We note that if we expand $I(\omega+a)$ in powers of a, we obtain for the coefficient of a

$$\lim_{a\to 0}\frac{I(\omega+a)-I(\omega)}{a}=-2\int_{-D}^{0}d\epsilon_1\int_{-D}^{0}d\epsilon_2\int_{-D}^{0}d\epsilon_3 \times[(\omega-\epsilon_1)^2(\omega-\epsilon_2)(\omega-\epsilon_1-\epsilon_2+\epsilon_3)]^{-1}-J. \qquad \text{(B3)}$$

On the other hand, from Eq. (A13) we find

$$dI(\omega)/d\omega=(1/\omega)\ln^2(D/\omega)+O((1/\omega)\ln(D/\omega)), \qquad \text{(B4)}$$

so that if we set

$$H(\omega)=\int_{-D}^{0}d\epsilon_1\int_{-D}^{0}d\epsilon_2\int_{-D}^{0}d\epsilon_3 \times[(\omega-\epsilon_1)^2(\omega-\epsilon_2)(\omega-\epsilon_1-\epsilon_2+\epsilon_3)]^{-1}, \qquad \text{(B5)}$$

We find from Eqs. (B2)-(B4)

$$H(\omega)=-(2\omega)^{-1}\ln^2\frac{D}{\omega}. \qquad \text{(B6)}$$

Equations (4.3)-(4.5) follow directly upon application of Eqs. (B2) and (B6).

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Specific Heat of Dilute Magnetic Alloys*

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An integral equation derived previously from the lowest-order nontrivial decoupling of the equations of motion for the *s-d* exchange model is solved exactly. The Green's function given by this solution is well-behaved at all temperatures. An approximate expression for the correlation energy of a single impurity is derived and used to calculate the specific heat. The specific heat is found to be of the order of Boltzmann's constant per local moment in magnitude, to have a peak at one-third of the Kondo temperature, and to go to zero as $T^{0.57}$ when T approaches zero.

I. INTRODUCTION

THE low-temperature properties of dilute magnetic alloys have been the subject of intensive investigation since Kondo's discovery of the scattering anomaly in these systems.[1] In a recent paper[2] (hereinafter denoted I), one of the authors showed that the equation of motion method applied to the *s-d* exchange model yields predictions in qualitative agreement with experiment for the resistivity and magnetic susceptibility of dilute alloys. In this paper the exact solution is found to an integral equation derived and solved approximately in I. This solution permits a considerably more careful calculation of the specific heat than was possible in I, yielding a qualitatively different result which is in reasonable agreement with experiment.

The interactions among magnetic impurities provide a mechanism which can explain the excess specific heat C_v observed in many alloys. The shape of the C_v versus temperature curves predicted from this mechanism is dependent on the impurity concentration.[3] However, in some alloy systems, Cu(Fe) for example, the shape is quite concentration-independent.[4] Strong low-temperature correlations between individual impurity spins and the conduction electrons have been invoked to qualitatively explain a number of other properties of this alloy.[5] The specific-heat anomaly occurs in the right temperature range to be related to these correla-

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* The portion of this work which was performed at the University of Pennsylvania was supported by the Advanced Research Projects Agency.

[1] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 27 (1964).

[2] D. R. Hamann, Phys. Rev. **158**, 570 (1967).

[3] S. H. Liu, Phys. Rev. **157**, 411 (1967), and references therein.

[4] J. P. Franck, F. D. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961); F. J. Chatenier and J. De Nobel, Physica **32**, 1097 (1966).

[5] M. D. Daybell and W. A. Steyert, Phys. Rev. Letters **18**, 398 (1967); M. A. Jensen, A. J. Heeger, L. B. Welsh, and G. Gladstone, *ibid.* **18**, 997 (1967); C. M. Hurd, *ibid.* **18**, 1127 (1967); R. B. Frankel, N. A. Blum, Brian B. Schwartz, and Duk Joo Kim, *ibid.* **18**, 1051 (1967).

tions. This evidence seemed sufficient for us to distrust the result of I, where no excess specific heat was found.

