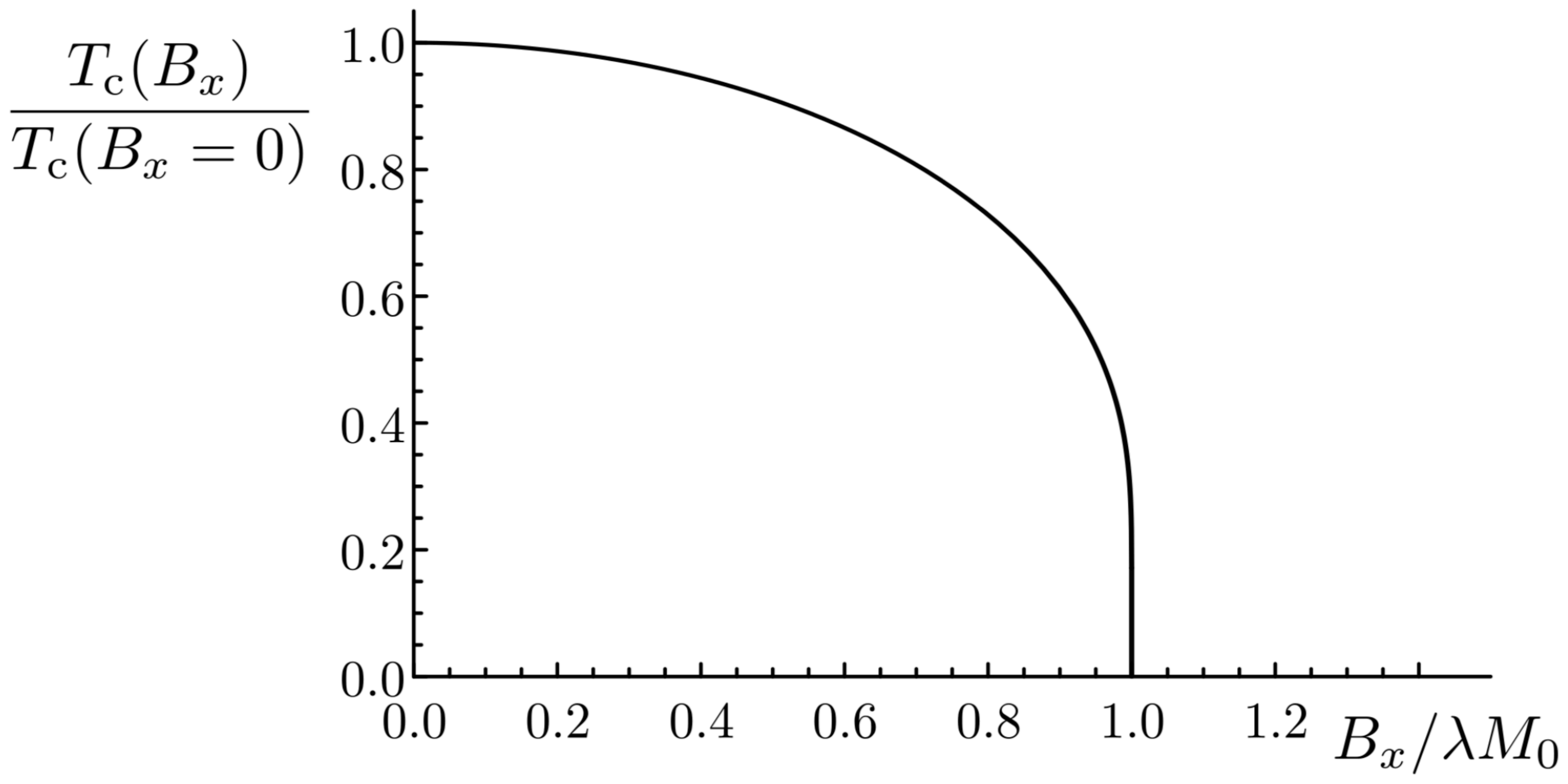
$$\frac{T_c(B_x)}{T_c(B_x = 0)} = \frac{2B_x/\lambda M_0}{\ln(\lambda M_0 + B_x) - \ln(\lambda M_0 - B_x)}$$

