Sign change of the Grüneisen parameter and magnetocaloric effect near quantum critical points

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We consider the Grüneisen parameter and the magnetocaloric effect near a pressure and magnetic field controlled quantum critical point, respectively. Generically, the Grüneisen parameter (and the thermal expansion) displays a characteristic sign change close to the quantum-critical point signaling an accumulation of entropy. If the quantum critical point is the endpoint of a line of finite temperature phase transitions, \( T_c \propto (p_c - p)^{\nu_z} \), then we obtain for \( p < p_c \): (1) a characteristic increase \( \Gamma \sim T^{-1/(\nu_z)} \) of the Grüneisen parameter \( \Gamma \) for \( T > T_c \), (2) a sign change in the Ginzburg regime of the classical transition, (3) possibly a peak at \( T_c \), (4) a second increase \( \Gamma \sim -T^{-1/(\nu_z)} \) below \( T_c \) for systems above the upper critical dimension and (5) a saturation of \( \Gamma \propto 1/(p_c - p) \).

We argue that due to the characteristic divergencies and sign changes the thermal expansion, the Grüneisen parameter and magnetocaloric effect are excellent tools to detect and identify putative quantum critical points.

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I. INTRODUCTION

The competition between two different ground states at a quantum phase transition leads to novel behavior in thermodynamics as well as in transport. A prominent example are the heavy fermion compounds whose non-Fermi liquid behavior is attributed to the presence of a quantum critical point (QCP) associated with a magnetic instability.

We recently pointed out\textsuperscript{1} that the Grüneisen parameter, \( \Gamma \), is an important tool to identify and classify a quantum critical point since it necessarily diverges near a pressure-driven quantum phase transition with characteristic exponent \( \nu_z \). In this article we focus on another aspect, i.e., the sign change of the Grüneisen parameter \( \Gamma \) for \( T > T_c \).

A quantum phase transition (QPT) occurs at zero temperature upon tuning an external parameter like doping, pressure, electric field, magnetic field, etc. to a critical value. The underlying QPT manifests itself at finite temperatures in an unusual sensitivity of thermodynamics on these tuning parameters. In the following we will focus on QCPs which are tuned with pressure, \( p \) and/or magnetic field, \( H \). Generalizations are straightforward. At \( T = 0 \) the distance to the QCP is determined by the control parameter which depends on pressure and/or magnetic field, \( r = r(p,H) \). Near the QCP the control parameter can be linearized around the critical pressure or the critical magnetic field,

\[ r(p,H) = (p - p_c)/p_0 = (H - H_c)/H_0 \]

where \( p_0 \) and \( H_0 \) are a constant pressure and magnetic field scale, respectively. Generically, the critical magnetic field will depend smoothly on pressure, \( H_c = H_c(p) \), and vice versa. Note that a linearization in magnetic field is only possible if the critical field is large, \( H/H_c \ll 1 \); in particular, this is not fulfilled in the case of a zero-field QCP.

The critical contribution to the free energy density is a function of this control parameter and temperature, \( f = f(r,T) \). The sensitivity on the tuning fields is thermodynamically measured by the derivatives of the free energy density with respect to \( r \). For a pressure-tuned QCP an example is provided by the thermal expansion,

\[ \alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_{p,H} = \frac{1}{V_m} \left. \frac{\partial S}{\partial p} \right|_{T,H} = \frac{1}{V_m} \left. \frac{\partial^2 f}{\partial r \partial T} \right|_{T,H}, \]

where \( V_m \) is the molar volume. With Eq. (1) follows that the thermal expansion is directly proportional to the mixed derivative \( \partial^2 f/\partial r \partial T \). When the QPT can be tuned by magnetic field the same derivative can be accessed by the thermodynamic quantity \( (dM/dT)_H \). If the QCP is sensitive to both, \( p \) and \( H \), the critical part of the thermal expansion and of the temperature derivative of the magnetization are expected to be proportional to each other near the QCP,

\[ \frac{V_m \alpha}{(dM/dT)_H} = \left. \frac{dH_c}{dp} \right|_{p=p_c}. \]

Their ratio gives the dependence of the critical magnetic field on pressure. Similar relationships hold for the magnetostriiction, compressibility and differential susceptibility which all yield \( \partial^2 f/\partial r^2 \).

The main quantity of our interest is the Grüneisen parameter which is measured by the ratio of thermal expansion and molar specific heat \( C_p = T \left. \frac{\alpha}{\partial T} \right|_p \),