Despite the plethora of recent theoretical papers on isolated magnetic impurities in metals, relatively few workers have studied the specific heat. Engelsberg[6] and Yosida and Miwa[7] concluded from finite order perturbation calculations that there was no observable excess C_v. Abrikosov reached a similar conclusion based on an infinite order sum of perturbation theory with anomalous pairing.[8] A specific heat anomaly around the Kondo temperature T_K might be anticipated on the basis of ground state energy calculations by several workers.[9] Nagaoka, who was the first to apply the equation of motion method to this problem,[10] calculated a C_v with a peak of order k around T_K, and going as $k(T/T_K)$ as $T\to 0$, where k is Boltzmann's constant. His calculation[11] will be discussed in detail in Sec. III.

In Sec. II, the key integral equation derived in I is solved exactly. In Sec. III, an expression for the correlation energy is derived and the results of the specific heat calculation, a portion of which was carried out numerically, are presented.

II. SOLUTION OF THE INTEGRAL EQUATION

In I, the double-time Green's function method was applied to the *s-d* exchange model and the equations of motion were truncated at the lowest nontrivial order, following Nagaoka.[10] The retarded one-electron Green's function was expressed in I, Eq. (I2.8), as

$$G_{kk'}{}^R(\omega) = (2\pi)^{-1}\left[\frac{\delta_{kk'}}{(\omega-\epsilon_k+i\delta)}+\frac{t^R(\omega)}{(\omega-\epsilon_k+i\delta)(\omega-\epsilon_{k'}+i\delta)}\right], \tag{2.1}$$

and t was identified as the one-particle t "matrix" for non-spin-flip scattering by analogy with one-particle scattering theory. The advanced functions G^A and t^A are defined similarly, with the sign of the $i\delta$'s changed. They are in fact complex conjugates of the retarded functions.

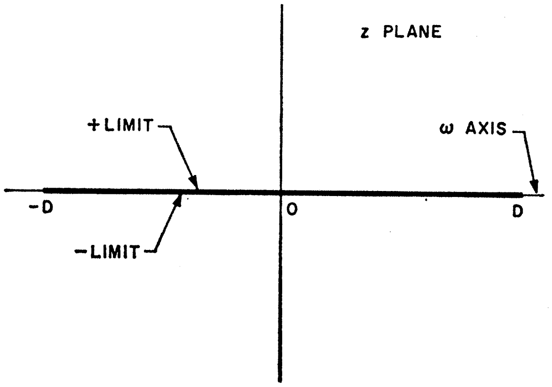

FIG. 1. The cut z plane defining the sectionally holomorphic functions introduced in Sec. II.

The truncated equations of motion were reduced to a single integral equation for t, Eq. (I2.22). This equation has been solved exactly by one of the authors for the case in which the conduction band density of states is approximated by a Lorentzian function, using methods similar to those described here.[12] In I, the equation with the Lorentzian density of states was simplified by retaining only those parts of the integral operators which contributed Fermi surface singularities of the Kondo type.[1] It was consistent with this approximation to replace the smooth Lorentzian cutoff of the integrands at energies of the order of the Fermi energy D by a sharp cutoff. The resulting Eq. (I2.29) is thus the result of an approximate treatment of a smooth density of states, and is *not* an exact consequence of Eq. (I2.22) and a square density of states. A change of dependent variable, Eq. (I2.30), to

$$\psi^R(\omega)=1-2\pi i\rho t^R(\omega), \tag{2.2}$$

where ρ is the Fermi surface density of states, simplified the equation considerably. The advanced quantity ψ^A is defined similarly, with a plus sign and t^A on the right, and is the complex conjugate of ψ^R. The integral equation for ψ^R, Eq. (I2.31), is[13]

$$\psi^R(\omega)=\left(1-S(S+1)(\tfrac{1}{2}\gamma\pi)^2+\gamma\int_{-D}^{D}d\omega'\,\frac{f(\omega')-\frac{1}{2}}{\omega-\omega'+i\delta}\right)\Big/\left(1+S(S+1)(\tfrac{1}{2}\gamma\pi)^2+\gamma\int_{-D}^{D}d\omega'\,\frac{f(\omega')-\frac{1}{2}}{\omega-\omega'+i\delta}\,\psi^A(\omega')\right), \tag{2.3}$$

where S is the magnitude of the local spin, f is the Fermi function, and $\gamma=(J\rho/N)$ is the dimensionless coupling constant, J being the *s-d* exchange. In cases of interest, γ is small and negative. The complex conjugate equation gives ψ^A. Since we believe the approximations leading to Eq. (2.3) are basically sound, and since it may be solved much more simply than the full equation,[12] we have used it as the basis of an initial specific-heat calculation.

