Kinks in the Electronic Specific Heat

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We find that the heat capacity of a strongly correlated metal presents striking changes with respect to Landau Fermi-liquid theory. In contrast with normal metals, where the electronic specific heat is linear at low temperature (with a T^3 term as a leading correction), a dynamical mean-field study of the correlated Hubbard model reveals a clear kink in the temperature dependence, marking a rapid change from a low-temperature linear behavior and a second linear regime with a reduced slope. Experiments on LiV_2O_4 support our findings, implying that correlated materials are more resistive to cooling at low T than expected from the intermediate temperature behavior.

If we trace from low to high temperatures the specific heat capacity $c_V = \partial E/\partial T$ of a solid, it provides for a rich variety of information. For a metal it increases linearly, $c_V = \gamma_0 T$, with the prefactor γ_0 proportional to the density of the electronic states, i.e., $\gamma_0 \sim N(E_F)$. This result is also valid for correlated systems that maintain a normal metallic behavior. In this case we can rely on Landau's normal Fermi-liquid (FL) theory [1], which describes the low-energy excitations of correlated (interacting) electrons as "quasiparticles" (QP) which are adiabatically connected to the noninteracting electrons. As a result, only a QP renormalization factor Z_{FL} needs to be included in comparison to noninteracting electrons so that $c_V = \gamma_{FL} T$ with $\gamma_{FL} = \gamma_0/Z_{FL}$. This description is so universally applicable that special attention is paid to any deviation occurring in the vicinity of special points (e.g., quantum critical points [2], where the specific heat shows a logarithmic T dependence). Turning back to the normal case, the common understanding [3] is that the next electronic contribution to the specific heat is cubic, $\sim T^3$. This is of the same order as the contribution from the lattice degrees of freedom, where the prefactor is given by the stiffness of the lattice and the mass of its ions. This makes the "lattice" prefactor much larger than the electron contribution, so that the cubic phonon contribution is usually dominant [4]. At higher temperature, finally, the specific heat saturates with a value proportional to the number of degrees of freedom in the system (law of Dulong and Petit).

In this Letter we show that the above described common understanding of the low-temperature specific heat of a metal needs to be markedly corrected, if the movement of the electrons is strongly correlated because of their mutual Coulomb interaction. Our finding is based on numerical solution of the Hubbard model using dynamical mean-field theory (DMFT), combined with a field theory formula for the specific heat calculation given by Abrikosov *et al.* [3]

and recent results for the energy-momentum dispersion relation [5,6].

As mentioned above, the starting point of our consideration is the half-filled single-band Hubbard model, the minimal model which describes strongly correlated electrons on a lattice. This model is solved numerically using DMFT [7,8] for a semicircular DOS with bandwidth W, and exact diagonalization (ED) [9] as impurity solver with 7 energy levels in the bath.

Figure 1 shows the total energy E_{tot} as a function of T and the specific heat c_V obtained through numerical differentiation for a ratio Coulomb interaction (U) to bandwidth (W) of $U/W = 0.8$ (top panels) in the temperature
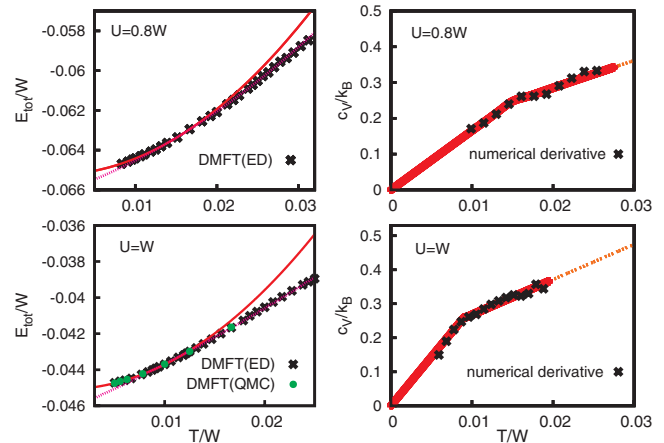

FIG. 1 (color online). Kinks in the electronic specific heat (right) for $U/W = 0.8$ (upper panel) and 1.0 (lower panel). The left panels show the DMFT(ED) results for the total energy E_{tot} from which the specific heat has been obtained as a numerical derivative after a spline interpolation. Also shown are two parabolic fits (see text) valid for $T < T^*$ (red solid line) and $T > T^*$ (violet dotted line) and the DMFT(QMC) results of Ref. [12] (green dots).