\[ \Gamma = \frac{\alpha}{C_p} = \frac{\left. \partial^2 f/\partial r \partial T \right|_{T,H}}{V_m T \left. \frac{\partial S}{\partial T} \right|_p}. \]
Accordingly, one obtains directly from (5)
\[ dS = 0 \]
which the entropy is constant, \( m = \text{magnetic field} \). The solid line shows a generic isentrope along which the qualitative behavior of \( \Gamma \) can be extracted from the scaling form of the free energy
\[ f(r, T) = b^{-(d+z)} f(r b^{1/\nu}, T b^z), \]
where \( b \) is an arbitrary scaling parameter, \( d \) is the dimensionality and \( \nu \) and \( z \) are the correlation length and dynamical critical exponent, respectively. As can be read off directly from Eq. (4), \( \Gamma \) scales like \( 1/r \) or equivalently,
\[ \dim[\Gamma_{cr}] = -\dim[r] = -1/\nu. \]  
(6)
Accordingly, one obtains directly from (5)
\[ \Gamma_{cr} \propto \frac{1}{T^{1/\nu z}}. \]  
(7)
in the quantum-critical regime, i.e. for \( T \gg |r|^{\nu z} \) (see Fig. 1). On the other hand, in the two low-temperature regimes on the right and left hand side of the QCP in
\[ T \sim |r|^\nu z \]
Fig. (1) the Grüneisen parameter diverges with the inverse of the control parameter \( r \propto p - p_c \),
\[ \Gamma_{cr} = -G_r \frac{1}{V_m (p - p_c)}. \]  
(8)
Surprisingly, due to the third law of thermodynamics, i.e. by assuming a vanishing residual entropy at zero temperature, it is possible to determine even the prefactor \( G_r \) of the divergence from a scaling analysis. It is given by a simple combination of critical exponents
\[ G_r = -\nu \frac{y_0^+ z - d}{y_0^-}, \]  
(9)
where the exponents \( y_0^+ \) and \( y_0^- \) are associated with the low-temperature behavior of the specific heat, \( C_p \sim T^{y_0^+} \), on the right and left hand side of the QCP, respectively. As was shown in Ref. [1], these results might even hold (up to possible logarithmic corrections) in situations where the simple scaling Ansatz (6) fails, i.e. for systems above the upper critical dimension.

Equation (9) implies not only a divergence of \( \Gamma \) but also a sign change (assuming that \( G_r \) has the same sign on both sides of the QCP)! Obviously the question arises where and how this drastic sign change takes place in the finite-temperature phase diagram. This will be one of the main topics discussed in this paper.

The following section will discuss the sign changes using qualitative arguments. Sec. II investigates quantum critical points where there is no phase transition at finite temperature and briefly discusses experiments close to metamagnetic quantum phase transitions. In Sec. IV we study how thermal expansion, Grüneisen parameter and magnetocaloric effects are influenced by a phase-transition at finite \( T \) in proximity to a QCP. An overview of our main results is given in Sec. IV.

II. SIGN OF THE GRÜNEISEN PARAMETER

In order to obtain insight into the meaning of the sign of the Grüneisen parameter it proves useful to consider a line of constant entropy within the pressure-temperature plane \( (p, T) \),
\[ dS = \frac{\partial S}{\partial T} \bigg|_p dT + \frac{\partial S}{\partial p} \bigg|_T dp = 0. \]  
(10)
Using the definition of the thermal expansion and the specific heat we obtain for \( \Gamma \),
\[ \Gamma = \frac{1}{V_m T} \frac{dT}{dp} \bigg|_S. \]  
(11)
The Grüneisen parameter measures the variation of temperature upon pressure changes under constant entropy conditions. The Grüneisen parameter thus corresponds to a pressure-caloric effect. As already alluded to, for

![Diagram showing different regimes in the phase diagram of a quantum phase transition. The dotted lines correspond to crossovers between the low-T and the quantum critical regime, \( T \sim |r|^\nu z \). The control parameter might be sensitive to pressure and/or magnetic field. The solid line shows a generic isentrope along which the entropy is constant, \( dS = 0 \).]
a QPT that can be driven by magnetic field the quantity analogous to the Grüneisen parameter is the magnetocaloric effect

$$\Gamma_H = -\frac{(dM/dT)_H}{C_H} = \frac{1}{T} \frac{dH}{dS} \bigg|_S,$$  \hspace{1cm} (12)

where \(C_H\) is the specific heat at constant \(H\). Experimentally, the quantities \(\Gamma\) and \(\Gamma_H\) can be directly accessed by measuring the change in temperature at constant entropy upon pressure and magnetic field variations, respectively. In mathematical terms both yield the slope of the constant entropy curves, i.e. isentropes in the phase diagram.

How do the isentropes look like near a quantum phase transition? We expect that we have an accumulation of entropy near the quantum critical point since directly at the QCP the system is frustrated of two different possible ground states. From this expectation follows that the isentropes are tilted towards the QCP with a minimum in its vicinity, see Fig. 1. The minima of the isentropes indicate how the entropy accumulates around the QCP and sit at the positions where the system is maximally undecided which ground state to choose. According to Eq. (11), the Grüneisen parameter is proportional to the slope of the isentropes, i.e. it has a different sign on each side of the QCP. It thus follows from a generic entropy distribution around the QCP that the Grüneisen parameter will change sign in its vicinity. The sign change occurs at the location of the isentrope minima and therefore tracks the accumulation of entropy in the phase diagram. In this way, the Grüneisen parameter maps out the entropy landscape near a quantum critical point.

Since the specific heat is always positive the sign change of the Grüneisen parameter coincides with that of the thermal expansion. As the thermal expansion is given by the negative derivative of the entropy with respect to pressure, \(\alpha \propto -\partial S/\partial p\), a negative thermal expansion is present whenever the entropy increases as a function of pressure. This happens naturally in the vicinity of a pressure-controlled QPT. The sign change of the thermal expansion and hence of the Grüneisen parameter occurs at a pressure value where the entropy reaches a maximum. Similarly, for magnetic field tuning the magnetocaloric effect and the quantity \((dM/dT)_H\) will change its sign at the accumulation point of entropy.