Classical ($b_x = 0$) find $m_z = \sqrt{3}(1-t)^{1/2}$

Quantum ($t = 0$) find $m_z = \sqrt{2}(1-b_x)^{1/2}$

Comparison with experiment





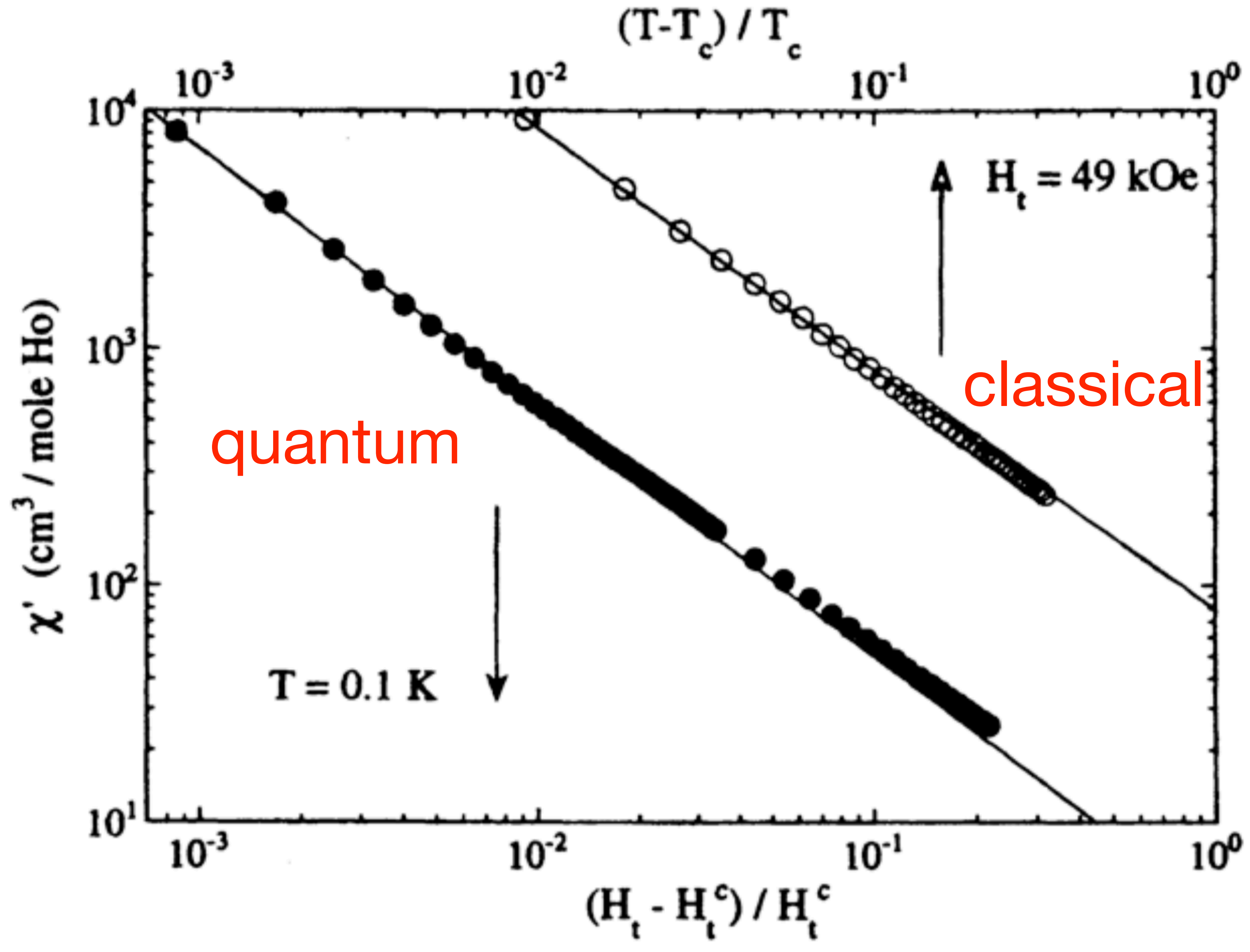
4.8.7 Dimensionality and critical exponents

Plausibility argument

- Critical exponents — *spatial dimensionality* is important — indeed for $d \geq d_{\rm m}$, mean field will hold. $d_{\rm m} = 4$ for short-range interactions $= 3$ for dipole interaction
- Partition function involves summation of Boltzmann factors $e^{-\beta\mathscr{H}}$.
- Compare with quantum generator of time evolution: $e^{\mathrm{i}\mathscr{H}t/\hbar}$.
- So Boltzmann factor is like an (imaginary) extra dimension.
- As $T \to 0$, or $\beta \to \infty$, spatial displacement gets larger (thermodynamic limit)
- Sums in partition function cover the spatial extent of the system
- So in $T \to 0$ limit there is an additional dimension to be traversed.

