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ON THE THERMODYNAMICS OF THE M-IMPURITY s–d MODEL*

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An argument is given showing that in the limit of small impurity concentrations, the statistical sum Z_{K} of the M-impurity s–d model equals $Z_{\mathrm{K}}(M) = M(Z_{\mathrm{K}r}(1) - Z_r(0)) + Z_r(0)$, where $Z_r(M)$ denotes the statistical sum of the M-impurity reduced s–d model and $Z_{\mathrm{K}r}(1)$ that of a single impurity interacting with the free electron gas and mean field of the reduced s–d model.

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The s–d exchange Hamiltonian introduced by Kasuya [1]

$$H_{\mathrm{K}}(M) = H_0 + V_{\mathrm{K}}(M) = \sum_{\boldsymbol{k}\sigma} \varepsilon_k a^*_{\boldsymbol{k}\sigma} a_{\boldsymbol{k}\sigma} - J \sum_{\alpha=1}^{M} \boldsymbol{\sigma}(\boldsymbol{R}_\alpha) \boldsymbol{S}_\alpha, \quad J < 0, \quad (1)$$

describing the interaction of conduction electrons with M spin S magnetic impurities located at $\boldsymbol{R}_1, \ldots, \boldsymbol{R}_M$ in a Dilute Magnetic Alloy (DMA) with N host atoms, has been the subject of extensive studies (*e.g.* Refs. [1–9]).

In the early eighties Andrei and Wiegmann independently diagonalized the single impurity version of this model ($M = 1$) [3–6]. The thermodynamics of $H(1)$ was studied by Andrei *et al.* in [4, 7]. They found general agreement between predictions of their theory and experimental measurements of specific heat and magnetization of DMA, in particular (LaCe)Al_2, in the vicinity of the Kondo temperature T_{K}.

Properties of DMA, in particular resistivity, specific heat, susceptibility are known to vary with impurity concentration $c = MN^{-1}$ (*e.g.* [2,10–15]). The theories developed on the grounds of the Andrei–Wiegmann solu-

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tion for H_{K} do not involve c, due to the presence of only one impurity in the model and therefore cannot account for these variations. An example of a successful theory which explains the c-dependence and temperature dependence of the properties of DMA is that of Kondo [2]. It was extended to temperatures close to 0 K in Refs. [16–18], by exploiting a reduced version $H_r(M)$ of $H_{\mathrm{K}}(M)$, which involves c, as the Hamiltonian of the unperturbed system.

Our proposal here is to use the Hamiltonian $H_r(M)$ as a means to solve the thermodynamics of $H_{\mathrm{K}}(M)$, in the limit of small c. The starting point of our considerations is a perturbation expansion of the free energy

$$f(H_{\mathrm{K}}(M,n),\beta) = -\lim_{M,n\to\infty}(n\beta)^{-1}\ln \mathrm{Tr}\exp(-\beta H_{\mathrm{K}}(M,n)), \tag{2}$$

in powers of $H_{\mathrm{K}}(M,n)$—$H_r(M,n)$ discussed in Ref. [19], n denoting the number of conduction electrons and the limit in (2) being approached at $c = MN^{-1}$ =const., $c_e = nN^{-1}$ =const. and the density of conduction electrons $d = n|\Lambda|^{-1}$ =const. The expansion of $f(H_{\mathrm{K}}(M,n),\beta)$ in powers of $H_{\mathrm{K}}(M,n) - H_r(M,n)$ in this limit simplifies to an expansion in powers of V_{K}.

The reduced Hamiltonian $H_r(M,n) = H_0(n) + V_r(M,n)$, where

$$V_r(M,n) = -\frac{J}{N}\sum_{\alpha=1}^{M}\sum_{i=1}^{n}\boldsymbol{S}_\alpha\cdot\boldsymbol{\sigma}_i\chi(p_i)A(n)\,, \tag{3}$$

with

$$\chi(p) = \begin{cases} 1 & \text{for } p\in[p_{\mathrm{F}}-\Delta,\ p_{\mathrm{F}}+\Delta] = \mathcal{P} \\ 0 & \text{for } p\notin\mathcal{P}. \end{cases}$$

