Thermodynamics of the Kondo Model

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The exact thermodynamic equations of the Kondo model are solved in the scaling regime and the impurity magnetization, susceptibility, and specific-heat curves are obtained as functions of the temperature for different magnetic fields. This is done for the case where the impurity has spin $\frac{1}{2}$, 1 and $\frac{3}{2}$.

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The Kondo Hamiltonian describes magnetic impurities dissolved at very low concentrations in a nonmagnetic metal and interacting with the conduction electrons via spin exchange interaction. It has attracted a great deal of interest, especially from theorists. Fundamental properties such as scaling and crossover behavior from a weak-coupling to a strong-coupling regime as the temperature is lowered were shown a decade ago.[1] The zero-field susceptibility as a function of temperature for the impurity-spin $S=\frac{1}{2}$ case was determined more recently by the use of the renormalization-group technique.[2,3]

In the present Letter we use the recent diagonalization[4,5] of the Hamiltonian and the resulting formulation of the thermodynamics[6-9] to explicitly determine various physical quantities, such as specific heat, susceptibility, and magnetization. These quantities are obtained as functions of temperature for various values of magnetic field. We consider the cases of the impurity spin $S=\frac{1}{2}$, 1, and $\frac{3}{2}$, and make a comparison of the theory with some of the large body of experimental data available.

The thermodynamics will be studied in the scaling regime. $H, T \ll D$, where $D=N_e/L$ is the density of the electrons (which also serves as a cutoff). The physics in this regime is completely parametrized by a dynamically generated scale,[1] which in our cutoff scheme[4,7] takes the form $T_0 = D\exp(-\pi/c)$ where $c = 2J/(1-\frac{3}{4}J^2)$. The scaling regime is best studied by taking the limit ($D\to\infty$, $c\to 0$, T_0 fixed) of the theory. The results thus obtained are universal and independent of the particular defining scheme.[10] The impurity free energy F^i is given for the spin-S case by

$$F^i = -(k_B T/2\pi)\int d\zeta\,\mathrm{sech}[\zeta - \ln(T_0/T)]\ln[1+\eta_{2S}(\zeta, H/T)], \tag{1}$$

where η_{2S} is the $2S$th member of the set of functions $\{\eta_n\}$, $n=1,2,\ldots,$ satisfying the following set of coupled integral equations:

$$\ln\eta_1 = -2e^{\zeta} + G\ln(1+\eta_2), \tag{2a}$$

$$\ln\eta_n = G\ln(1+\eta_{n-1}) + G\ln(1+\eta_{n+1}), \quad n\geq 2, \tag{2b}$$

with the boundary condition[11]

$$[n]\ln(1+\eta_{n+1}) - [n+1]\ln(1+\eta_n) \to 2\mu H/k_B T, \tag{2c}$$

where G and $[n]$ are integral operators with kernels $(2\pi)^{-1}\mathrm{sech}\zeta$ and $\pi^{-1}(n\pi/2)[(n\pi/2)^2+\zeta^2]^{-1}$, respectively.

The coupling constant J and the cutoff D enter the thermodynamics only through the combination defining T_0 which is the strong-coupling scale (in the spin-$\frac{1}{2}$ case) and is related to the conventionally defined Kondo temperature T_K by the ratio $W = T_K/T_0 = 1.290\,268\ldots$.[7]

We would like to remark, however, that to discuss the problem of spin impurities with $S\geq 1$ dissolved in a metal, a preferable approach is provided by the SU($2S+1$) generalization[12] of the basic SU(2) Kondo model, rather than the use of higher *spin representation.* The SU(n) version of the Kondo model is also solvable[13,14] and its thermodynamics will be studied in the future.