range where $c_V(T)$ is monotonically increasing [10]. Thanks to the extremely dense temperature mesh, our results clearly show a rapid but continuous change of slope (kink) of c_V at $T^* \sim 0.015W$, a feature entirely unexpected for a normal FL [3]. This kink becomes more and more pronounced when electronic correlations are further enhanced by increasing the Coulomb interaction (we show in the bottom panels of Fig. 1 the case of $U/W = 1$), i.e., when moving towards the metal-to-insulator (phase) transition. At the same time, the value of T^*, where the kink appears, is reduced, displaying a clear relation with the increasing correlations which reduce Z_{FL}.

A proper fit to the numerical data hence needs to consist of two slopes (renormalization factors) γ_{FL} and γ_2 instead of a single one: $c_V = \gamma_{FL}T$ for $T < T^*$ and $c_V = B + \gamma_2 T$ for $T > T^*$ with a rather sharp crossover in between. This has been achieved through fitting $E_{tot}(T) = [E_{tot}(0) + \gamma_{FL}T^2/2]f(T - T^*) + (E_{tot}(T^*) + BT + \gamma_2 T^2/2) \times [1 - f(T - T^*)]$ using a Fermi-function-like change $f(x) = 1/(1 + e^{\tilde{\beta}x})$ for the crossover at T^*. Note that this fit (solid red line in left panels of Fig. 1) is valid in the temperature range where $c_V(T)$ is monotonically increasing, i.e., approximately $0 < T \lesssim 2T^*$. To assess the reliability of our impurity solver, we compared our results with precise DMFT(QMC) data [12] (green dots in Fig. 1, second row, first panel). The comparison of the total energy shows an excellent agreement with our DMFT (ED) calculations. Notice that a direct observation of the kinks in DMFT(QMC) may require a much finer grid in the temperature regime considered. In our opinion, however, a first hint for a kink is already provided by the Taylor expansion of $c_V(T)$ in Ref. [12]: The coefficients of the higher order terms become huge, an indication that the Taylor expansion is not appropriate as in the presence of a kink.

To support our finite-T numerical findings, we carry out an analytical theory for the surprising appearance of kinks in correlated systems, which relies on the knowledge of the $T = 0$ Green function. The analytical approach is based on a formula by Abrikosov, Gor'kov, and Dzyaloshinski (AGD) for the entropy of a fermionic system at low temperatures [3]. The AGD formula allows us to compute the entropy using the low-frequency behavior of the self-energy $\Sigma(\omega)$ at zero temperature; therefore, it connects the dynamical information (frequency dependence) to the thermal response (temperature dependence). More precisely, it relates the low-T behavior of the entropy (and consequently of the specific heat) to the poles of the $T = 0$ retarded Green function, which in turn follows from the self-energy on the real axis. A correlated system is expected to show a kink for a frequency $\omega^* \ll W$ in the $T = 0$ self-energy under generic conditions [6]. Also experimentally, kinks in the angular-resolved photoemission spectrum have been observed for several strongly correlated materials such as cuprates [13], vanadates [14], and ruthenates [11,15].

For a normal metal, the AGD formula reproduces the standard Fermi-liquid result $\gamma = \gamma_0/Z_{FL}$, with $Z_{FL} = [1 - \frac{\partial\Sigma(\omega=0)}{\partial\omega}]^{-1}$. In this Letter we show that AGD formula also works beyond this linear Fermi-liquid regime, and it actually describes a kink in the specific heat at a temperature T^*, if the proper "kinky" $T = 0$ self-energy for a correlated electron system is used.