p_{F} denoting the Fermi momentum and $A(n)$ the antisemmetrizer with respect to conduction electron variables, was introduced in [16] on the grounds that it represents the most relevant part of $V_{\mathrm{K}}(M,n)$ in the range of low temperatures: V_r comprises only spin–flip processes which are not accompanied by momentum exchange processes. As shown by Kondo in [2], spin–flip processes and not momentum exchange processes account primarily for the anomalous resistivity of DMA in low temperatures and momentum exchange in this range of T can be discarded in the crudest approximation on the grounds of the inequalities $k_{\mathrm{B}}T \approx \varepsilon_k - \varepsilon_{k'} \ll p_{\mathrm{F}}\Delta m^{-1} \ll \varepsilon_{\mathrm{F}}$. The presence of an external magnetic field $\boldsymbol{B}$ is accounted for by the term

$$V(\boldsymbol{B}) = -\sum_{i=1}^{n}\chi(p_i)\boldsymbol{\sigma}_i\cdot\boldsymbol{B} - g'\sum_{\alpha}\boldsymbol{S}_\alpha\cdot\boldsymbol{B}\,, \tag{4}$$

which should be added to the relevant Hamiltonian.

It was demonstrated in Ref. [17] that $H_r(M,n,\boldsymbol{B}) = H_r(M,n) + V(\boldsymbol{B})$ is equivalent in the thermodynamic limit to

$$\begin{aligned} h_r(M,n,B) &= A(n)\Big(H_0(n) + g_0 \sum_{j=1}^{n} \chi(p_j)(\boldsymbol{y}_m - \boldsymbol{x}_m)\cdot\boldsymbol{\sigma}_j\Big)A(n) \\ &\quad + \gamma \sum_{\alpha=1}^{M} (\boldsymbol{z}_m + \boldsymbol{x}_m)\cdot \boldsymbol{S}_\alpha + \frac{1}{2} n\left(x_m^2 - y_m^2 - z_m^2\right) + V(\boldsymbol{B}), \quad (5) \\ \gamma g_0 &= |J| N^{-1}, \end{aligned}$$

in the sense of the equality

$$\lim_{M,n\to\infty} f(H_r(M,n,\boldsymbol{B}),\beta) = \lim_{M,n\to\infty} f(h_r(M,n,\boldsymbol{B}),\beta) = f(\boldsymbol{x}_m,\boldsymbol{y}_m,\boldsymbol{z}_m,\beta)\,, \tag{6}$$

where $\boldsymbol{x}_m, \boldsymbol{y}_m, \boldsymbol{z}_m$ are the solutions of the equations

$$\frac{\partial f}{\partial \boldsymbol{x}} = 0, \qquad \frac{\partial f}{\partial \boldsymbol{y}} = 0, \qquad \frac{\partial f}{\partial \boldsymbol{z}} = 0, \tag{7}$$

which minimize $f(\boldsymbol{x},\boldsymbol{y},\boldsymbol{z},\beta)$. The system represented by $h_r(M,n,0)$ exhibits a second order phase transition at $T_c = (\sqrt{2}k_{\mathrm{B}})^{-1}\sqrt{\delta}c|J|$, $\delta = 3\Delta c_e(cp_{\mathrm{F}})^{-1}$ accompanied below T_c by antiparallel alignment of impurity and conduction electron spins. At $T > T_c$, $h_r = H_0$, if $B = 0$.

The presence of the low temperature ferromagnetic phase of $H_r(M,n,0)$ is consistent with conclusions about the phase diagram of $H(1,n,0)$ drawn by Anderson *et al.* [20] and the presence of such phase in numerous alloys and compounds with s–d exchange *e.g.* in (LaGd)Al_2 [21, 22], PbSnMnTe [23], $CePd_2Ga_3$ [24], Ce_2Pd_2In justifying our choice of $H_r(M,n,\boldsymbol{B})$ as the unperturbed system.

