Workshop on Novel States and Phase Transitions in Highly Correlated Matter

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Universally diverging Grüneisen parameter and magnetocaloric effect close to quantum critical points

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These are preliminary lecture notes, intended only for distribution to participants.
Universally diverging Grüneisen parameter and magnetocaloric effect close to quantum critical points

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Outline

- Introduction quantum phase transitions
- Thermodynamical quantities
- Scaling analysis
- Expectations & experiment
- Summary
Quantum fluctuations induce 2nd order phase transition at zero temperature.

depending on the material.

controlled by

- pressure $r = \frac{p-p_c}{p_c}$
- doping $r = \frac{x-x_c}{x_c}$
- magnetic field $r = \frac{H-H_c}{H_c}$

(Quantum critical point)

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Why is the quantum phase transition interesting?

**Singular QCP determines the physics in its vicinity, even at finite temperatures!**

⇒ Thermodynamics can probe its properties!

**HOW? → this talk!**
Why is the quantum phase transition interesting?

QCP may be the endpoint of a line, $T_c(r)$, of finite temperature, i.e., "classical" phase transitions.

Finite temperature transition has its "own" criticality;
differs qualitatively from the quantum phase transition at $T = 0$! belongs to different universality class.
Can we nevertheless discern the QC contribution to thermodynamics?

YES!

Classical criticality is additive; sits on top of the quantum critical background.

We are interested in this BACKGROUND!

Classical critical divergencies dominate over the QC background only within a tiny wedge housing the phase boundary.
What does thermodynamics probe?

Variations of the free energy $F(r, T)$ along the two directions of the phase diagram: control parameter $r$ and temperature $T$.

Derivatives probe the sensitivity

\[
\frac{\partial^n}{\partial T^n} F(r, T) \quad \text{wrt variation of } T \\
\frac{\partial^m}{\partial r^m} F(r, T) \quad \text{wrt variation of } r \\
\frac{\partial^{n+m}}{\partial T^n \partial r^m} F(r, T) \quad \text{wrt variation of both.}
\]
<table>
<thead>
<tr>
<th>QPT driven by</th>
<th>pressure $p$</th>
<th>magnetic field $H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\partial^2 F}{\partial T^2}$</td>
<td>specific heat coeff. $\gamma$</td>
<td>specific heat coeff. $\gamma$</td>
</tr>
<tr>
<td>$\frac{\partial^2 F}{\partial r \partial T}$</td>
<td>thermal expansion</td>
<td>temperature dependence of magnetization: $\frac{\partial M}{\partial T}</td>
</tr>
<tr>
<td>$\frac{\partial^2 F}{\partial r^2}$</td>
<td>compressibility</td>
<td>differential susceptibility</td>
</tr>
</tbody>
</table>

$\alpha = \frac{1}{V} \frac{\partial V}{\partial T} |_p$

$\kappa = -\frac{1}{V} \frac{\partial V}{\partial p} |_T$

$\frac{\partial M}{\partial H} |_T$
Important in the following:

**Single** prefered direction to approach the classical phase transition.

\[ T = \Rightarrow \]

\[ T \rightarrow T_c \]

\[ \alpha \sim C_p \sim |T - T_c|^{-\alpha} \]
Important in the following:

**Two (orthogonal) directions** to approach the QCP.

Specific heat $C_p$ and thermal expansion $\alpha$ yield *complementary* information about the QPT!
Grüneisen parameter

quotient of thermal expansion

\[ \alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_p = \frac{1}{V} \frac{\partial^2 F}{\partial T \partial p} = -\frac{1}{V} \frac{\partial S}{\partial p} \left|_T \right. \]

and molar specific heat at constant pressure

\[ C_p = -\frac{T}{N_A} \left. \frac{\partial^2 F}{\partial T^2} \right|_p = \frac{T}{N_A} \gamma = \frac{T}{N_A} \frac{\partial S}{\partial T} \left|_p \right. \]

\[ \Gamma = \frac{\alpha}{C_p} \]
If physics is dominated by single energy scale $E^*$:

scaling form of the molar entropy
\[
\frac{S}{N_A} = \Psi \left( \frac{T}{E^*} \right)
\]

\[
\Gamma = -\frac{N_A \partial S/\partial p|_T}{V T \partial S/\partial T|_p} = \frac{1}{V_m E^*} \frac{\partial E^*}{\partial p}
\]

$V_m$: molar volume

usually $E^*$ varies slowly with pressure, for example for phonons $E^* = \omega_D$

\[
\implies \text{Grüneisen law: } \Gamma \approx \text{const.}
\]

HOWEVER, violated near a quantum critical point!