Let us now prove this result. The specific heat can be expressed via the entropy as $c_V(T) = T\frac{dS}{dT}$. For a metallic system at low T, the entropy is computed according to AGD [3] as

$$S(T) = \frac{1}{2\pi i T} \int_{-\infty}^{\infty} d\epsilon N(\epsilon) \int_{-\infty}^{\infty} d\omega\, \omega \frac{\partial f(\omega)}{\partial \omega}$$
$$\times [\log G_R^{-1}(\epsilon, \omega) - \log G_A^{-1}(\epsilon, \omega)], \qquad (1)$$

where $N(\epsilon)$ is the noninteracting DOS [we use a semicircular DOS $N(\epsilon) = \frac{4}{\pi D^2}\sqrt{D^2 - \epsilon^2}$] with bandwidth $W = 2D$, $f(\omega) = \frac{1}{e^{\omega/T}+1}$ is the Fermi-Dirac distribution function, and $G_{R/A}(\epsilon)$ the retarded/advanced $T = 0$ Green functions, respectively. Equation (1) has been obtained in Ref. [3] by a low-T expansion of the self-energy. Introducing the auxiliary dimensionless variable $y = \omega/T$ ($k_B \equiv 1$), and performing a straightforward derivative with respect to T, the specific heat is eventually computed as

$$c_V(T) = T\frac{dS(T)}{dT}$$
$$= T\frac{1}{2\pi i} \int_{-\infty}^{\infty} d\epsilon N(\epsilon) \int_{-\infty}^{\infty} dy\, y\, \frac{e^y}{(e^y + 1)^2}$$
$$\times \left[G_A(\epsilon, yT)\frac{d}{dT}G_A^{-1}(\epsilon, yT) - G_R(\epsilon, yT) \right.$$
$$\left. \times \frac{d}{dT}G_R^{-1}(\epsilon, yT) \right]. \qquad (2)$$

In the case of a FL, where just one renormalization factor Z_{FL} is present for the low-frequency behavior of the self-energy, the standard FL formula [$c_V(T) = \gamma_0/Z_{FL}T$] is easily recovered. The same Eq. (2), however, yields completely different results for strongly correlated metals: When the interactions are strong enough, the spectral function displays a typical "three-feature" structure (the QP peak, and the two Hubbard subbands), which survives to moderate doping. In this situation two distinct renormalization factors can be identified in the low-frequency regime with a kink in the real part of $\Sigma(\omega)$ in between [6]. Specifically, Ref. [6] shows that while the lowest frequencies follow the FL behavior $\text{Re}\Sigma(\omega) = (1 - 1/Z_{FL})\omega$ there is a rapid (but continuous) change of slope (kink) in $\text{Re}\Sigma(\omega)$ at frequency $\omega^* \ll W$ [e.g., $\omega^* \simeq (\sqrt{2} - 1)Z_{FL}W/2$ in the case of the semicircular DOS]. For larger frequency, $\text{Re}\Sigma(\omega) = -b + (1 - 1/Z_{CP})\omega$ with a reduced slope $Z_{CP} > Z_{FL}$ (typically by about a factor 2), see the inset of Fig. 2 and Ref. [6]. The constant $b = (1/Z_{FL} - 1/Z_{CP})\omega^*$ ensures the continuity of $\Sigma(\omega)$.
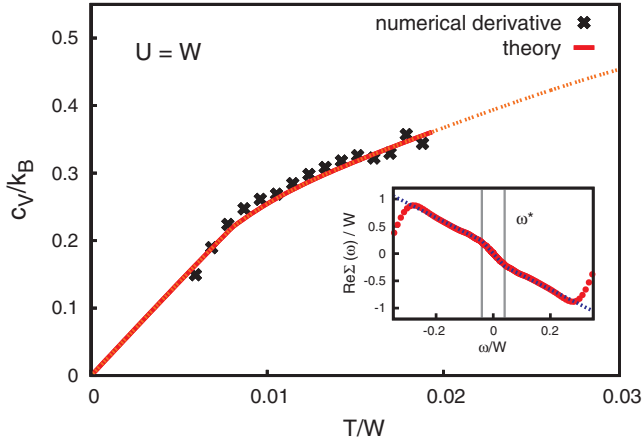
FIG. 2 (color online). Analytical theory describing kinks in the specific heat (red solid line) on the basis of the AGD formula (see text). The blue dashed line in the inset was fitted to the (red) numerical renormalization group data of Ref. [16]; note that the deviation at larger frequencies ω does not significantly affect the specific heat in the plotted temperature range. The agreement of the analytical calculation with our numerical results (black crosses) is excellent.

