Universally Diverging Grüneisen Parameter and the Magnetocaloric Effect Close to Quantum Critical Points

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At a generic quantum critical point, the thermal expansion α is more singular than the specific heat c_p. Consequently, the "Grüneisen ratio," $\Gamma = \alpha/c_p$, diverges. When scaling applies, $\Gamma \sim T^{-1/(\nu z)}$ at the critical pressure $p = p_c$, providing a means to measure the scaling dimension of the most relevant operator that pressure couples to; in the alternative limit $T \to 0$ and $p \neq p_c$, $\Gamma \sim 1/(p - p_c)$ with a prefactor that is, up to the molar volume, a simple *universal* combination of critical exponents. For a magnetic-field driven transition, similar relations hold for the magnetocaloric effect $(1/T)\partial T/\partial H|_S$. Finally, we determine the corrections to scaling in a class of metallic quantum critical points.

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Introduction.—The anomalous behavior observed in an increasing number of systems, ranging from insulating magnets and heavy fermion compounds to cuprate superconductors, has been attributed to the presence of quantum critical points (QCPs). These occur in systems where a continuous quantum phase transition (QPT) at $T = 0$ is induced by tuning some control parameter such as pressure p, doping, or magnetic field H. Such zero-temperature critical points can determine the properties of materials in a wide range of temperatures. In general, quantum critical points are more difficult to characterize compared to their classical counterparts. At a classical critical point, thermodynamic quantities typically diverge; the associated critical exponents historically played a central role in our eventual understanding of scaling and universality. Some of these divergences, however, have to disappear at a QCP: There are constraints placed by the third law of thermodynamics due to the very fact that the transition takes place at zero temperature. Here we show that the Grüneisen ratio [1,2] diverges at any QCP, in a way that provides a novel thermodynamic means of probing quantum phase transitions.

We define the Grüneisen ratio Γ [1–3] in terms of the molar specific heat $c_p = \frac{T}{N}\frac{\partial S}{\partial T}|_p$ and the thermal expansion $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}|_{p,N} = -\frac{1}{V}\frac{\partial S}{\partial p}|_{T,N}$:

$$\Gamma = \frac{\alpha}{c_p} = -\frac{1}{V_m T}\frac{\partial S/\partial p}{\partial S/\partial T}, \tag{1}$$

where S is the entropy and $V_m = V/N$ the molar volume. In ordinary situations, pressure dependences are regular and a finite Grüneisen ratio is expected as is indeed observed in all previous measurements of this quantity in the literature. Such a regular dependence is typically described by assuming that the system is dominated by a single energy scale E^* (e.g., the Fermi energy in a metal or the Debye energy if acoustic phonons dominate), so the molar entropy takes the form $S/N = f(T/E^*)$. The Grüneisen ratio is then temperature independent and given by [1,2,4,5] $\Gamma = [1/(V_m E^*)](\partial E^*/\partial p)$. However, this formula already suggests that a diverging Γ can be expected when some energy scale E^* vanishes as it happens at a QCP.

Divergence of the Grüneisen ratio at QCPs.—A quantum critical point is reached in a singular fashion by tuning some external parameter and, in general, this external parameter is thermodynamically coupled to pressure. In the low temperature limit, the singular terms of S and T in Eq. (1) cancel out leaving Γ to depend only on singularities associated with the pressure p. As the pressure controls the QPT, such a singularity always exists and the Grüneisen ratio diverges at any QCP. This divergence is entirely determined by the scaling dimension of the control parameter, which is the most relevant operator to which the pressure couples. As shown below, this leads to a T dependence, $\Gamma \sim 1/T^{1/\nu z}$ [see Eq. (8)]. *In other words, the temperature exponent of the Grüneisen ratio provides a direct means to measure νz and, as a result, characterize a QCP.* Put in a slightly different way, the thermal expansion contains valuable information complementary to that obtained from the specific heat: While c_p measures the response to T (y axis in Fig. 1), α describes the response to the tuning parameter of the QPT, the second relevant variable at a QCP (x axis in

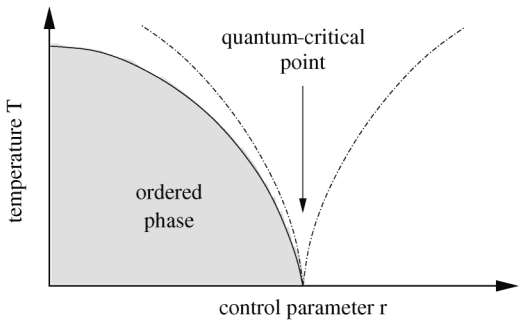

FIG. 1. Schematic phase diagram with a QCP.