- So in $T \to 0$ limit there is an additional dimension to be traversed.
- A $d-$dimensional quantum transition is like a $d+1$ dimensional classical one (should have same critical exponents)

Susceptibility measurements



- Slope of the fit lines is -1.
- This gives the susceptibility critical exponent $\gamma = 1$.
- Since $d_{\mathrm{m}} = 3$ (dipole Ising) we expect $\gamma = 1$ for classical (upper), and $\gamma = 1$ *definitely* for quantum (lower) — as with β, above.

1.7 The Third Law of Thermodynamics

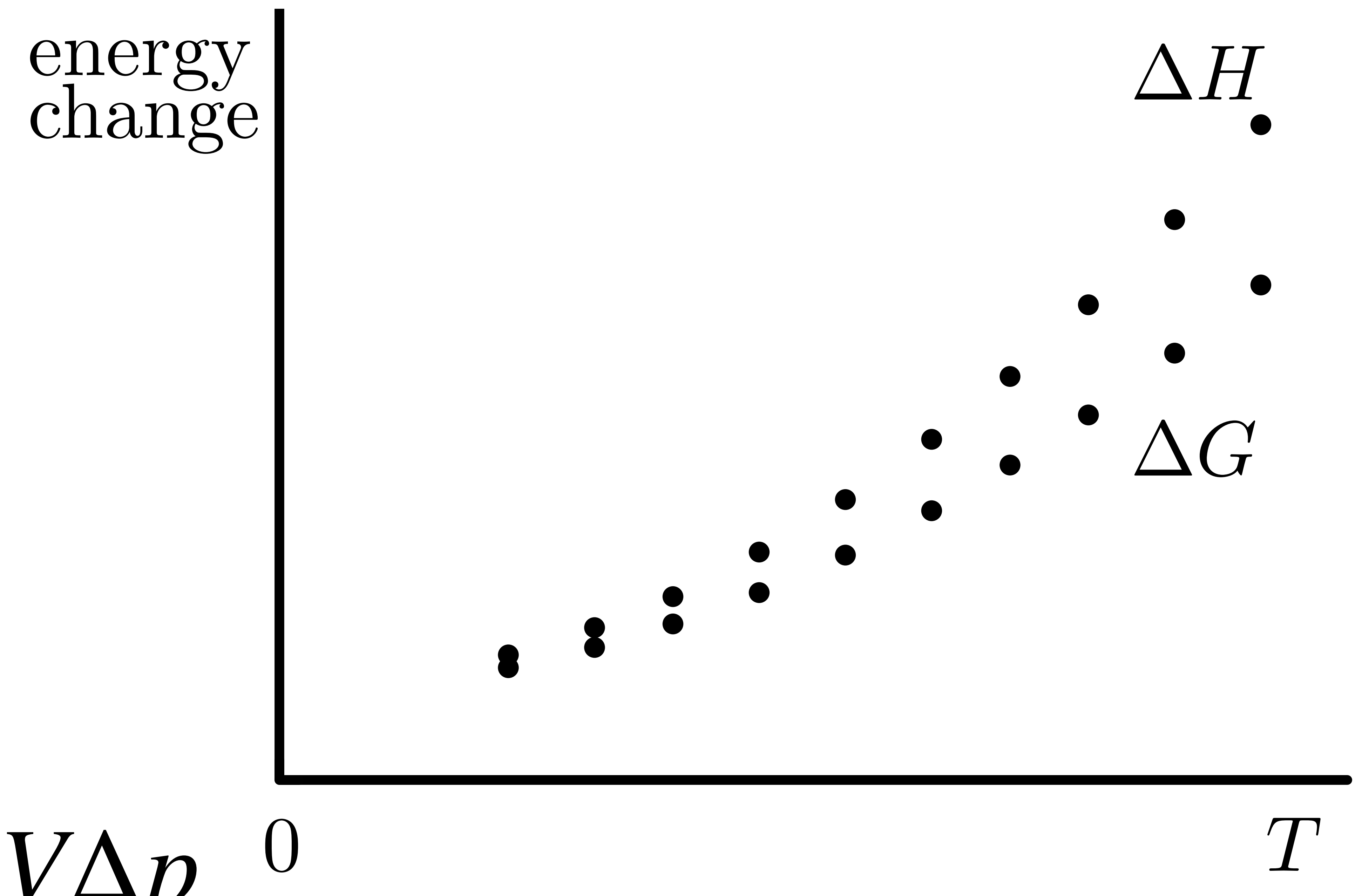
1.7.1 History of the Third Law

- Walter Nernst: chemist! – Nernst 'heat theorem' – 1906
- History and controversies – see Dugdale's book and Wilks's book.
- Question of status of Third Law.

- Nernst measured / inferred the change in Gibbs free energy and the change in enthalpy for chemical reactions which started and finished at the same temperature.

- Nernst's conclusion: As $T \to 0$ the changes in H and G tend to same:

$$\Delta H - \Delta G \to 0 \quad \text{as} \quad T \to 0$$



- Nernst used thermodynamic arguments to infer behaviour of S at low T:

$$\Delta H = T\Delta S + V\Delta p, \quad \Delta G = -S\Delta T + V\Delta p$$

so $\Delta G = \Delta H - T\Delta S - S\Delta T$, or, at constant T, $\Delta G = \Delta H - T\Delta S$

- Thus Nernst inferred that $T\Delta S \to 0$ as $T \to 0$

— No surprise, but . . . . . .

1.7.2 Entropy

- How fast does $\Delta H - \Delta G$ go to zero?

- Nernst observed it went *faster* than linearly, i.e.

$$\frac{\Delta H - \Delta G}{T} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0.$$

  but $\Delta H - \Delta G = T\Delta S$.