As mentioned above, already the scaling result for the Grüneisen parameter in the low-temperature regime, Eq. (8), suggested a sign change of \(\Gamma\) provided that the prefactor \(G_r\) has the same sign in both low-\(T\) regimes. That this is the case is again ensured by entropic constraints. The sign of \(G_r\) is determined by the relative size of the exponents \(y_0^\pm\) and \(d/z\). These exponents determine the behavior of the specific heat or, alternatively, the entropy, \(S\), in the low-\(T\) regime, \(S \sim T^{y_0^\pm}\), and the quantum critical regime, \(S \sim T^{d/z}\), see Fig. 1. Using again the argument, that the competition between two different ground states leads to an enhanced entropy close to the QCP, we expect on physical grounds that the entropy as a function of \(T\) decreases in the low-\(T\) regime at least as fast as in the quantum critical regime. This implies that \(d/z \leq y_0^\pm\) and finally

$$\Gamma_r \leq 0 \hspace{1cm} (13)$$

in both low-temperature regimes. There are examples of critical theories with exponents \(d/z = y_0\), so that \(\Gamma_r = 0\), e.g. an insulating Heisenberg antiferromagnet with \(z = 1\) and \(y_0 = d\) on the ordered side of the phase diagram or an itinerant antiferromagnet with \(d = z = 2\) and \(y_0 = 1\). In the latter example, logarithmic corrections ensure that the entropy at the critical point is higher.

In the low-temperature regime we can determine the critical isentropes explicitly by using the scaling result Eq. (8). We obtain for \(T \ll |r|^{\nu z}\)

$$T(r)|_S \propto |r|^{-G_r}. \hspace{1cm} (14)$$

The isentrope behaves as a powerlaw near the QCP with an exponent given by \(G_r\), Eq. (10). A minimum of the isentrope directly follows if \(G_r\) is negative.

In the following we will give examples of two possible scenarios. If the entropy landscape at finite temperature is only determined by the zero-temperature transition we expect that the minima of the isentropes are located approximately above the QCP, i.e. at \(r \approx 0\). In this scenario, considered in Sec. III, the Grüneisen parameter and the magnetocaloric effect change their sign near the critical pressure \(p_c\) and critical field \(H_c\). If the QCP is however an endpoint of a line of classical finite temperature transitions we expect that the entropy landscape is distorted with the minima in the vicinity of the critical temperature as sketched in Fig. 1. We will show that the sign change of the Grüneisen parameter then occurs within the Ginzburg region of the symmetric phase. This scenario is considered in Sec. IV.

### III. SIGN CHANGE OF \(\Gamma\) NEAR A QCP WITHOUT ORDER AT FINITE \(T\)

#### A. Ising chain in a transverse field

A simple example of a QPT where the entropy landscape is solely determined by the underlying QCP is provided by the model of an Ising chain in a transverse field. The Ising chain shows a QPT as a function of transverse magnetic field \(H\) between a magnetic and a paramagnetic ground state. We are interested in the behavior of the magnetocaloric effect (12) near the critical field \(H_c\), which was also considered in Ref. 6. The continuum theory describing the transition is given by (Majorana-) fermions with a relativistic spectrum

$$\epsilon_k = \sqrt{r^2 + k^2}, \hspace{1cm} (15)$$

where \(r \propto H - H_c\). The important exponents of the critical theory are \(z = d = \nu = 1\). Furthermore, the spectrum is gapped away from the QCP which leads to a
specific heat that decays exponentially with temperature. The exponent $y^\pm_0$ appearing in (9) can effectively be set to infinity on both sides of the QCP, so that the prefactor in both low-temperature regimes simplifies to
\[ G_r = -\nu z = -1. \]  
(16)

The thermodynamic quantities can be computed from the free energy density
\[ f(r,T) = -T \int_{-\infty}^{\infty} \frac{dk}{2\pi} \log \left[ 2 \cosh \frac{\epsilon_k}{2T} \right]. \]  
(17)

The isentropes near the critical field $H_c$ are sketched in Fig. 2. Since the control parameter enters the free energy only quadratically the entropy landscape is symmetric with respect to the reflection $r \rightarrow -r$. This symmetry is rooted in the self-duality of the theory describing the QPT\(^8\). This has the consequence that in the case of the Ising chain the sign change of the magnetocaloric effect occurs directly at $r = 0$. The self-duality symmetry thus causes the prefactor of the divergence (7) to vanish in the quantum critical regime. The resulting magnetocaloric effect is shown in Fig. 3 for a temperature sweep at constant magnetic field and (b) a magnetic field sweep at constant temperature. As shown in the inset, the saturation value in the low-$T$ regime has the universal prefactor, $-G_r = \nu z = 1$.

B. Experiments on metamagnetic quantum criticality

An especially interesting example of a QCP without an associated finite-$T$ phase transition are the so-called "metamagnetic quantum critical endpoints\(^9\). The QCP is here understood to be the endpoint, $(H_c,T^*)$, of a line of first order transitions where the temperature $T^*$ is tuned to zero. As the control parameter (i.e. the magnetic field) couples here linearly to the order parameter, the quantum-critical properties of such systems differ in some aspects from the examples considered in this paper – for a detailed discussion we refer to Ref. 10. The notion of metamagnetic quantum criticality\(^9\) was originally motivated by experimental\(^11\) on Sr\(_3\)Ru\(_2\)O\(_7\). The metamagnetic transition is sensitive to pressure and magnetic field variations suggesting that both $p$ and $H$ can be used as tuning parameters, $r = r(p,H)$, and relations such as Eq. (3) are expected to hold. In fact, the differential susceptibility and magnetostriction nicely track each other\(^13\) near the critical field, $H_c \approx 7.9T$, confirming that pressure and magnetic field variations probe indeed the same thermodynamic information. The thermal expansion\(^10\) shows a change of sign near the critical field indicating the accumulation of entropy in the $(H,T)$ plane above.
H = H_c.