Fig. 1). This has to be contrasted with a classical phase transition. There, generically, only one relevant operator exists to which both T and p couple. Accordingly, Γ will be constant close to a classical transition.

To observe the singular behavior of Γ or the thermal expansion, the pressure has to couple sufficiently strongly to the critical dynamics. This is, for example, the case in heavy fermion compounds where the intricate competition between magnetic interactions and the Kondo effect can be tuned by pressure, doping, or magnetic field to yield a QPT, typically from a metallic antiferromagnet to a metallic paramagnet. The high sensitivity to pressure arises from the exponential dependence of the Kondo temperature on system parameters. Whether the transitions in these systems conform to the Gaussian picture associated with $T = 0$ spin-density wave (SDW) transitions [6,7] or are non-Gaussian as in a locally quantum critical point [8] is a question of great current interest.

If the control parameter of the QPT is not pressure but an external magnetic field H, the role of the Grüneisen ratio is played by the ratio of the T derivative of the magnetization M (per mole) to the molar specific heat, for either fixed pressure or fixed volume,

$$\Gamma_H = -\frac{(\partial M/\partial T)_H}{c_H} = -\frac{1}{T}\frac{(\partial S/\partial H)_T}{(\partial S/\partial T)_H} = \frac{1}{T}\frac{\partial T}{\partial H}\bigg|_S. \quad (2)$$

It can be determined directly from the magnetocaloric effect—the change of temperature in response to an adiabatic ($S = \text{const}$) change of H.

In the following, we go beyond these general considerations by carrying through (i) a more detailed analysis based on the assumption of scaling and (ii) a model study on the spin-density-wave (SDW) QCPs in metallic systems. The latter is a model system that is above or equal to the upper critical dimension, so corrections to scaling are important; it is of direct interest in comparing with experiments in heavy fermion compounds.

Scaling analysis.—Close to any QCP, the correlation length ξ diverges as a function of a control parameter r, $\xi \sim |r|^{-\nu}$, where, e.g., $r = (p - p_c)/p_c$ or $r = (H - H_c)/H_c$. Correspondingly, a typical correlation (imaginary) time, $\xi_\tau \sim \xi^z$, diverges as the QCP is approached. The "dynamical critical exponent" z depends on the dynamics of the order parameter and relates time and length scales.

If one assumes that the critical behavior is governed by ξ and ξ_τ (a more careful discussion of this assumption is given below), the critical contribution to the free energy per mole, $F_{cr} = F - F_{\text{reg}}$, can be cast into the following standard scaling ansatz (using hyperscaling):

$$\frac{F_{cr}}{N} = -\rho_0 r^{\nu(d+z)} \tilde{f}\left(\frac{T}{T_0 r^{\nu z}}\right) = -\rho_0 \left(\frac{T}{T_0}\right)^{(d+z)/z} f\left(\frac{r}{(T/T_0)^{1/(\nu z)}}\right), \quad (3)$$

where ρ_0 and T_0 are nonuniversal constants, while $f(x)$ and $\tilde{f}(x)$ are universal scaling functions. Obviously, $f(x \to 0) \approx f(0) + xf'(0) + \cdots$ is regular as there is no phase transition at $r = 0$, $T > 0$ (see Fig. 1). The limit $\tilde{f}(x \to 0) = \tilde{f}(0) + cx^{y_0+1}$ describes the low temperature behavior of the phases to the left or right side of the QCP (in general different for $r > 0$ and $r < 0$). Note that the exponent $y_0 > 0$ has to be positive due to the third law of thermodynamics. It characterizes the power-law behavior of the specific heat $c_p \sim T^{y_0}$, e.g., $y_0 = 1$ for a Fermi liquid, $y_0 = 2$ for a d-wave superconductor in $d = 2$, or $y_0 = d$ and $d/2$ for an insulating antiferromagnet and ferromagnet, respectively.