- So Nernst concluded $\quad \Delta S \rightarrow 0 \quad \text{as} \quad T \rightarrow 0$

  The entropy change in a process tends to zero at $T = 0$. The entropy thus remains a constant in any process at absolute zero.

- The entropy of a body at zero temperature is a constant, independent of all other external parameters. — Nernst heat theorem.

1.7.3 Microscopic viewpoint

- Nernst heat theorem: $S \to$ const as $T \to 0$.
- What is the constant? Look to microscopics.
- Boltzmann entropy $S = k \ln \Omega$. Ω is no of microstates in the macrostate.
- At $T = 0$ system will be in its *unique* ground state. Thus $\Omega = 1$ and so $S = 0$.
- Nernst's constant is zero.
- Third Law:
  As the absolute zero of temperature is approached the entropy of all bodies tends to zero.

$$\frac{\partial S}{\partial \text{ anything}} \to 0 \text{ as } T \to 0$$

- Applies to systems in equilibrium.

Degeneracy?

- What about degeneracy of ground state? – Then argument breaks down.
- Note S is extensive; must be considered in the thermodynamic limit.
- Should examine how the intensive S/N behaves in the limit $N \to \infty$.
- If degeneracy of the ground state is g then must look at $\ln(g)/N$.
- This will tend to zero in the thermodynamic limit so long as g increases with N no faster than exponentially. This is the fundamental quantum-mechanical principle behind the Third Law.
- See Leggett article for deeper discussion.

Quantum necessity

- The Third Law would fail if classical mechanics were to apply down to $T = 0$.
- Gibbs entropy: $S = -k \sum P_j \ln P_j$

  in classical case: $S = -\dfrac{1}{h^{6N}} k \int \rho \ln \rho \, \mathrm{d}^{3N}p \, \mathrm{d}^{3N}q$

  where ρ is density of points in phase space.