A metamagnetic anomaly of a different type but with qualitative similar signatures is also observed in the heavy-fermion compound CeRu_2Si_2 [14,15]. The thermal expansion as a function of H again shows a pronounced sign change near the metamagnetic field H_m ≈ 7.8T suggesting the vicinity to a QCP. According to Eq. (3), the zero-temperature limit of the Gruneisen parameter is expected to diverge as \( \Gamma \sim 1/(H - H_c) \) which also seems to be compatible with experimental observations, see Fig. 16 of Ref. [14].

IV. SIGN CHANGE OF 1 NEAR A QCP WITH ORDER AT FINITE T

It is a common situation that the symmetry-broken phase of the QPT extends to finite temperature, T. The QCP is then in fact the endpoint of a line of classical transitions along which derivatives of the free energy show a singular behavior at a finite critical temperature \( T_c \). Entropy is expected to accumulate near the phase boundary and the entropy landscape is correspondingly distorted as shown in Fig. 11.

As a consequence, the Gruneisen parameter is expected to change its sign near the critical temperature \( T_c \). This is observed for example in the heavy fermion compound CeCu_6−xAu [16] and in the spin-gap compound TiCuCl [22]. An especially nice example is the superconducting heavy fermion system URu_2Si_2. The thermal expansion shows a pronounced jump at the superconducting transition at \( T_c = 1.18K \) accompanied with a change of sign suggesting the vicinity of an associated QCP. The superconducting condensate of URu_2Si_2 forms in fact within a so-far unidentified “hidden order” phase which can be suppressed by an applied magnetic field of \( H_c = 35.9T \). Moreover, an additional reentrant phase is located in a magnetic field range of \( H = 36−39T \). The magnetocaloric effect has been measured and the isentropes around the second order transition at \( H \approx 36T \) have a similar shape as in Fig. 1 with minima near the critical temperature, \( T_c \). Another example is the heavy-fermion alloy U(Pt,Pd)_3 where a Gruneisen parameter inversion was also observed.

As an illustration of such a scenario we will consider the quantum phase transition of the dilute Bose gas. This example will capture many features which we believe are generic for a QCP with order at finite temperature. We assume that the chemical potential is sensitive to pressure so that a quantum phase transition can be induced by tuning the pressure to a critical value \( p_c \). Moreover, for dimensions \( d > 2 \) a finite temperature transition is present which distorts the entropy landscape in a manner as sketched in Fig. 11. The dilute Bose gas is relevant for the field-driven QPT in the spin-gap compounds which is interpreted as the Bose condensation of magnons [20,21,22,23,24,25].

FIG. 4: Sketch of a phase diagram with a symmetry-broken phase extended to finite temperature; here the QCP is the endpoint of a line of classical second order transitions. The minima of the isentropes, which identify the position of the sign change of the Gruneisen parameter, are located within the Ginzburg regime in the symmetric phase. Furthermore, in the Ginzburg regime the isentrope tend to nestle to the phase boundary as explained in the main text. For later reference the different regimes were labeled as: I/I’ low-temperature regime, \( T \ll |r|^z \), and II/II’ quantum critical regime, \( T \gg |r|^z \), in the symmetric/ordered phase, and III the Ginzburg regime that houses the phase boundary, \( T_c \sim (−r)^{\nu} \).

The action of the dilute Bose gas has the form [7]

\[
S[\phi, \phi^*] = \int_0^\beta d\tau \int d^d r \left[ \phi^*(\tau, r) \left( \frac{\partial}{\partial \tau} - \nabla^2 - \mu_0 \right) \phi(\tau, r) + \frac{u}{2} |\phi(\tau, r)|^4 \right].
\] (18)

We will limit ourselves to a discussion of this model above the upper critical dimension of the QPT, \( d + z > 4 \) and therefore \( d > 2 \), where the correlation length and the dynamical exponent of the QPT are given by their Gaussian values,

\[
\nu = 1, \quad z = 2.
\] (19)

First let us consider the theory on the mean-field level, however, including the one-loop correction to the chemical potential. The Landau potential takes the form

\[
V_{MF}(\phi, \phi^*) = R|\phi|^2 + \frac{u}{2} |\phi|^4.
\] (20)

where the effective mass \( R \) is temperature dependent as it is renormalized by the critical fluctuations,

\[
R = -\mu_0 + 2u \int \frac{d^dk}{(2\pi)^d} \coth \left( \frac{k^2}{2T} \right) = r - r_{cr}(T).
\] (21)
In the last equation we introduced the control parameter $r$ given in terms of the renormalized zero-temperature chemical potential, $r \equiv -\mu = -\mu_0 + u \int \frac{dk}{(2\pi)^d}$. If the QCP is sensitive to pressure changes, $r$ can be linearized in the applied pressure, $r = (p - p_c)/p_0$ (assuming a finite magnetic field in the case of critical spin-gap when the mass vanishes, $R = 0$). The phase transition occurs when the mass vanishes, $R = 0$. The phase boundary in the plane $(r, T)$ is thus given by

$$r_{cr}(T) = -\frac{\zeta(d/2)}{2^{d-1} \pi^{d/2}} u T^{1/\psi}. \quad (22)$$

where the exponent reads $1/\psi = (d + z - 2)/z = d/2$. Note that the temperature dependence of the phase boundary, $T_c \propto (p_c - p)^\nu$, is due to the dangerously irrelevant quartic coupling $u$.