It was noted in I that insofar as t is identified with

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[6] S. Engelsberg, Phys. Rev. **139**, A1194 (1965).

[7] K. Yosida and H. Miwa, Phys. Rev. **144**, 375 (1966).

[8] A. A. Abrikosov, Physics (to be published).

[9] K. Yosida, Phys. Rev. **147**, 223 (1966); Progr. Theoret. Phys. (Kyoto) **36**, 875 (1966); A. Okiji, *ibid.* **36**, 714 (1966); J. Kondo, Phys. Rev. **154**, 644 (1967).

[10] Y. Nagaoka, Phys. Rev. **138**, A1112 (1965).

[11] Y. Nagaoka, Progr. Theoret. Phys. (Kyoto) **37**, 13 (1967).

[12] P. Bloomfield (to be published).

[13] An equation similar to this was independently derived by D. Falk and M. Fowler, Phys. Rev. **158**, 567 (1967).

the t matrix of one-particle scattering theory, ψ is analogous to the s matrix (for non-spin-flip orbital angular-momentum zero scattering). This analogy should not be pushed too far. Away from the Fermi surface, ψ is not the s matrix since the density of states is not ρ. The identification of ψ as the s matrix is completely wrong when it is continued away from the physical region of the ω axis. The only requirement that ψ^R and ψ^A must satisfy is that they be the boundary values of two functions analytic in the upper and lower half complex planes, respectively.[14] This is sufficient to insure the consistency of the derivation of Eq. (2.3). The complete set of requirements derived in scattering theory for the s matrix, while essential for the consistency of Suhl's dispersion-theoretic formulation of this problem,[15] do not apply to our ψ.

We will solve Eq. (2.3) by analytically continuing it and its complex conjugate into the complex plane. At this point, we will introduce a few conventions which will be used in the remainder of this paper. We deal with functions defined in the z plane cut along its real axis (ω axis, Re $z=\omega$) from $-D$ to D, Fig. 1. When we write z as the argument of a function, we imply that it is defined in the whole cut plane. When we write ω as the argument of a function, we refer only to its value on the real axis between $-D$ and D. In this case we attach a superscript + or − to the function indicating that the cut is to be approached from above or below. We call functions of z which are analytic except on this cut sectionally holomorphic (SH).[16] When we refer to a function as analytic, we mean that it is analytic in the entire uncut z plane. An analytic function is also SH. The reader should carefully distinguish these conventions from those of Fowler,[17] who studied the analytic continuation of Eq. (2.3) across the cut. The singularities he discusses are on the second Riemann sheet of our cut z plane, which we will never need to consider.

Let us now introduce abbreviated notation for the quantities appearing on the right of Eq. (2.3), after first dividing the numerator and denominator by γ:

$$X(z)=\gamma^{-1}-S(S+1)(\pi/2)^2\gamma+\int_{-D}^{D}d\omega'\frac{f(\omega')-\frac{1}{2}}{z-\omega'},\quad(2.4)$$

$$\varphi_1(z)=\int_{-D}^{D}d\omega'\frac{f(\omega')-\frac{1}{2}}{z-\omega'}\psi^A(\omega'),\quad(2.5)$$

$$\varphi_2(z)=\int_{-D}^{D}d\omega'\frac{f(\omega')-\frac{1}{2}}{z-\omega'}\psi^R(\omega').\quad(2.6)$$

The three functions defined above are SH.[16] $X^+(\omega)$ is minus the function $X(\omega)$ which was used in I, and given approximately in Eq. (I3.19). In terms of these quantities, the integral Eq. (2.3) and its conjugate can be written

$$\psi^R(\omega)=X^+(\omega)/[a+\varphi_1^+(\omega)],\quad(2.7)$$

$$\psi^A(\omega)=X^-(\omega)/[a+\varphi_2^-(\omega)],\quad(2.8)$$

where

$$a=\gamma^{-1}+S(S+1)(\pi/2)^2\gamma.\quad(2.9)$$

Note the difference between a and the constant entering the right side of Eq. (2.4), which is crucial.