Classical entropy $$S \propto -\int \rho \ln \rho \, \mathrm{d}^{3N}p \, \mathrm{d}^{3N}q$$

- As T decreases the mean energy of the system will decrease.
- So the 'volume' of phase space occupied will decrease — density increases.
- Momentum coordinates p will vary over a smaller and smaller range.
- As $T \to 0$ the p range will become localised closer and closer to $p = 0$.
- Volume of occupied phase space $\to 0$, so $S \to -\infty$.

in agreement with classical gas: $S = Nk \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{V}{N} e^{5/2} \right]$

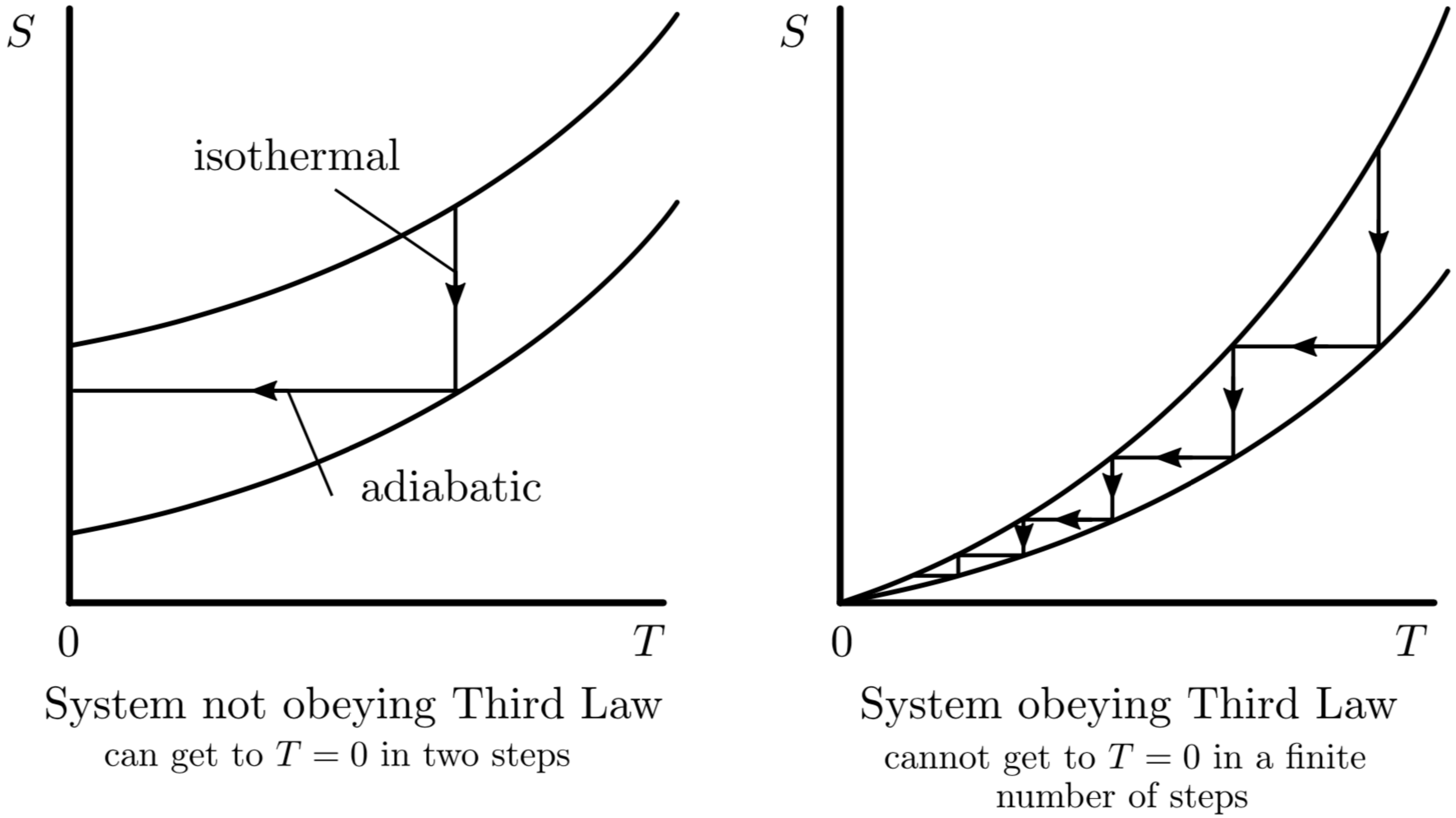
↓

- The Uncertainly Principle of quantum mechanics limits the low temperature position-momentum of a system; you cannot localise points in phase space to a volume smaller than the appropriate power of Planck's constant.