Thermodynamical quantities are easily obtained from (3). The critical contribution c_{cr} to the specific heat at $r = 0$ is given by

$$c_{cr}(T, r = 0) = \frac{(d + z)d}{z^2}\frac{\rho_0}{T_0} f(0)\left(\frac{T}{T_0}\right)^{d/z}, \quad (4)$$

and for $T \to 0$, $r \neq 0$,

$$c_{cr}(T \to 0, r) = \frac{\rho_0 c y_0 (y_0 + 1)}{T_0}\left(\frac{T}{T_0}\right)^{y_0} r^{\nu(d - y_0 z)}. \quad (5)$$

Similarly, in the case of a pressure tuned QCP with $r = (p - p_c)/p_c$, the critical contribution α_{cr} to the thermal expansion reads

$$\alpha_{cr}(T, r = 0) = -\frac{d + z - \frac{1}{\nu}}{z}\frac{\rho_0 f'(0)}{T_0 p_c V_m}\left(\frac{T}{T_0}\right)^{[d-(1/\nu)]/z}, \quad (6)$$

and, for $r \neq 0$,

$$\alpha_{cr}(T \to 0) = -\frac{\rho_0 (y_0 + 1) c \nu (d - y_0 z)}{T_0 V_m}\frac{r^{\nu(d-y_0 z)}}{p_c r}\left(\frac{T}{T_0}\right)^{y_0}. \quad (7)$$

The thermal expansion is more singular than the specific heat leading to a Grüneisen ratio,

$$\Gamma_{cr}(T, r = 0) = \frac{\alpha_{cr}}{c_{cr}} = -G_T T^{-1/(\nu z)}, \quad (8)$$

where the prefactor $G_T = \{[(d + z - 1/\nu) z f'(0)]/[(d + z) d f(0)]\}[T_0^{1/(\nu z)}/(p_c V_m)]$ contains some nonuniversal parameters (p_c and T_0). *We reach the important conclusion that the temperature exponent of the Grüneisen ratio is equal to* $1/\nu z$.

In the other limit $T \to 0$, $r \neq 0$, we obtain the universal result

$$\Gamma_{cr}(T \to 0, r) = -G_r \frac{1}{V_m (p - p_c)}. \quad (9)$$

Remarkably, even the (generally unknown) scaling functions cancel out in the amplitude G_r, leaving only a combination of critical exponents and the dimensionality:

$$G_r = \frac{\nu(d - y_0 z)}{y_0}. \quad (10)$$

Note that the universality of this prefactor is connected to the third law of thermodynamics—a finite residual entropy per volume ($y_0 = 0$) would spoil this result.

It is rather difficult to measure thermal expansion inside a pressure cell. However, in many systems doping acts similar to "chemical pressure." If doping x and pressure p can be quantitatively related, $p - p_c = c(x - x_c)$, a measurement of Γ for different samples at ambient pressure can be used to check the prediction (9) quantitatively. For generic tuning parameters, we need to substitute $(\partial r/\partial p)$ for $1/p_c$ in Eqs. (6) and (7) and modify Eqs. (8) and (9) accordingly.

Similarly, for a QCP tuned by magnetic field [$r = (H - H_c)/H_c$], one obtains the following for the magnetocaloric effect:

$$\Gamma_{H,cr}(T \to 0, r) = -\frac{(\partial M/\partial T)_H}{c_{cr}} = -G_r \frac{1}{H - H_c}. \quad (11)$$

Again, in the $T \to 0$ limit, the prefactor (10) is universal. The T dependence of $\Gamma_{H,cr}$ at $r = 0$ is also given by (8).

It is interesting to compare the above with the case of a quantum critical *line*, where the critical behavior is not restricted to a single point but to a finite (pressure) interval. Here, since only marginal and irrelevant operators exist for $T = 0$, Γ_{cr} can diverge at most logarithmically:

$$\Gamma_{cr} \sim \pm \log T. \quad (12)$$

Conversely, if Γ diverges algebraically for $T \to 0$, a critical line scenario can be excluded.

Applicability of scaling.—The applicability of the scaling results (3)–(11) depends on a number of assumptions. Most importantly, in an actual experiment not $\Gamma_{cr} = \alpha_{cr}/c_{cr}$ but $\Gamma = \alpha/c$ is measured and sometimes noncritical contributions can dominate (for an example see below). To verify Eqs. (8) and (9) in a situation where c_{cr} is subleading, one would have to subtract carefully the noncritical contributions to the specific heat.