Now using the Plemelj formulas,[18] we can show from Eqs. (2.4)–(2.6) that

$$\varphi_1^+(\omega)-\varphi_1^-(\omega)=[X^+(\omega)-X^-(\omega)]\psi^A(\omega),\quad(2.10)$$

$$\varphi_2^+(\omega)-\varphi_2^-(\omega)=[X^+(\omega)-X^-(\omega)]\psi^R(\omega).\quad(2.11)$$

Note that the functions φ_1^- and φ_2^+ introduced here do not occur in the integral equations, but represent analytic continuations of the "physical" functions φ_1^+ and φ_2^- around the ends of the cut. If we substitute Eqs. (2.8) and (2.7) in Eqs. (2.10) and (2.11), respectively, we find

$$\varphi_1^+-\varphi_1^-=(X^+-X^-)X^-/(a+\varphi_2^-),\quad(2.12)$$

$$\varphi_2^+-\varphi_2^-=(X^+-X^-)X^+/(a+\varphi_1^+),\quad(2.13)$$

where ω is understood as the argument of all functions. If we multiply Eq. (2.12) by $(a+\varphi_2^-)$ and Eq. (2.13) by $(a+\varphi_1^+)$ and add the resulting equations, we find that all plus-minus product terms cancel, and we can write the sum as

$$[a\varphi_1^++a\varphi_2^++\varphi_1^+\varphi_2^+-(X^+)^2]$$
$$=[a\varphi_1^-+a\varphi_2^-+\varphi_1^-\varphi_2^--(X^-)^2].\quad(2.14)$$

Let us consider the function of z of which the two sides of Eq. (2.14) are boundary values. It is at least SH since it consists of sums and products of SH functions. Equation (2.14) states that it is continuous across the ω axis from $-D$ to D. Therefore it is analytic. From Eqs. (2.4)–(2.7), we see that it goes to the constant $-b^2$ at infinity, where

$$b=\gamma^{-1}-S(S+1)(\pi/2)^2\gamma.\quad(2.15)$$

Therefore it must be a constant everywhere:

$$a\varphi_1(z)+a\varphi_2(z)+\varphi_1(z)\varphi_2(z)-X^2(z)=-b^2.\quad(2.16)$$

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[14] D. N. Zubarev, Uspek. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

[15] H. Suhl, Phys. Rev. **138**, A515 (1965); Physics **2**, 39 (1965); Phys. Rev. **141**, 483 (1966); H. Suhl and D. Wong, Physics **3**, 1 (1967); H. Suhl, in *Proceedings of the International School of Physics "Enrico-Fermi," Course 37* (Academic Press Inc., New York, 1967).

[16] N. I. Muskhlishvili, *Singular Integral Equations*, translated by J. R. M. Radok (P. Noordhoff Ltd., Groningen, The Netherlands, 1953), p. 229.

[17] M. Fowler, Phys. Rev. **160**, 463 (1967).

[18] Better known as $1/(x\pm i\epsilon)=P/x\mp i\pi\delta(x)$. See Ref. 16, p. 42.

Thus we have been able to exploit the analytic structure of the integral equation to find a relation between φ_1 and φ_2.

To proceed, let us solve (2.16) for φ_2,

$$\varphi_2(z)=[X^2(z)-b^2-a\varphi_1(z)]/[a+\varphi_1(z)]. \quad (2.17)$$

Taking the minus limit of Eq. (2.17) and substituting it in Eq. (2.12), we find after a little algebra

$$\begin{aligned}&(a+\varphi_1^+)/(a+\varphi_1^-)\\ &\qquad=[X^+X^-+a^2-b^2]/[(X^-)^2+a^2-b^2], \quad (2.18)\end{aligned}$$

where all functions have argument ω. Note that

$$a^2-b^2=S(S+1)\pi^2. \quad (2.19)$$

Equation (2.18) is an example of the Riemann-Hilbert boundary problem of the theory of analytic functions. It occurs in the solution of linear singular integral equations, and has been studied extensively.[19] Let us define the right side of Eq. (2.18) as