  This fundamental limitation of the density of phase points recovers the Third Law. Thus again we see the intimate connection between quantum mechanics and the Third law.

- The Second Law tells us that there is an absolute zero of temperature. Now we see that the Third Law tells us there is an absolute zero of entropy.

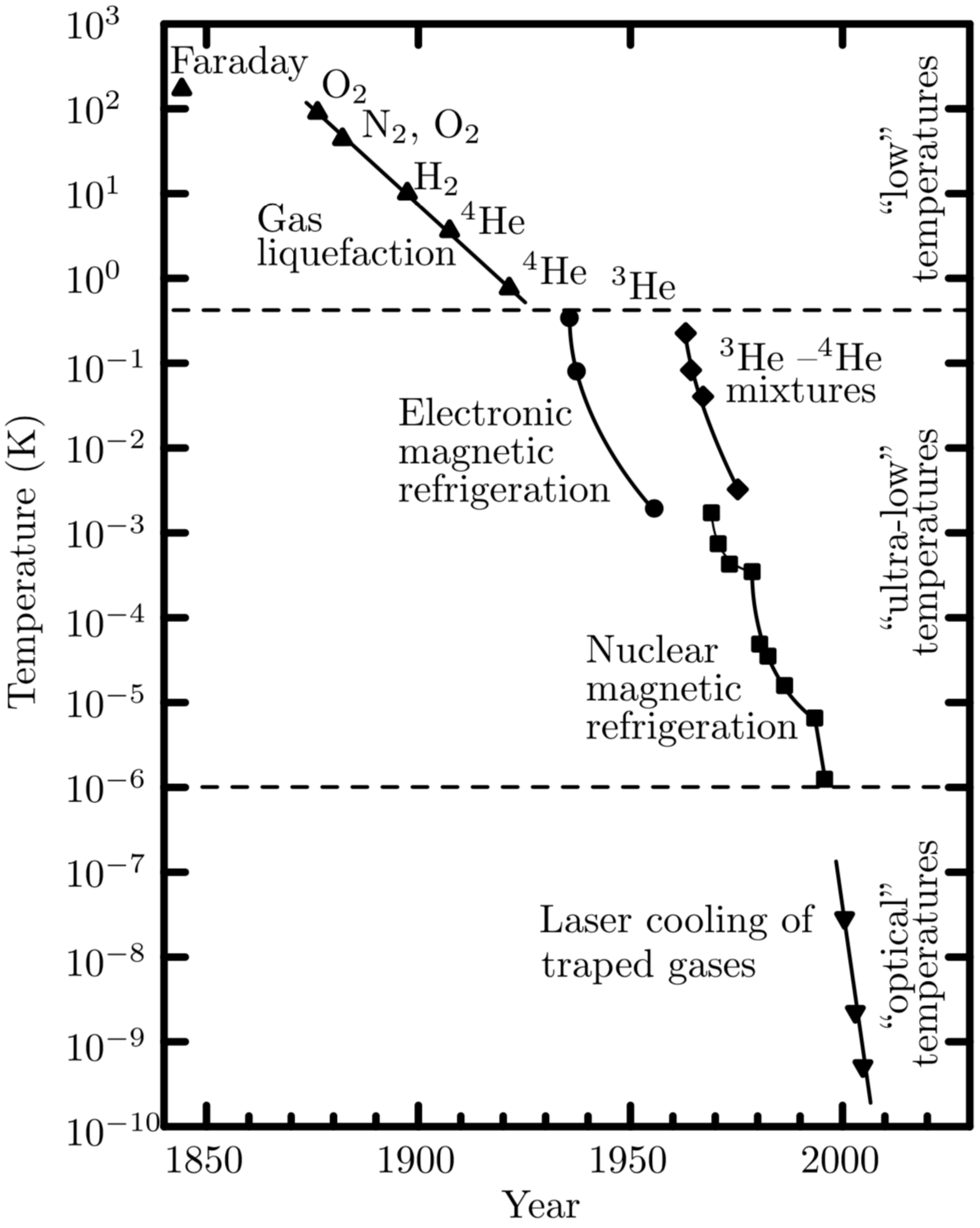
1.7.4 Unattainability of absolute zero



Sequence of adiabatics and isothermals between two values of some external parameter (cyclic process), Third Law implies that you cannot get to $T = 0$ in a finite number of steps. This is, in fact, another possible statement of the Third Law.