Above the upper critical dimension, $d + z > 4$, irrelevant couplings will in general invalidate the simple scaling form of the critical free energy density given in Eq. (8). In the present example the dependence on the quartic coupling, $u$, must be incorporated into a generalized scaling form

$$f(r, T, u) = b^{-(d+z)} f(r b^{1/\nu}, T b^z, u b^{d+z-4}). \quad (23)$$

The dependence on $u$ may spoil the predictions for the Grüneisen parameter drawn from Eq. (8). This is for example the case within the wedge of the Ginzburg region indicated in Fig. 2 which contains the phase boundary. Bearing this in mind we now go beyond the mean field treatment by including the contribution of fluctuations in the free energy density.

### A. Gaussian approximation

Depending on the regime in the phase-diagram plane, Fig. 3, the physics of the dilute Bose gas is determined by different fixed points.

In the low-temperature regime I within the symmetry-broken phase, $T \lesssim -r$, the physics of the Grüneisen parameter will be controlled by the Goldstone modes; an expansion around the Gaussian theory in the quartic coupling $u$ is plagued with IR divergencies in this regime indicating the crossover to the stable Goldstone fixed point. This regime is conveniently treated by decomposing the fluctuations into massive amplitude- and gapless phase modes. The thermodynamics will be determined by the phase modes leading to a specific heat which decreases in temperature as $C_p \sim (T/\sqrt{-r})^\nu$ with $y_0 = d$. The prefactor, $G_r$, of the Grüneisen divergence is here given by

$$-G_r |_{+} = -\frac{\nu (d - z y_0)}{y_0} = 1/2. \quad (24)$$

On the other hand, the thermodynamics in the low-temperature regime I within the symmetric phase, $T \lesssim r$, is determined by the Gaussian fluctuations around the $T = 0$ theory. The specific heat decreases exponentially with temperature, $C_p \sim r^{d/2}(r/T)^{1/2} e^{-r/T}$, reflecting the gap in the fluctuation spectrum. Correspondingly, in this regime the prefactor $G_r$ is given by

$$-G_r |_{+} = \nu z = 1. \quad (25)$$

The most interesting regime for our discussion is the quantum critical regime, $T \gg |r|$. Here thermodynamics is almost always (in regions indicated as II and II') dominated by ideal gas behavior with a specific heat, $C_p \sim T^{d/2}$ and thermal expansion $\alpha \sim T^{d/2-1}$. Only sufficiently near the classical critical transition in regime III, thermodynamics will be controlled by the classical critical fixed point which for the dilute Bose gas belongs to the XY-universality class. This crossover occurs at the Ginzburg temperature when the Ginzburg parameter is of order one,

$$G \equiv u T |R|^{(d-4)/2} = \mathcal{O}(1). \quad (26)$$

Note that the effective classical quartic coupling is given by $u T$. The description of the classical critical properties within this Ginzburg regime is beyond the simple approximation scheme employed here. It is within the Ginzburg regime where the thermal expansion and the Grüneisen parameter change sign. However, as we will explain in detail below the sign change is not a property associated to classical criticality but is rather to be attributed to the underlying quantum phase transition. The sign change is a property of the quantum critical background on which the classical singularities develop.

For its description we will evoke a Gaussian approximation which captures the correct thermodynamics in the quantum critical regime, $T \gg |r|$, except in the Ginzburg region where it will fail yielding singularities with wrong Gaussian exponents. In the quantum critical regime within the symmetric phase the Gaussian fluctuations determine the free energy density

$$f(r, T) = T \int \frac{d^4k}{(2\pi)^4} \log \left[ 1 - \exp \left( -\frac{R(r, T) + k^2}{T} \right) \right]. \quad (27)$$

For the following it will be crucial that here and in Eq. (25) the temperature dependent mass $R(r, T)$ enters, see Eq. (21), which measures the distance from the classical transition. Note that in Eq. (21) we have set $R = 0$ on the right-hand side, using only critical fluctuations when computing the mass renormalization. For our discussion it is essential that this approximation is justified outside of the Ginzburg regime, as corrections are of order of the Ginzburg parameter, $\delta R/R = \mathcal{O}(G)$. Outside the Ginzburg regime, we therefore obtain similar results as other approximation schemes like the self-consistent Hartree-Fock or the Popov approximation. Those approximations have, however, the disadvantage that they wrongly predict a first-order transition within the Ginzburg regime, while our approximation describes a
second-order phase transition with Gaussian (and therefore wrong) critical exponents.

In the symmetry-broken phase the field fluctuates around the solution of the mean-field potential \( \Psi \). The condensate then attains the finite value, \(|\phi|^2 = -R/u\), and contributes to the free energy. The fluctuations around the finite condensate have the Bogoliubov spectrum,

\[
f_- = \frac{R(R - 2r)}{2u} + T \int \frac{d^4k}{(2\pi)^4} \log \left[ 1 - \exp \left( -\frac{\sqrt{k^2(-2R + k^2)}}{T} \right) \right].
\]

(28)

Note that by virtue of \( \Psi \), the resulting entropy derived within this Gaussian approximation is indeed continuous at the critical temperature as is appropriate for a second order phase transition.