Equation (2) seems almost linear in $\ln(1+\eta_n)$. We can bring out this fact and simplify numerical computation by introducing a new set of functions ξ_n defined by

$$\eta_n = (\sinh^2 nx_0/\sinh^2 x_0)\exp(2\xi_n) - 1 \tag{3}$$

in terms of which the thermodynamic equations

become

$$\xi_1 = \tfrac{1}{2}\ln[1 + 2\cosh x_0 \exp(-2e^{\zeta})\exp(2G\xi_2)], \quad (4a)$$

$$\xi_n = G(\xi_{n+1} + \xi_{n-1}) + b_n, \quad n \geq 2, \quad (4b)$$

$$\lim_{n\to\infty}\{[n]\xi_{n+1} - [n+1]\xi_n\} = 0, \quad (4c)$$

where $x_0 = \mu H/k_B T$ and

$$b_n = -\tfrac{1}{2}\ln\left[\frac{1 + (1 - e^{-2\xi_n})}{(\sinh^2 n x_0/\sinh^2 x_0 - 1)}\right]. \quad (5)$$

The functions ξ_n are monotomically decreasing and have the limits

$$\xi_n(-\infty) = \ln[\sinh(n+1)x_0/\sinh n x_0], \quad \xi_n(\infty) = 0. \quad (6)$$

As n increases, the remainder term b_n tends rapidly to zero. If the remainder terms are neglected for $n \geq N$ we can solve Eq. (4b) in a closed form as

$$\xi_N = [1]\xi_{N-1}. \quad (7)$$

The error in this approximation can be shown to be of order of $2\exp[-(N-1)|x_0|]$ when $x_0 \neq 0$ and of the order of $2/N^2$ when $x_0 = 0$. Thus by taking N to be suitably large we can achieve the desired accuracy. When $x_0 = 0$, this convergence is very slow, and hence additional effort is necessary to carry out the calculation.

The calculation was greatly expedited by converting the integral equations (4) into a set of matrix equations and the integral operators G and $[n]$ into matrix operators which were computed ahead of time and stored. The resulting matrix equations were iterated until the functions $\xi_n(\zeta, x_0)$ were determined to the desired accuracy. The free energy was determined from Eq. (1) and numerically differentiated to yield the susceptibility, specific heat, and magnetization. The accuracy of these are estimated to be better than 1% when $H = 0$, and a few percent when $H \neq 0$. The resulting graphs are displayed in Figs. 1 through 4.

In Fig. 1 we have plotted $k_B T\chi/(g\mu_B)^2$ for zero field and $S = \frac{1}{2}$, 1, and $\frac{3}{2}$ as a function of temperature. This is a measure of the effective spin of the impurity. At low temperature (strong-coupling regime) half a unit of the impurity spin is screened by the electrons.[15] For spin-$\frac{1}{2}$ impurity, this means that its magnetic moment is completely screened. As the temperature is raised we cross over to the asymptotic-freedom regime where the free result $S(S+1)/3$ is logarithmically approached. The comparison of our result with those of the renormalization-group calculation[2] shows very good agreement.

In Fig. 2 we have plotted the specific heat as a function of temperature at zero field and for $S = \frac{1}{2}$, 1, and $\frac{3}{2}$. The impurity makes its strongest contributions to specific heat around $T = T_K$. As the spin of the impurity increases, its contribution decreases. This is a manifestation of an

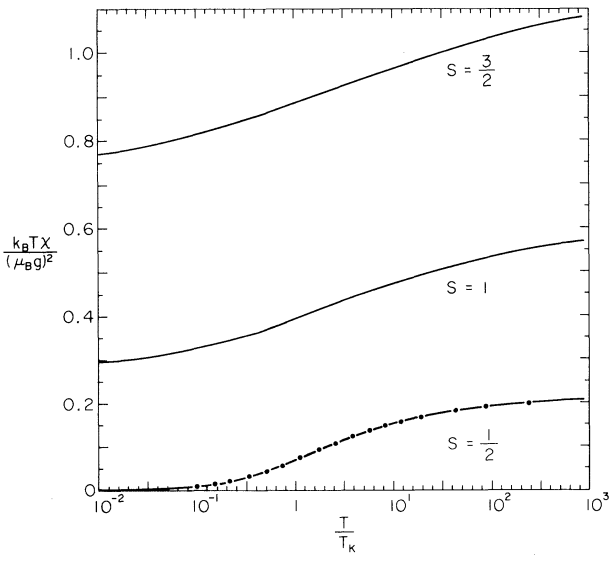

FIG. 1. $k_B T\chi/(g\mu_B)^2$ vs $\log_{10}(T/T_K)$ for $S = \frac{1}{2}$, 1, and $\frac{3}{2}$ impurities. The points are renormalization-group calculation results from Ref. 2.