- Although one cannot get all the way to $T = 0$, it is possible to get closer and closer.

  The figure (adapted and extended from Pobel's book),
  indicates the success in this venture.



Consequences of the Third Law

$$\frac{\partial S}{\partial\ \text{anything}} \to 0 \text{ as } T \to 0$$

1.7.5 Heat capacity

Heat capacity $$C = \frac{\partial Q}{\partial T} = T\frac{\partial S}{\partial T}.$$

Third law $\Longrightarrow$ $$\frac{\partial S}{\partial T} \to 0 \quad \text{as} \quad T \to 0.$$

Therefore $$C \to 0 \quad \text{as} \quad T \to 0.$$

Contrast equipartition $C_V = \frac{3}{2}Nk$ for *classical* gas.

But Fermi and Bose gas C_V does go to zero as $T \to 0$.

Solid heat capacity
Classical equipartition

Einstein and Debye

Expansion coefficient

- Application of the Third Law often involves the use of a Maxwell relation.

The relevant Maxwell relation here is $\left.\dfrac{\partial V}{\partial T}\right|_p = -\left.\dfrac{\partial S}{\partial p}\right|_T .$

— Left side has expansion coefficient.
— Right side connects with Third Law.

Third Law $\Longrightarrow$ $\left.\dfrac{\partial S}{\partial p}\right|_T \to 0$ as $T \to 0$

So expansion coefficient $\to 0$ as $T \to 0$.

Magnetic susceptibility

- Get the variables right (analogy with $p - V$ system)

$$\Delta W = -p\Delta V \quad \text{compare with} \quad \Delta W = -M\Delta B$$

So take $p - V$ results and substitute $p \to M$ and $V \to B$. — "magnetic recipe"

Magnetic susceptibility: $$\chi = \frac{\mu_0}{V}\frac{\partial M}{\partial B}.$$

Recipe says $$\chi V/\mu_0 \to \frac{\partial p}{\partial V}$$

but there is no Maxwell relation for this. So . . . . . .

- Look at $\partial\chi/\partial T$:

$$\frac{\partial(\chi V/\mu_0)}{\partial T} = \frac{\partial^2 M}{\partial T \partial B}$$
$$\rightarrow \frac{\partial^2 p}{\partial T \partial V} \quad .$$

- Swap order of differentiation

$$\frac{\partial}{\partial B}\frac{\partial M}{\partial T} \rightarrow \frac{\partial}{\partial V}\frac{\partial p}{\partial T}$$

Now we do have a Maxwell relation

$$\left.\frac{\partial p}{\partial T}\right|_V = \left.\frac{\partial S}{\partial V}\right|_T \rightarrow \left.\frac{\partial M}{\partial T}\right|_B = \left.\frac{\partial S}{\partial B}\right|_T$$

Now the right hand side of these $\rightarrow 0$ by the Third Law. ↓

- Look at $\partial\chi/\partial T$:

$$\frac{\partial(\chi V/\mu_0)}{\partial T} = \frac{\partial^2 M}{\partial T \partial B}$$
$$\rightarrow \frac{\partial^2 p}{\partial T \partial V} \ .$$

- Swap order of differentiation

$$\frac{\partial}{\partial B}\frac{\partial M}{\partial T} \rightarrow \frac{\partial}{\partial V}\frac{\partial p}{\partial T}$$

Now we do have a Maxwell relation

$$\left.\frac{\partial p}{\partial T}\right|_V = \left.\frac{\partial S}{\partial V}\right|_T \rightarrow \left.\frac{\partial M}{\partial T}\right|_B = \left.\frac{\partial S}{\partial B}\right|_T$$

Now the right hand side of these $\rightarrow 0$ by the Third Law.

Conclusion:

$$\frac{\partial \chi}{\partial T} \rightarrow 0 \text{ as } T \rightarrow 0$$

or

$$\chi \rightarrow \text{const} \quad \text{as } T \rightarrow 0$$

Curie's law !!!