The equality (6) provides the grounds for a further simplification of the perturbation expansion of $f(H_{\mathrm{K}}(M,n,\boldsymbol{B}),\beta)$. At $T > T_c$, the unperturbed system $H_r(M,n,0)$ can be replaced by virtue of Eq. (6) by H_0. The latter is diagonal in the plane wave representation $\{ukd_\alpha\}$. As a consequence all terms of the perturbation expansion (*cf.* Ref. [19])

$$\begin{aligned} Z_{\mathrm{K}}(M,n,0 &= \mathrm{Tr}\exp(-\beta H_{\mathrm{K}}(M,n,0)) \qquad (8) \\ &= \sum_{l=0}^{\infty} \mathrm{Tr}\left(\mathrm{e}^{-\beta H_0}\frac{(-1)^l}{l!}\int_0^\beta \mathrm{d}t_l \ldots \int_0^\beta \mathrm{d}t_1 T_{\mathrm{o}}[V_{\mathrm{K}}(M,t_l)\ldots V_{\mathrm{K}}(M,t_1)]\right) \end{aligned}$$

T_{o} denoting the ordering operator with respect to $t_1,\ldots,t_n$, proportional to c differ only by the factor $cN = M$ from those which arise in an analogous expansion of $Z_{\mathrm{K}}(1,n,0)$. (This simplification of the r.h.s. of Eq. (8) is due to the equality $\sum_\alpha \boldsymbol{R}_\alpha(\boldsymbol{k}d_\alpha - \boldsymbol{k}'_\alpha) = 0$ which holds for $\boldsymbol{R}_1 = \ldots = \boldsymbol{R}_M$ under the resulting restrictions on $\{\boldsymbol{k}d_\alpha, \boldsymbol{k}d'_\alpha\}$ for which the trace of expressions proportional to c is non-vanishing.) For sufficiently dilute alloys all terms of the expansion (8) proportional to powers of c higher than the first can be discarded. This approximation to $Z_{\rm K}(M,n,0)$ amounts to the same one which Kondo applied in his calculation of DMA resistivity [2]: neglect of correlations between localized spins and summation of contributions from each impurity separately.

Thus we arrive at the conclusion that in the limit of sufficiently small c

$$\begin{aligned} Z_{\rm K}(M,n,0) &\approx \operatorname{Tr}\left(\mathrm{e}^{-\beta H_0}\left(1 + cN\sum_{l=1}^{\infty}\frac{(-1)^l}{l!}\right.\right.\\ &\qquad \left.\left.\times\int_0^\beta \mathrm{d}t_l \ldots \int_0^\beta \mathrm{d}t_1 T_{\rm o}\Big[V_{\rm K}(1,t_l)\ldots V_{\rm K}(1,t_1)\Big]\right)\right)\\ &= cN(Z_{\rm K}(1,n,0) - Z_0) + Z_0\,, \end{aligned} \tag{9}$$

where $Z_0 = \operatorname{Tr}\exp(-\beta H_0)$.

In the range of small concentrations c and low temperatures *viz.* $T < T_{\rm c}$, $H_{\rm K} + V(B)$ can be split into the unperturbed part $H_{\rm u}$ and perturbation $H_{\rm p}$ ($H_{\rm K} + V(B) = H_{\rm u} + H_{\rm p}$) in the following manner:

$$\begin{aligned} H_{\rm u} &= h_r(0,n,\boldsymbol{B})\,,\\ H_{\rm p} &= V_{\rm K}(M,n) - V_r(M,n) + \sum_\alpha(\gamma(\boldsymbol{z}_m + \boldsymbol{x}_m) - g'\boldsymbol{B})\cdot\boldsymbol{S}_\alpha\,. \end{aligned} \tag{10}$$

Then an argument, analogous to the one which led to Eq. (5), yields the equality

$$Z_{\rm K}(M,n,\boldsymbol{B}) \approx cN(Z_{{\rm K}r}(1,n,\boldsymbol{B}) - Z_r(0,n,\boldsymbol{B})) + Z_r(0,n,\boldsymbol{B})\,, \tag{11}$$

where $Z_r(0,n,\boldsymbol{B}) = \operatorname{Tr}\exp(-\beta h_r(0,n,\boldsymbol{B}))$, since the vectors $\boldsymbol{x}_m - \boldsymbol{y}_m$ and $\boldsymbol{B}$ are either parallel or antiparallel, allowing to introduce a diagonal representation of $h_r(0,n,\boldsymbol{B})$ in the same plane wave basis (Ref. [25]). $Z_{{\rm K}r}$ denotes the statistical sum of a single impurity interacting with $h_r(1,n,\boldsymbol{B})$.