As a consequence of this self-energy kink, the Green functions and their temperature derivatives appearing in Eq. (2) have to be written separately for the two regimes, namely $G_R = (yT/Z_{FL} - \epsilon + i0^+)^{-1}$ and $\frac{d}{dT}G_R^{-1}(\epsilon, yT) = y/Z_{FL}$ for $\omega < \omega^*$, while for frequencies larger than ω^* one has $G_R = (yT/Z_{CP} - \epsilon + b + i0^+)^{-1}$ and $\frac{d}{dT}G_R^{-1}(\epsilon, yT) = y/Z_{CP}$ with $Z_{CP} > Z_{FL}$. The parameters have been extracted from fitting $\Sigma(\omega)$ of Ref. [16] (the use of the numerical renormalization group as an impurity solver allowing for very accurate low-frequency results). In the inset of Fig. 2 we show $\Sigma(\omega)$ and the fit (blue dashed line). We recall in passing that it is Z_{CP} which controls the width of the "quasiparticle" peak in the interacting DOS, while Z_{FL} characterizes only the asymptotic properties in the limit $\omega \to 0$ (or $T \to 0$) [6].

The evaluation of Eq. (2) is performed by splitting explicitly the integral over y in the two regions:

$$c_V(T) = T\left[\frac{1}{Z_{FL}}\int_{|y|<\frac{\omega^*}{T}} N\left(\frac{yT}{Z_{FL}}\right)\right.$$
$$\left. + \frac{1}{Z_{CP}}\int_{|y|>\frac{\omega^*}{T}} N\left(\frac{yT}{Z_{CP}} + b\right)\right]dy\,\frac{y^2 e^y}{(e^y + 1)^2}. \quad (3)$$

This equation is the final result of our analytical calculation. It allows us to compute, through a simple integral, the specific heat from the noninteracting density of states $N(E)$, the two renormalization factors Z_{FL} and Z_{CP}, and the kink frequency ω^*. Using the parameters extracted from Ref. [16] we obtain the solid line shown in Fig. 2. It is easy to verify that the standard Fermi-liquid behavior is recovered from Eq. (3) in the limit of large ω^* (i.e., when only one low-frequency scale is present). In the opposite limit $\omega^* \to 0$ a standard Fermi-liquid behavior is also

recovered, though with a different renormalization factor $\gamma = \gamma_0/Z_{CP}$. More interesting is the intermediate situation we are considering here, when ω^* lies in the low-frequency range. In this case, the specific heat behavior shows a kink at a temperature $T^* \propto \omega^*$ (with a proportionality factor of about $1/5$ for the case of the semicircular DOS): As one can see in Fig. 2 the standard FL behavior $c_V(T) = \frac{\gamma_0}{Z_{FL}}T$ is recovered only for $T < T^*$, while at $T = T^*$ a sharp change of slope is observed. For $T > T^*$, the specific heat is still essentially linear, but with a completely different slope (determined by the value of Z_{CP} and the coefficient b). Eventually, the AGD formula loses its validity at higher T, where the maximum of c_V is reached (see again [10]).

We emphasize that the AGD formula reproduces the finite low-T DMFT(ED) solution not only qualitatively but also at a quantitative level. This allows us to precisely relate the value of T^* with ω^* and, hence, with the characteristic parameters of the system [e.g., the estimate $T^* \sim 1/10(\sqrt{2} - 1)Z_{FL}W$ works well for the case of a semicircular DOS]. The agreement with the AGD formula is particularly remarkable if we notice that, strictly speaking, the AGD formula is only applicable to the linear-T regime, since it does not include all additional terms leading to the aforementioned T^3 contribution. However, this term is small at low temperatures. Hence, if the correlation is strong enough, it can push the kink in the very small T regime, where the AGD formula is expected to work. This explains why our analytical calculation is able to reproduce our numerical results to a very good accuracy in Fig. 2. Let us emphasize that it was not at all clear *a priori* whether an AGD-like calculation was possible beyond the regime of Landau's QP, i.e., after the kink in the energy-momentum dispersion which indicates the basic excitations are no longer Landau QP.