The temperature dependence of the free energies, \( f_\pm \), is two-fold: there is an explicit \( T \)-dependence and an implicit dependence via the effective mass \( R \) which is induced by the dangerously irrelevant quartic coupling \( u \), see Eq. (5). In the following it will be useful to distinguish between a quantum critical and a classical critical contribution to thermodynamics. We will define the quantum critical contribution to be the one which derives from the explicit temperature dependence of the free energies. The classical contribution to thermodynamics will arise from the implicit \( T \)-dependence via the effective mass \( R \) which is induced by the dangerously irrelevant quartic coupling \( u \), see Eq. (5). This latter contribution will dominate thermodynamics near the classical transition since near \( T_c \) the free energy is very sensitive to variation of \( R \).

To illustrate this point let us rewrite the free energy densities \( f_\pm \)

\[
f_\pm = \Psi_\pm(r, R) + T^{(d+z)/2} F_\pm(R T^{-1/(\nu z)}),
\]

(29)

where \( \Psi_+ = 0 \) and \( \Psi_-(r, R) = (R(R - 2r))/(2u) \) is the contribution from the condensate. The part of the free energies that depends explicitly on temperature obeys scaling with \( z = 1/\nu = 2 \) and the scaling functions

\[
F_\pm(x) = \frac{K_d}{2} \int_0^\infty dt t^{(d-2)/2} \log \left[ 1 - e^{-\omega_\pm(t, x)} \right]
\]

(30)

where \( K_d^{-1} = 2^{d-1}\pi^{d/2}/\Gamma(d/2) \) and

\[
\omega_+(t, x) = t + x, \quad \omega_-(t, x) = \sqrt{t(t - 2x)}.
\]

(31)

The Gaussian approximation yields an expression for the free energy density which conforms to the general scaling form \( \Psi \). The dependence on the quartic coupling, \( u \), however appears only via the thermal renormalization of the mass \( R = R(r, T) \). Apart from this implicit temperature dependence induced by the dangerously irrelevant quartic coupling, \( u \), the expression \( \Psi \) resembles the quantum critical scaling form \( \Psi \). Thermodynamic contributions that only derive from the explicit temperature dependence will therefore conform with the results obtained from Eq. (5). In this sense it is appropriate to call these contributions quantum critical. The implicit temperature dependence via \( R = R(r, T) \) results in additional classical contributions to thermodynamics which are subleading except in the Ginzburg regime where the Gaussian approximation breaks down. The purpose of including the thermal renormalization of the mass is to ensure the correct threshold behavior at \( T_c \). The sign change of \( R(r, T) \) across the phase transition will reflect itself in a sign change of the Grüneisen parameter. This sign change persists even outside the Ginzburg region as is explained below.

### B. Sign change of the Grüneisen parameter

We will show in the following that the sign change of the Grüneisen parameter stems from the quantum critical contribution to the thermal expansion and is in fact a property of the functions \( F_\pm \). Consider the contribution to the thermal expansion at the critical temperature \( T_c \) deriving from the explicit temperature dependence,

\[
\alpha_\pm \equiv \frac{1}{V_m p_0} \lim_{R \to 0} \frac{\partial^2}{\partial R \partial T} f_\pm
\]

(32)

\[
= \frac{1}{V_m p_0} \nu(2d + 2) - 1 - T_c \frac{\nu d - 1}{\nu z} F_\pm(0).
\]

Although the scaling function itself is continuous at the phase transition, \( F_+(0) = F_-(0) \), its derivative is not. In our specific example we have

\[
F_+(0) = -F_-(0),
\]

(33)

i.e. the quantum critical contribution to the thermal expansion is discontinuous and changes sign at the phase transition. Note that the quantum critical contribution to the specific heat is smooth at \( T_c \).

Making use of Eq. (21), the associated anomaly in the thermal expansion, \( \Delta \alpha_\text{QCP} = \alpha_\text{QCP}^+ - \alpha_\text{QCP}^- \), can be related to the derivative of the phase boundary,

\[
\Delta \alpha_\text{QCP} = -\frac{1}{V_m p_0 u} \left. \frac{\partial r_{\text{cr}}(T)}{\partial T} \right|_{R=0} = -\frac{1}{V_m p_0 u} \left. \left( \frac{dT_c}{dp} \right)^{-1} \right|_{R=0}.
\]

(34)

The same anomaly follows also from the renormalized mean-field potential \( \Psi \). In this sense the anomaly \( \Delta \alpha_\text{QCP} \) and the resulting sudden sign change of the Grüneisen parameter near \( T_c \) can be interpreted as a finite temperature manifestation of the mean-field character of the underlying quantum phase transition. Although the sharp jump will be smeared out by the classical critical fluctuations in spatial dimensions \( d < 4 \), the smearing is confined to the Ginzburg regime which is vanishingly small near the QCP. A pronounced jump
near $T_c$ in the thermal expansion and in the Grüneisen parameter with an accompanying sign change will result.

The smearing of the jump will also shift the exact position of the sign change away from the critical temperature $T_c$. In the following we will argue that this shift is towards the symmetric phase.