The equality (11) shows that the thermodynamics of the M-impurity s–d model reduces to that of the 1-impurity model in the temperature dependent mean field

$$W_r(1,n) = \gamma(\boldsymbol{z}_m + \boldsymbol{x}_m)\boldsymbol{S}_1 + g_0 A(n)\sum_{j=1}^{n}\chi(p_j)(\boldsymbol{y}_m - \boldsymbol{x}_m)\boldsymbol{\sigma}_j A(n)\,. \tag{12}$$

Diagonalization of $H_{W_r}(1,n,\boldsymbol{B}) = H_{\rm K}(1,n,\boldsymbol{B}) + W_r(1,n)$ analogous to that of $H_{\rm K}(1,n,\boldsymbol{B})$ solved by Andrei and Wiegmann, allows to evaluate $Z_{{\rm K}r}(1,n,\boldsymbol{B}) = {\rm Tr}\exp(-\beta H_{W_r}(1,n,\boldsymbol{B}))$. The presence of c in $Z_{{\rm K}r}(M,n,\boldsymbol{B})$ accounts for the variation of thermodynamics of DMA with c and the phase transition of $H_r(M,n,\boldsymbol{B})$ resembles the transition to the magnetically ordered phase observed in DMA. Full analysis of these effects will be carried out in subsequent papers.

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REFERENCES

[1] T. Kasuya, *Prog. Theor. Phys.* **16**, 45 (1956).

[2] J. Kondo, *Prog. Theor. Phys.* **32**, 37 (1964).

[3] N. Andrei, *Phys. Rev. Lett.* **45**, 379 (1980).

[4] N. Andrei, K. Furuya, J.H. Lowenstein, *Rev. Mod. Phys.* **55**, 331 (1983).

[5] P.B. Wiegmann, *Pis'ma Zh. Eksp. Teor. Fiz.* **31**, 392 (1980); P.B. Wiegmann, *JETP Lett.* **31**, 364 (1980).

[6] P.B. Wiegmann, *Quantum Theory of Solids*, Ed. I.M. Lifshits, MIR Publishers, Moscow 1982.

[7] V.T. Rajan, J.H. Lowenstein, N. Andrei, *Phys. Rev. Lett.* **49**, 497 (1982).

[8] J. Kondo, *Prog. Theor. Phys.* **40**, 683 (1968).

[9] K. Yosida, H. Miwa, *Prog. Theor. Phys.* **41**, 1416 (1969).

[10] B.B. Tripplett, W.E. Philips, *Phys. Rev. Lett.* **27**, 1001 (1971).

[11] J.P. Franck, F.D. Manchester, D.L. Martin, *Proc. R. Soc.* **A263**, 494 (1961).

[12] C. Rizzuto, *Rep. Prog. Phys.* **37**, 147 (1974).

[13] W. Felsch, K. Winzer, G.V. Minnigerode, *Z. Phys.* **B21**, 151 (1975).

[14] N.W. Ashcroft, N.D. Mermin, *Solid State Physics*, Ed. Sunders, Philadelphia, New York, Tokyo 1976.

[15] C.D. Bredl, F. Steglich, K.D. Schotte, *Z. Phys.* **B29**, 327 (1978).

[16] J. Maćkowiak, *Physica* **A199**, 165 (1993).

[17] J. Maćkowiak, *Phys. Rep.* **308**, 235 (1999).

[18] M. Wiśniewski, PhD thesis, N. Copernicus University, Toruń 1999, unpublished.

[19] J. Maćkowiak, M. Wiśniewski, *Physica* **A242**, 482 (1997).

[20] P.W. Anderson, G. Yuval, *Phys. Rev. Lett.* **23**, 89 (1969).

[21] M.B. Maple, *Solid State Commun.* **12**, 653 (1973).

[22] M.H. Bennet, B.A. Coles, *Physica* **B86–88**, 844 (1977).

[23] T. Story, R.R. Gałązka, R.B. Frankel, P.A. Wolff, *Phys. Rev. Lett.* **56**, 777 (1986).

[24] E. Bauer, G. Schaudy, G. Hilscher, L. Keller, P. Fischer, A. Dönni, *Z. Phys.* B **94**, 359 (1994).

[25] J. Maćkowiak, M. Wiśniewski, *Physica* **A212**, 382 (1994).