Typical energy scale vanishes: $\omega_c \sim \xi^{-z}$. 
Scaling analysis

Upon scaling the unit length by $l$:

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Scaling</th>
<th>Scaling Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta x$</td>
<td>$\Delta x' = \Delta x , l^{-1}$</td>
<td>-1</td>
</tr>
<tr>
<td>$r$</td>
<td>$r' = r , l^{1/\nu}$</td>
<td>$1/\nu$</td>
</tr>
<tr>
<td>$T$</td>
<td>$T' = T , l^z$</td>
<td>$z$</td>
</tr>
<tr>
<td>$F$</td>
<td>$F' = F , l^\phi$</td>
<td>$\phi = d + z$</td>
</tr>
</tbody>
</table>

Definition of a QCP:

free energy $F$: scale invariant – physics independent of microscopic details

$$F(r, T) \to l^{d+z} \, F(r, T) \, l^\frac{1}{\nu} = F(r \, l^{1/\nu}, T \, l^z)$$
Scaling dimension of the Grüneisen parameter:

\[ \Gamma(r, T) \sim -\frac{1}{T} \frac{\partial^2 F(r, T)}{\partial r \partial T} \]

\[ \sim -\frac{1}{T} \frac{\partial^2 l^{-(d+z)} F(r l^{1/\nu}, T l^z)}{\partial T^2} \]

Scaling dimension of \( \Gamma \) equals **minus** the scaling dimension of the control parameter \( r \):

\[ \text{dim}[\Gamma] = -\text{dim}[r] \]
Consequences: $\Gamma$ diverges at the QCP!

1. Quantum critical regime
   choose scale $T l^z = 1$
   \[ \Gamma(r, T) = \frac{1}{T^{\frac{1}{\nu z}}} \Gamma(r T^{-\frac{1}{\nu z}}, 1) \]
   \[ \rightarrow \frac{1}{T^{\frac{1}{\nu z}}} \Gamma(0, 1) \]

2. Low-T regime
   choose scale $|r| l^{1/\nu} = 1$
   \[ \Gamma(r, T) = \frac{1}{|r|} \Gamma(\text{sign}(r), T |r|^{-\nu z}) \]
   \[ \rightarrow \frac{1}{|r|} \Gamma(\text{sign}(r), 0) \]


Experiment I: Heavy fermion compound CeNi$_2$Ge$_2$

QCP located at ambient pressure $\rightarrow$ thermal expansion measurements feasible


$$\gamma_{cr} \sim -\sqrt{T} \quad \& \quad \frac{\alpha_{cr}}{T} \sim \frac{1}{\sqrt{T}} \quad \Rightarrow \quad \Gamma_{cr} \sim \frac{1}{T} = T^{-\frac{1}{\nu z}}$$

3D-AF SDW in the quantum critical regime: $\nu z = 1$

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Experiment II: Heavy fermion compound YbRh$_2$Si$_2$

in the quantum critical regime:

\[ \nu_z \approx 1.4 \]

(beware: energy scale 300mK)


Does not conform to standard Hertz’ theory!

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Critical Point vs. Critical Line

Disorder might wash out QCP to a quantum critical line?

![Diagram showing critical behaviour along a finite pressure interval along the line: control parameter marginal → zero scaling dimension. Grüneisen can diverge at most logarithmically!]

Algebraic divergence excludes quantum critical line scenario.

Divergence of $\Gamma$ criterion for the existence of a QCP!
Universality in the low-$T$ regime

choose $r l^{1/\nu} = 1$ in the scaling form, $F(r, T) = l^{-(d+z)} F(r l^{1/\nu}, T l^z)$, for the free energy: $F(r, T) = r^\nu(d+z) f(\frac{T}{r^\nu z})$ ⇒ entropy: $S(r, T) = -r^\nu d f'(\frac{T}{r^\nu z})$

constraint by the third law of thermodynamics: $f'(x) \approx -c x^{y_0}$

no constant contribution and $y_0 > 0$

thermal expansion with $r = (p - p_c)/p_c$

$$\alpha = -\frac{1}{V_m} \frac{\partial S}{\partial p}|_T \approx -\frac{c\nu(d-y_0 z)}{V_m p_c} r^\nu(d-y_0 z)^{-1} T y_0$$

specific heat

$$C_p = T \frac{\partial S}{\partial T}|_p \approx c y_0 r^\nu(d-y_0 z) T y_0$$

universal exponents, non–universal prefactors
In the low-T regime: absence of a residual entropy leads to

**Universal Grüneisen parameter**

\[ \Gamma = \frac{\alpha}{C_p} = -G_r \frac{1}{V_m(p - p_c)} \]

\( V_m \) molar volume

prefactor \( G_r \) given by critical exponents: \[ G_r = \frac{\nu(d - y_0z)}{y_0} \]
e.g. SDW transition \( G_r = \frac{d-z}{2} \)

for a gapped system, \( C_p \sim e^{-\Delta/T} \), **effectively** \( y_0 \rightarrow \infty: \)
\[ G_r = -\nu z. \]

**Assumption of scaling predicts** not only exponent, but also prefactor!
Constant entropy curves

\[ dS = \left. \frac{\partial S}{\partial p} \right|_T dp + \left. \frac{\partial S}{\partial T} \right|_p dT = -V_m \alpha dp + \gamma dT = 0 \]

\[ \Gamma = \frac{\alpha}{T \gamma} = \frac{1}{V_m T} \left. \frac{dT}{dp} \right|_S \]

Grüneisen parameter measures “pressure-caloric effect”

for a magnetic field driven QPT: role of the Grüneisen parameter is taken over by the magnetocaloric effect
Constant entropy curves: Sign change of $\Gamma$!