$$H(\omega)=[X^+X^-+S(S+1)\pi^2]/[(X^-)^2+S(S+1)\pi^2]. \quad (2.20)$$

Taking logarithms of both sides of Eq. (2.18),

$$\ln(a+\varphi_1^+)-\ln(a+\varphi_1^-)=\ln H. \quad (2.21)$$

Equation (2.21) is satisfied by the SH function

$$\ln[a+\varphi_1(z)]=\ln a-(2\pi i)^{-1}\int_{-D}^{D}d\omega'\,\frac{\ln H(\omega')}{z-\omega'}, \quad (2.22)$$

which may be verified using the Plemelj formulas.[18] The constant $\ln a$ is determined by the behavior of the left side as $|z|\to\infty$. Exponentiating Eq. (2.22) we see that a SH function satisfying Eq. (2.18) is

$$a+\varphi_1(z)=a\exp\frac{-1}{2\pi i}\int_{-D}^{D}d\omega'\,\frac{\ln H(\omega')}{z-\omega'}. \quad (2.23)$$

So far, we have only established that Eq. (2.23) is a particular solution. We can multiply the right hand side of Eq. (2.23) by any analytic function (polynomial) and still satisfy Eq. (2.18). However, doing so would violate the requirement that $\varphi_1(z)\to 0$ as $|z|\to\infty$ imposed by the definition of φ_1, Eq. (2.5). There is one other possibility. Suppose the right-hand side of Eq. (2.23) goes to zero at the ends of the cut as $(z+D)^n(z-D)^m$, where n and m are positive integers. Then the function

$$U(z)=[(z+D)^n(z-D)^m]^{-1}\exp\frac{-1}{2\pi i}\int_{-D}^{D}d\omega'\frac{\ln H(\omega')}{z-\omega'} \quad (2.24)$$

is also SH, satisfies Eq. (2.18) on the cut, and has no zeros in the finite z plane. The most general SH function satisfying Eqs. (2.5) and (2.18) is

$$a+\varphi_1(z)=P^{n+m}(z)\,U(z), \quad (2.25)$$

where P^{n+m} is any polynomial of degree $n+m$ (with leading term az^{n+m} as $|z|\to\infty$). The integer $n+m$ is called the index in the study of the general Riemann-Hilbert problem.

The index is determined by the net change in Im $\ln H(\omega)$ as ω goes from $-D$ to D. From Eq. (2.4), we see that $\mathrm{Im}X^{\pm}=\mp(f-\frac{1}{2})$, and that $\mathrm{Re}X^{\pm}$ is even and diverges logarithmically to $-\infty$ as ω approaches $\pm D$. Therefore $H(\pm D)=1$, and $\ln H(\omega)$ must go to integral multiples of $2\pi i$ at these points. The numerator in Eq. (2.20) is real and positive, since $X^+=(X^-)^*$. We can establish that the real part of the denominator is positive by noting that

$$\begin{aligned}\mathrm{Re}[(X^-)^2+S(S+1)\pi^2]&=(\mathrm{Re}X^-)^2-(\mathrm{Im}X^-)^2\\ &\qquad+S(S+1)\pi^2\\ &\geq S(S+1)\pi^2-(\mathrm{Im}X^-)^2\\ &\geq\tfrac{1}{2}\pi^2. \quad (2.26)\end{aligned}$$

Therefore, the phase of H stays between $\pm\frac{1}{2}\pi$, and $\ln H(\omega)$ has the same value at $\pm D$. This proves that the index is zero, since we can fix the branch of $\ln H$ by requiring $\ln H(\pm D)=0$. Then the integral in Eq. (2.24) cannot diverge logarithmically as $z\to\pm D$, so the exponential cannot have zeros at either point, and $n=m=0$.