C. Location of the sign change

Where is the position of the sign change and hence the minima of the isentropes exactly located? Let us first give some general arguments. Let us consider the behavior of the entropy upon approaching the phase boundary from the ordered phase, see Fig. 4. The entropy attributed to the QCP increases when the phase boundary is approached from the ordered side by increasing the control parameter, $\partial S/\partial r|_{T<T_c} > 0$. We enter the Ginzburg regime the change in entropy becomes dominated by the finite temperature phase transition. The symmetric phase can be entered by either increasing control parameter $r$ or temperature $T$. However, within the Ginzburg regime the tuning of $r$, i.e., pressure or temperature have the same effect since both parameters couple to the same relevant operator of the classical transition. Since the entropy always increases as a function of temperature we also have $\partial S/\partial r|_{T=T_c} > 0$. The entropy as a function of $r$ should therefore attain its maximum, $\partial S/\partial r = 0$, above the critical temperature $T_c$. As a consequence, it follows that the sign change of the thermal expansion and the Grüneisen parameter should occur within the symmetric phase.

We can obtain an explicit expression for the Grüneisen parameter at the critical temperature, $T_c$, when the specific heat is sufficiently singular at the classical second order phase transition. The derivation follows standard arguments. Near the finite temperature transition the singular part of the molar entropy can be written in the form

$$S_{CL} = S_{CL}(T - T_c(p), p).$$

(35)

Near the critical temperature, the leading contribution to the thermal expansion will derive from the pressure dependence of the first argument. We thus obtain for the critical thermal expansion

$$V_m \alpha_{cr} \sim -\frac{\partial S_{CL}}{\partial p} \bigg|_{T} \sim \frac{\partial S_{CL}}{\partial T} \bigg|_{p} \sim \frac{C_{cr}}{T_c} \frac{dT_c}{dp}.$$  

(36)

If the classical critical contribution is sufficiently singular such that the background contribution can be neglected the Grüneisen parameter at $T_c$ is just given by the slope of the phase boundary,

$$\Gamma(T = T_c) = \frac{1}{V_m T_c} \frac{dT_c}{dp} = - \frac{\Psi}{V_m(p_c - p)} \bigg|_{T = T_c(p)}.$$  

(37)

In the last equation we made use of $T_c \propto (p_c - p)^\gamma$. The negative slope of the phase boundary, i.e. the suppression of $T_c$ with increasing pressure, $r = (p - p_c)/p_0$ as depicted in Fig. 4 results in a negative Grüneisen parameter at the critical temperature, $\Gamma(T = T_c) < 0$. The Grüneisen parameter thus has the same sign at the critical temperature as in the ordered phase. We again find that the sign change must occur within the symmetric phase.

In order to locate the sign change we consider the thermal expansion of the dilute Bose gas within the symmetric phase. The quantum critical contribution reads

$$\alpha_{QCP} = \frac{1}{V_m p_0} \frac{\partial^2 f_+(R(r,T),T)}{\partial R \partial T} = \frac{1}{2uV_m p_0} \frac{\partial R}{\partial T} \left(1 + O(uTR^{(d-4)/2})\right)$$

(38)

In addition to $\alpha_{QCP}$, the implicit temperature dependence via the effective mass, $\tilde{R}$, yields a classical contribution

$$\alpha_{CL} = \frac{1}{V_m p_0} \frac{\partial^2 f_+(R(r,T),T)}{\partial R^2} \frac{\partial R}{\partial T}.$$  

(39)

We obtain for their ratio

$$0 > \frac{\alpha_{CL}}{\alpha_{QCP}} \sim 2u \frac{\partial^2 f_+}{\partial R^2} \sim O(uTR^{(d-4)/2}).$$  

(40)

The classical part of the thermal expansion has a sign opposite to the part attributed to the QCP. The classical part therefore reduces the contribution $\alpha_{QCP}$ upon approaching the phase boundary from the symmetric phase. This finally leads to the sought-after sign change.
The two contributions are of the same order when the Ginzburg criterion \(^{20}\) is fulfilled. The position of the sign change of the Grüneisen parameter is hence located within the Ginzburg regime of the classical finite temperature transition. Sufficiently near the QCP the Ginzburg regime is vanishingly small so that the position of the sign change of \(\Gamma\) almost coincides with the critical temperature \(T_c(p)\).

The temperature evolution of the specific heat, thermal expansion and the Grüneisen parameter is shown in Fig. 5. The control parameter has been chosen negative such that the critical temperature is crossed during the temperature sweep. The temperature region shown in Fig. 5 corresponds to the quantum critical regime, \(|r| \ll T^{1/(\nu z)}\), where the expressions \(^{27}\) and \(^{28}\) for the free energy are applicable. In this regime the Grüneisen parameter is determined by temperature and obeys the scaling form \(^{1}\). Since we have \(\nu z = 1\) it behaves as \(\Gamma \propto 1/T\). The curve follows this behavior except within the small Ginzburg regime where the Grüneisen parameter strikingly changes its sign and forms a sharp peak at the critical temperature. Since within our Gaussian approximation the classical critical specific heat is divergent with the Gaussian exponent, \(\alpha_{\text{Gauss}} = 2 - d/2 > 0\), the peak value is given by Eq. \(^{37}\), where for the dilute Bose gas we have \(\Psi = 2/d\). In particular, at the phase transition the Grüneisen parameter is now determined by the distance to the QCP, \(p - p_c\). Since the phase boundary is located well inside the quantum critical regime, \(T \gg |p - p_c|\), where \(\Gamma\) is usually determined by temperature, \(\Gamma \propto 1/T\), the Grüneisen parameter is strongly enhanced at \(T_c\). The crossover to this enhanced value occurs within the narrow Ginzburg regime leading to a peak structure at \(T_c\). The peak of \(\Gamma\) at the critical temperature manifests itself in an additional tilt of the isentropes within the Ginzburg regime as sketched in Fig. 4. Indeed, remembering that the Grüneisen parameter just measures the slope of the isentropes, Eq. \(^{11}\), it follows from expression \(^{37}\) that the isentrope locally follows the phase boundary at \(T_c\).