Near the QCP: system has to decide between two different groundstates. 

$\Rightarrow$ Accumulation of entropy near the quantum critical point.

**Scenario I**

- $\Gamma$ sign change at $T_c$
- $dS = 0$

**Scenario II**

- $\Gamma$ sign change above QCP
- $dS = 0$
**Scenario I:** Dilute Bose Gas in $d = 3$

\[ S = \int dx \left( \phi^*(x) \left[ \frac{\partial}{\partial \tau} - \nabla^2 - \mu_0 \right] \phi(x) + \frac{u}{2} |\phi(x)|^4 \right) \]

shows QPT as a function of $\mu_0$

- scaling exponents: $z=2$, $d=3$, $\nu = \frac{1}{2}$

- symmetric phase: gapped spectrum

- condensed phase: Goldstone boson – linear spectrum

applicable to TICuCl$_3$

“Bose-Einstein condensation of magnons”
Hartree-Fock-Bogoliubov approximation:

Pronounced sign change of the thermal expansion at $T_c$

$1^{st}$ order jump at finite $T_c$: artefact of the approx.
Grüneisen parameter of the dilute Bose gas

rescaled parameter saturate at the universal values:

symmetric phase: gapped spectrum $y_0 \to \infty \quad \implies \quad -G_r = \nu z = 1$

condensed phase: linear spectrum $y_0 = 3 \quad \implies \quad -G_r = \frac{\nu(y_0z - d)}{y_0} = \frac{1}{2}$
Scenario I: Heavy fermion compound CeCu$_6-x$Au$_x$

\[ \frac{C_p}{T} \quad \text{J mol}^{-1} \text{K}^{-2} \]
\[ \frac{\alpha_v}{T} \quad (10^{-6} \text{K}^2) \]

\[ T (\text{K}) \]

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workshop Trieste July 2004 [25]
Scenario II: Ising Chain in a Transverse Field

\[ H = -J \sum_i \sigma_i^z \sigma_{i+1}^z + h \sum_i \sigma_i^x \]

as a function of magnetic field \( h \):
QPT between a magnetic and a paramagnetic ground state
continuum theory: fermions with relativistic spectrum

\[ \epsilon_k = \sqrt{r^2 + k^2} \]

where \( r = \frac{h - h_c}{h_c} \)

free energy: \[ F = -T \int_{-\infty}^{\infty} \frac{dk}{2\pi} \log \left[ 2 \cosh \frac{\epsilon_k}{2T} \right] \]

scaling exponents: \( z = d = \nu = 1 \)
Temperature sweeps at constant magnetic field:

\[ \gamma \frac{3}{\pi^2} \sim e^{-|r|/T} \]

\[ \frac{dM}{dT} |_{\Delta} \]

\[ r = 0.01 \]
\[ r = 0.02 \]
\[ r = 0.03 \]

\[ r = -0.01 \]
\[ r = -0.02 \]
\[ r = -0.03 \]
Magnetic Field sweeps at constant temperature:
Scenario II: Heavy fermion compound CeRu$_2$Si$_2$


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Restrictions

A simple scaling ansatz might fail.

1. If there are more critical time scales
e.g. spin fluctuations and fermionic quasiparticles.
   — local QCP

2. above the upper critical dimension
   → “dangerously irrelevant” operator may spoil scaling
   → explicit calculation necessary!

3. scaling exponent “resonances”

4. Scaling analysis yields only critical part!
   CAUTION: possibly non-critical contributions
Hertz’ theory of itinerant magnetism

describes spin–density wave (SDW) instability of certain heavy fermions

\[ S = \frac{1}{\beta V} \sum_{\omega_n, k} \frac{1}{2} \Phi^T \left[ \delta_0 + \xi_0^2 k^2 + \frac{|\omega_n|}{T^* k^{z-2}} \right] \Phi + u \Phi^4 \]

e.g. in the quantum critical regime for \( d=3 \)

<table>
<thead>
<tr>
<th></th>
<th>( d = 3, z = 2 )</th>
<th>( d = 3, z = 3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{cr} )</td>
<td>( T^{1/2} )</td>
<td>( T^{1/3} )</td>
</tr>
<tr>
<td>( c_{cr} )</td>
<td>( -T^{3/2} )</td>
<td>( T \log \frac{1}{T} )</td>
</tr>
<tr>
<td>( \Gamma_{cr} )</td>
<td>( -T^{-1} )</td>
<td>( \left( T^{2/3} \log \frac{1}{T} \right)^{-1} )</td>
</tr>
</tbody>
</table>

logarithmic corrections to scaling
for \( d=z=3 \) “resonance”
Summary: PRL 91 (2003) 066404-1

- Grüneisen parameter and magnetocaloric effect \textit{diverge} at the QCP
- in the low-T regime \textit{universal} behaviour
- thermal expansion more divergent than specific heat
- criterion for the existence of a simple QCP
- characterization of universality class: \( \nu, z \)
- provides mapping of the entropy landscape