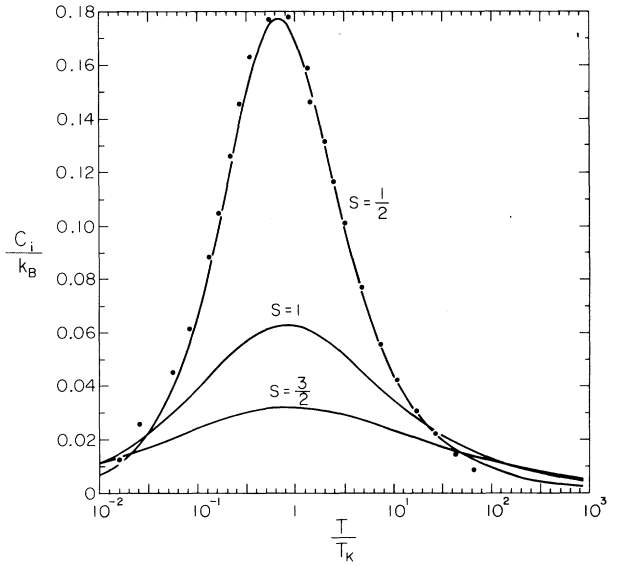

FIG. 2. C_v/k_B vs $\log_{10} T/T_K$ for $S = \frac{1}{2}$, 1, and $\frac{3}{2}$ impurities. The points are the renormalization-group calculation results from Ref. 16.

asymptotic-freedom phenomenon in the spin S with the higher-spin impurity acting more and more like a free spin.

We have also plotted the result of a recent renormalization-group calculation[16] on the graph. This calculation was done on the generalized resonance-level model which provides a long-time approximation to the Kondo model. We find the agreement to be good, though not as good as that of the renormalization-group calculation[3] of χ performed on the Kondo model itself and given in Fig. 1.

In Fig. 3 we have plotted the specific heat of the $S=\frac{1}{2}$ impurity for various values of the magnetic field. Though the curves tend to approach the free-spin Schottky anomaly $C_v{}^f/k_B = x_0{}^2\,\mathrm{sech}^2 x_0$ ($x_0 = \mu H/k_B T$) with increasing magnetic field, still, even at the value of $\mu H/k_B T_K = 9$, they differ significantly, manifesting the logarithmic nature of the corrections in the asymptotic regime.

We have also plotted experimental measurement of the specific-heat of $(La, \mathrm{Ce})\mathrm{Al}_2$.[17] The Ce ground state in this material has an effective spin of $\frac{1}{2}$, according to magnetic susceptibility measurements which suggest that the cubic crystal field splits the Ce^+ $J=\frac{5}{2}$ multiplet into an excited-state quartet and a ground-state doublet, with a splitting of ~150 K.[18] We find the material to be characterized by $T_K = 0.20 \pm 0.02$ K, which fits well the different measurements.[19] This is the only parameter which needs to be determined. In addition, we are given $g=\frac{10}{7}$. The agreement between theory and experiment is good, for both zero and nonzero fields.

In Fig. 4, we plot the impurity magnetization as a function of $\mu H/k_B T$ for $S=\frac{1}{2}$ and for various values of the magnetic field. At high temperature or high field, the magnetization approaches the free-spin value $M_f{}^i = \mu \tanh(\mu H/k_B T)$ very slowly, with logarithmic corrections characteristic of asymptotic freedom. The scales of the corrections[7] in temperature and field are, respectively, $T_K = 1.290\,368\ldots T_0$ and $T_H = (\pi/e)^{1/2} T_0$.