The well-pronounced peak of the Grüneisen parameter at \(T_c\) is only expected for a sufficiently singular classical critical specific heat such that relation \(^{37}\) holds. The Gaussian approximation employed here overestimates the classical critical specific heat exponent of the dilute Bose gas. In fact, the specific heat exponent of the \(d = 3\) XY-universality class is negative, i.e., the specific heat is not divergent at \(T_c\). Nevertheless, we still expect it to dominate over the quantum critical background such that a narrow peak in \(\Gamma\) should evolve at \(T_c\).

As can be seen in the inset of Fig. 5 near the QCP the anomaly in the specific heat, \(\Delta C_p\), near \(T_c\) is small in comparison with the one in the thermal expansion, \(\Delta \alpha\). This is expected since the large anomaly in the thermal expansion is attributed to the quantum critical point, \(\Delta \alpha = \Delta \alpha_{\text{QCP}}\), see Eq. \(^{41}\), whereas the anomaly of the specific heat originates only from the classical contribution to thermodynamics due to the temperature dependence induced in the effective mass, \(R\), by the dangerously irrelevant quartic coupling, \(u\).

This is also in agreement with the Ehrenfest relation \(^{2}\) which compares the size of the anomalies, i.e., the jumps in thermal expansion and specific heat at the classical transition that derive from the mean-field potential \(^{20}\),

\[
\frac{\Delta \alpha}{\Delta C_p} = \frac{1}{V_m} \frac{d \log T_c(p)}{dp} = \frac{\psi}{V_m(p - p_c)} \bigg|_{T=T_c(p)} < 0.
\]

(41)

In the second equation we made again use of Eq. \(^{22}\). As the quantum critical point is approached the relative size of the anomalies is expected to diverge as \(\sim 1/(p - p_c)\) resulting in a dominant anomaly in the thermal expansion. Note that although it has the same functional form as Eq. \(^{22}\) the Ehrenfest relation contains different information. In particular, the Ehrenfest relation does not discuss the absolute size of the Grüneisen parameter \(\Gamma\).

At low temperatures the Grüneisen parameter will eventually saturate after crossing over into the low-temperature regime \(\Gamma\) (not shown) and converges to a value now given by Eq. \(^{3}\). The behavior of the thermal expansion and the Grüneisen parameter in the various regimes of the phase diagram are summarized in Fig. 6 and 7.

V. SUMMARY

The Grüneisen parameter, \(\Gamma\), and the magnetocaloric effect change sign near generic quantum critical points.
We showed that the position of the sign change indicates the accumulation of entropy in the phase diagram. Two scenarios have been distinguished: a QCP with and without a symmetry broken phase at finite temperature. For the latter, treated in Section III the sign change is expected to be located near the critical value of the control parameter, e.g., near the critical pressure $p_c$. We discussed two examples where such a scenario is realized: the Ising chain in a transverse field and metamagnetic quantum critical materials.

An overview of our main results for the second scenario, where a symmetry-broken phase at finite $T$ is present, is given in Figs. 4 and 5. While explicit calculations have been performed for a QPT of the dilute Bose gas, we expect that all of our qualitative results are equally valid for other quantum phase transitions where the control parameter couples quadratically to the order parameter. Note that the exponents for $\Gamma$ in Fig. 5 were obtained by considering the ratio of the critical parts of thermal expansion and specific heat; for comparison with experiments a possible non-critical background contribution might have to be subtracted, cf. discussion in Ref. 1.

Most interesting is a situation where one investigates the behavior on the ordered side of the phase diagram close to the QCP. Upon lowering temperature one crosses according to Fig. 4 four different regimes.

In regime II one observes the usual power-laws in thermal expansion and Grüneisen parameter (or equivalently magnetocaloric effect) which are associated to the quantum-critical part of the phase diagram. The main result of our paper is the characteristic jump of thermal expansion and Grüneisen parameter in the Ginzburg regime located slightly above the classical phase transition. The jump in $\Gamma$ proportional to $\left(\frac{p_c - p}{p_c}\right)$, where $\Psi$ characterizes the form of the phase boundary, $T_c \propto (p_c - p)^\nu$, gets more and more pronounced upon approaching the QCP. If the classical specific heat is diverging, there is also a sharp maximum in $\Gamma$ at $T_c$ with the universal value $\Gamma(T_c) = \Psi/(V_m(p - p_c))$. In situations where the classical specific heat is not so singular, a peak can still occur but a lower maximal value is expected. In the ordered phase outside of the Ginzburg regime, i.e. in regime II’, the Grüneisen parameter increases again as in II but with an opposite sign as the system is located on the other side of the phase transition. Finally, at lowest temperatures a saturation of $\Gamma$ sets in to an universal value given by Eq. 5. For a magnetic-field tuned quantum phase transition an analogous behavior is expected for the magnetocaloric effect 12. In cases where the QCP is below its upper critical dimension, one has $\Psi = \nu z$ and region II’ is absent.

It is an interesting open question how the above results are modified for quantum phase transitions which involve different types of fluctuations possibly characterized by different time-scales as for example in the case of itinerant ferromagnetism. 11,32

To summarize, the divergence of the Grüneisen parameter and magnetocaloric effect near a QCP in combination with their sign change result in very strong signatures. They are thus important thermodynamic probes to detect and classify QCPs.

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