Generally, the scaling ansatz (3) holds only below the upper critical dimension ($d + z < 4$ within Φ^4 theories). At the upper critical dimension, logarithmic corrections to scaling arise. Above the upper critical dimension, the scaling argument can be spoiled by the presence of so-called "dangerously irrelevant operators": the free energy is a singular function of irrelevant variables. Explicit calculations (see below) for the case of an SDW transition [6,7] show that on the paramagnetic side the irrelevant operator at most leads to logarithmic corrections.

A more subtle question is whether one of the basic assumptions underlying the scaling approach (3) holds: Is there a single diverging time scale close to the QCP? For example, in a nearly magnetic metal the answer to this question is not obvious as there are at least two types of low-energy degrees of freedom: magnetic fluctuations and fermionic quasiparticles [9–11]. This can indeed lead to a breakdown of simple scaling relations as shown, e.g., by Belitz *et al.* [9]. In the case of a *local* critical point induced by a (nonlocal) magnetic transition, as has been suggested by one of the authors in [8], two scaling dimensions need to be considered: one associated with the tuning of the long-wavelength fluctuations and the other with the tuning of the local fluctuations.

SDW transitions.—We now turn to more specific calculations at SDW quantum critical points, for two reasons. First, they allow us to address a number of questions concerning the scaling results: How do corrections to scaling arise at the upper critical dimension? Are the scaling results valid above this dimension? What happens, if the prefactor $d - y_0 z$ in Eqs. (9) and (11) vanishes? Second, our calculations are important for the purpose of assessing the relevance of SDW QCPs to the magnetic quantum phase transitions in heavy fermion compounds.

Our starting point is the Ginzburg-Landau-Wilson functional of Hertz [6]:

$$S[\phi] = \sum_{\mathbf{q}, i\omega_n} \left(\delta + q^2 + \frac{|\omega_n|}{\Gamma_q} \right) |\boldsymbol{\phi}_{\mathbf{q}, i\omega_n}|^2 + S^{(4)},$$
$$S^{(4)} = u \int_0^\beta d\tau \int d^d\mathbf{r} [\boldsymbol{\phi}(\mathbf{r}, \tau)]^4, \quad (13)$$

with $\Gamma_q = \Gamma_0 q^{z-2}$, where $z = 2$ for an antiferromagnetic SDW transition in a metal. The $z = 3$ theory may be used to describe the critical end point of a metamagnetic first order transition [12] in $d = 2, 3$. In the case of a ferromagnetic QCP in $d = 3$, the model (13) with $z = 3$ is valid only up to logarithmic corrections and breaks down in $d = 2$ [13]. For commensurate 2D magnetism coupled to 2D fermions, there are additional singularities in the fermion-collective-mode coupling [11]; these singularities are absent when the fermions are taken to be 3D [14]. Following the renormalization group scheme adopted by Millis [7,15] we have calculated the thermal expansion and the Grüneisen ratio for $d = 2, 3$ and $z = 2, 3$ on the nonmagnetic side of the phase diagram, $\delta \geq \delta_c$. Details of the calculation will be reported elsewhere.

The results are summarized in Tables I and II. Up to logarithmic corrections, the results obey the scaling forms (3)–(11) with $\nu = 1/2$, $y_0 = 1$. Note that for $d = z$ the prefactor in (7) and (9) and (11) vanishes. The $1/r$ dependence of α_{cr} for $d = z$ arises from a $T^2 \log 1/r$ correction to F_{cr} not captured by scaling. For the quantum critical regime in $d = 1/\nu = 2$, the thermal expansion is logarithmic. The argument of the logarithm is a power of T for $d + z > 4$ and is itself logarithmically dependent on T for $d + z = 4$; these features reflect the dangerously irrelevant or marginal nature of the quartic coupling u.

In addition to the critical contributions, the measured quantities also contain noncritical background components. We list here the full results for the purpose of comparisons with experiments in heavy fermion compounds undergoing an antiferromagnetic transition

TABLE I. Results for SDW-QCPs in the Fermi liquid regime $r = \delta - \delta_c \gg T^{2/z}$. For a pressure tuned QCP, one obtains $\Gamma_{cr} = (dr/dp)\Gamma_{r,cr}/V_m$ using $r = (p - p_c)/p_c$, and $\Gamma_{H,cr} = (dr/dH)\Gamma_{r,cr}$ for $r = (H - H_c)/H_c$. Nonuniversal prefactors of α_{cr} and c_{cr} are not shown. The prefactors of Γ_{cr} and $\Gamma_{H,cr}$ are (up to the logarithmic correction for $d = z$) universal. Note that for $d = 3$, $z = 2$ the specific heat is dominated by a noncritical contribution $c_p \sim T$.