The experimental data plotted in Fig. 4 have been gleaned from Felsche, Winzer, and Minnegrode[20] for the magnetization of $(La, \mathrm{Ce})\mathrm{Al}_2$, with $T_K = 0.20$ K. While there is qualitative agreement with the theoretical curves, there are significant quantitative deviations, possibly due to a Van Vleck contribution from the mixing of the ground state with the excited state 150 K above the ground state.[18] If we ignore the effect of conduc-

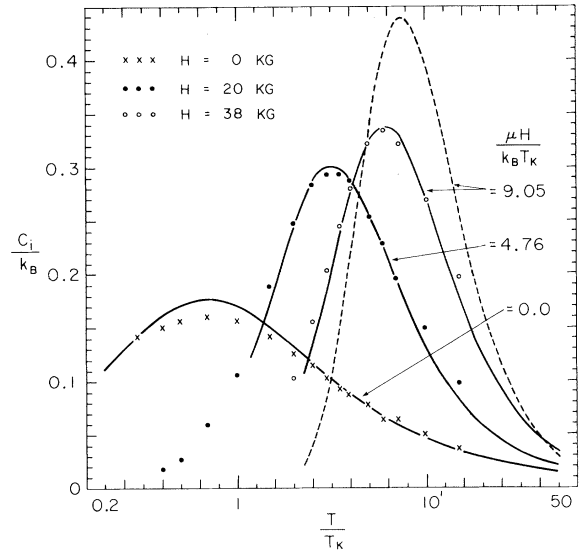

FIG. 3. The specific heat C_v/k_B vs $\log_{10} T/T_K$ for $S=\frac{1}{2}$ and magnetic field $\mu H/k_B T_K = 0.0$, 4.76, and 9.05. For $(La, \mathrm{Ce})\mathrm{Al}_2$ ($T_K = 0.20$), this corresponds to $H = 0$, 20, and 38 kG. The points are experimental results from Ref. 17. The dashed curve gives the free-spin specific heat (Schottke anomaly) for $H = 38$ kG.

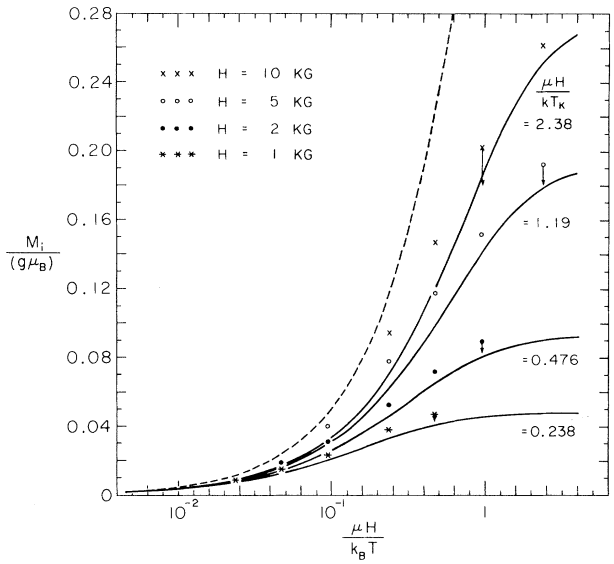

FIG. 4. The magnetization $M^i/g\mu_B$ as a function of $(\mu H/k_B T)$, for values of the magnetic field $\mu H/k_B T_K = 0.238$, 0.476, 1.19, and 2.38. For $(La, \mathrm{Ce})\mathrm{Al}_2$ ($T_K = 0.20$ and $g=\frac{10}{7}$), this corresponds to $H = 1$, 2, 5, and 10 kG. The points are experimental results from Ref. 20. The dashed curve gives the free-spin magnetization. The saturation value of $M^i/g\mu_B$ is 0.5. The arrows show the Van Vleck corrections to magnetization which are independent of temperature and are constant over each curve.

tion electrons, we can estimate the Van Vleck contribution to the magnetization to be $\sim 0.003\,\mu_B$/kG. In Fig. 4, we indicate with an arrow the appropriate temperature-independent Van Vleck contribution for each magnetic field.

In conclusion, we have been able to extract the full thermodynamics of the model and confront it with experiment. We have found agreement which is far better than one might have anticipated, given the simplified nature of the model. There is clearly a need for a new round of experiments to determine over what ranges of temperatures, fields, concentrations, and materials the Kondo effect dominates. Perhaps even more important, it should now be possible to explore a number of interesting properties of dilute alloys based on accurate measurements of *departures* from Kondo behavior.

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