The theoretical evidence of a low-temperature kink in the electronic specific heat of strongly correlated systems poses the question of its experimental observation, which was—so far—still lacking. The main problem is obviously the phonon contribution $c_V \sim T^3$ which—because of its large prefactor—usually overshadows the much smaller electronic contribution to the specific heat, already at temperatures of few 10 K. This restricts the choice to materials which show the kink at a very low T^*. That means in turn compounds with a strong renormalization ($Z_{FL} \ll 1$), i.e., heavy Fermion systems. Given our starting point, the Hubbard model, the ideal material is LiV_2O_4, the first d-electron system where heavy Fermion behavior was found [17]. Indeed, recent LDA + DMFT calculations [18], which take into account the realistic three-d-band structure of LiV_2O_4, have demonstrated that an effective description in terms of the single-band Hubbard model (very close to half-filling) is particularly appropriate for this compound.

In Fig. 3, we show that our theory nicely describes the experimental results for LiV_2O_4. We compare the data of Ref. [19] (displayed in a magnified low-T range with

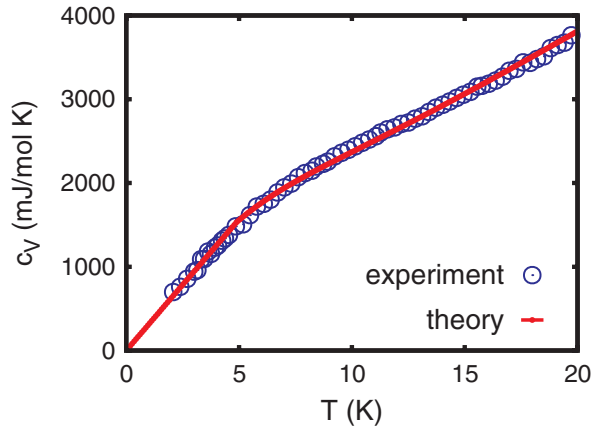FIG. 3 (color online). Kink in the low-temperature specific heat of LiV_2O_4 (open blue circles) visible at $T^* \sim 5$–6 K, and well reproduced by our analytical theory (red solid line).

respect to the original publication) with our analytical formula, fitting the free parameters to the experimental data. Indeed, a kink is clearly visible, as at the curve rapidly changes its slope at a temperature T^* of 5–6 K. The three fitting parameters ($Z_{FL} = 0.054$, $Z_{CP} = 0.092$, $\omega^* = 0.0035W$ with $W = 600$ meV for LiV_2O_4) assume very reasonable values. This clearly confirms the strong-correlation origin of the kink in the specific heat of this material.

We notice there are also kinks in the specific heat of f-electron heavy Fermions such as $YbRh_2Si_2$ [20] or $YbCu_{5-x}Al_x$ [21]. However, these materials are close to a quantum critical point, at which additional physical processes become important. In some systems also long range magnetic order leads to additional structures in the specific heat. Hence, at present, it is less clear how far these kinks are connected to our theory. Another material with strongly correlated Fermions showing similar kinks in the specific heat is ^{3}He (Refs. [22,23]) for which, however, the application of a lattice model such as the Hubbard model represents certainly quite a crude approximation.

In conclusion, we have demonstrated numerically, analytically, and experimentally that the textbook knowledge of the electronic specific heat at low temperatures needs to be modified for strongly correlated electrons. In the proximity of the Mott transition the leading correction to the linear Fermi-liquid temperature behavior is a quite rapid change of slope, i.e., a *kink*, which takes place well before (at smaller T) the standard T^3 behavior becomes relevant. Let us emphasize the reported kink is a generic feature of strongly correlated electron systems, in very contrast to existing theories for kinks stemming from the coupling to (potentially present) bosonic degrees of freedom. Since the slope of the specific heat is reduced after the kink, the behavior of c_V/T is just opposite to what one would expect from the standard theory; i.e., c_V/T is decreasing with

increasing temperature instead of the expected increase due to the cubic term. Hence, if one extrapolates from the behavior at intermediate temperatures (i.e., after the kink) without taking into account the kink, a much lower specific heat at low temperatures is obtained with respect to the actual result. In other words, a material with strongly correlated electrons can be unexpectedly resistant against cooling at low temperatures. Moreover, depending on the temperature range considered in the experiments, only one of the two regimes of linear behavior of $c_V(T)$ may be accessible. This can easily lead to remarkable inconsistencies in the analysis of the experimental data for strongly correlated materials.

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