	$d = 2$, $z = 3$	$d = 3$, $z = 2$	$d = 3$, $z = 3$	$d = 2$, $z = 2$
$\alpha_{cr} \sim$	$Tr^{-3/2}$	$Tr^{-1/2}$	Tr^{-1}	Tr^{-1}
$c_{cr} \sim$	$Tr^{-1/2}$	$-Tr^{1/2}$	$T \log\frac{1}{r}$	$T \log\frac{1}{r}$
$\Gamma_{r,cr} =$	$(2r)^{-1}$	$-(2r)^{-1}$	$(r \log\frac{1}{r})^{-1}$	$(r \log\frac{1}{r})^{-1}$

TABLE II. Results for SDW-QCPs in the quantum critical regime $r = \delta - \delta_c \ll T^{2/z}$ (cf. Table I).

	$d = 2$, $z = 3$	$d = 3$, $z = 2$	$d = 3$, $z = 3$	$d = 2$, $z = 2$
$\alpha_{cr} \sim$	$\log\frac{1}{T}$	$T^{1/2}$	$T^{1/3}$	$\log\log\frac{1}{T}$
$c_{cr} \sim$	$T^{2/3}$	$-T^{3/2}$	$T \log\frac{1}{T}$	$T \log\frac{1}{T}$
$\Gamma_{r,cr} \sim$	$T^{-2/3} \log\frac{1}{T}$	$-T^{-1}$	$(T^{2/3} \log\frac{1}{T})^{-1}$	$\frac{\log\log\frac{1}{T}}{T \log\frac{1}{T}}$

($z = 2$). Consider first $d = 3$. At the QCP ($r = 0$),

$$\alpha = a_1 T^{1/2} + a_2 T, \tag{14}$$

where the a_2 term comes from the (fermionic) background contribution. However, approaching the QCP in the Fermi-liquid regime

$$\alpha = (a_1/r^{1/2} + a_2)T. \tag{15}$$

For $d = 2$ and $z = 2$, we have at the QCP ($r = 0$)

$$\alpha = a_1 \log\left[b \log\frac{T_0}{T} \right] + a_2 T, \tag{16}$$

and, in the Fermi-liquid regime approaching the QCP,

$$\alpha = (a_1/r + a_2)T. \tag{17}$$

In two dimensions, the thermal expansion at $r = 0$ diverges in the zero-temperature limit in sharp contrast to the textbook statement that $\alpha(T \to 0) = 0$. Still, it is straightforward to show that our results satisfy the third law of thermodynamics. As $\alpha = -(1/V)\partial S/\partial p$, we can write, for generic pressure,

$$S(p, T) = S(p_c, T) - \int_{p_c}^{p_*} \alpha V \, dp - \int_{p_*}^{p} \alpha V \, dp, \tag{18}$$

where p_* characterizes the crossover between the QC and FL regimes. $S(p, T \to 0) \to 0$ due to a vanishing integration region $[(p^* - p_c) \propto T]$ over which α is divergent.

We now briefly discuss the experimental implications of our results. Many heavy fermion compounds have long been known to show a Grüneisen ratio that increases to a very large value as temperature is lowered [5,16]. Experiments are also becoming available in the heavy fermion metals tuned to an antiferromagnetic quantum critical point, making possible a systematic comparison with our theory [17]. It is hoped that the present paper will stimulate similar measurements in other kinds of (real and putative) quantum critical materials.

In conclusion, we argue that the Grüneisen ratio and the magnetocaloric effect are divergent at any QCP. In addition, they can be used to measure the scaling dimensions and to check the very existence of a quantum critical point.

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[17] Since the first submission of this manuscript, the divergence of the Grüneisen ratio predicted here has been observed in two quantum critical heavy fermions [$CeNi_2Ge_2$ and $YbRh_2(Si_{0.95}Ge_{0.05})_2$]: R. Küchler *et al.*, following Letter, Phys. Rev. Lett. **91**, 066405 (2003).