Since the index is zero, Eq. (2.23) is the unique solution to the boundary value problem to which the set of integral equations has been reduced. The retarded "s matrix" found by substituting Eq. (2.23) in Eq. (2.7) is

$$\psi^R(\omega)=(1/a)X^+(\omega)\,\exp(2\pi i)^{-1}\int_{-D}^{D}d\omega'\,\frac{\ln H(\omega')}{\omega-\omega'+i\delta}. \quad (2.27)$$

It is instructive to place this in another form. In Ap-

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[19] Reference 16, pp. 230–234. For a simple treatment, see R. Balescu, *Statistical Mechanics of Charged Particles* (Interscience Publishers, Inc., New York, 1963), pp. 390–405.

pendix B, we show that

$$[X^2(z)+S(S+1)\pi^2]^{1/2}=|a|\exp\frac{-1}{2\pi}\times\int_{-D}^{D}\frac{d\omega'}{z-\omega'}\operatorname{Im}\ln H(\omega'). \quad (2.28)$$

Multiplying the right side of Eq. (2.27) by unity expressed as the ratio of the two sides of Eq. (2.28), we can show

$$\psi^R(\omega)=\frac{-X^+}{[(X^+)^2+S(S+1)\pi^2]^{1/2}}\times\exp(2\pi i)^{-1}\int_{-D}^{D}d\omega'\frac{\ln|H(\omega')|}{\omega-\omega'+i\delta}. \quad (2.29)$$

The solution is now expressed as a product of the approximate solution found in I, Eq. (I3.21), and a correction factor formed by the exponential.

It is easy to find the magnitude of ψ^R using Eq. (2.29), since the principal value part of the integral only contributes to the phase. We obtain

$$|\psi^{R,A}|^2=X^+X^-/[X^+X^-+S(S+1)\pi^2]. \quad (2.30)$$

Within the parallels drawn in I between the quantities appearing in this theory and those in Suhl's theory, Eqs. (I3.27) to (I3.30), this result is identical to his.[15] Fowler conjectured that Eq. (2.30) should be true for this theory[17] by analogy with Suhl's theory.

It is important to recognize that Eq. (2.30) is not, by itself, the solution of the integral equations. Equation (2.30) only specifies this solution within a factor unimodular on the ω axis. As we have shown, the solution is uniquely specified by the integral equations.

There is a further parallel between this solution and that of Suhl's theory. The function $X(z)$ has no zeros at high temperatures. Below a particular temperature T_K (the Kondo temperature), it has a conjugate pair of zeros on the imaginary axis, which can be considered to "emerge" across the cut from the second sheet of X. It is clear from Eq. (2.27) that ψ^R acquires one of these zeros in its physical region (upper-half z plane). Suhl's early solution of his equations used an integral representation for the non-spin-flip s matrix which did not permit these zeros to emerge across the cut. This resulted in inadmissable poles in the physical region for the spin-flip scattering amplitude, which should have been canceled by the emerging zeros. Suhl and Wong overcame this difficulty by taking a factor containing these zeros out of the integral representation.[15] In our equation of motion theory, including both this treatment and the approximate treatment of I, this property emerged quite naturally.

The concept of index introduced in establishing the uniqueness of our solution Eq. (2.23) to the boundary problem Eq. (2.18) is sufficiently important to merit further discussion through an example. Falk and Fowler have shown[13] that the ansatz made by Nagaoka[10] in his treatment of the equation of motion method below T_K is in fact the solution of an integral equation obtained from Eq. (2.3) by dropping the $S(S+1)$ terms. Let us apply the present method of solution to this equation. Since the right side of Eq. (2.19) is made zero, Eq. (2.20) is replaced by

$$H_N(\omega)=X^+/X^-, \quad (2.31)$$

where we have appended the subscript N for "Nagaoka." Once again, we determine the index by examining the phase change of H_N from $-D$ to D. For high temperatures, the phase change is zero, so the index is zero. For temperatures below T_K, however, ReX goes to zero near $\omega=0$, the phase change becomes 4π, and the index becomes 2. The fundamental solution (that with no zeros) defined by Eq. (2.24) for this new boundary problem is easily shown to be

$$U_N(z)=X(z)/[(z+i\Delta)(z-i\Delta)], \quad (2.32)$$

where $\pm i\Delta$ are the positions of the zeros of X. The most general solution is now

$$a+\varphi_{1N}(z)=\frac{(z-z_1)(z-z_2)}{(z+i\Delta)(z-i\Delta)}X(z), \quad (2.33)$$

where z_1 and z_2 are arbitrary. There are only two choices of z_1 and z_2 which permit ψ^R and ψ^A to be analytic in the appropriate half planes and complex conjugates of each other, as we may establish by substituting Eq. (2.33) in Eqs. (2.16), (2.7), and (2.8). They are $z_1=i\Delta$, $z_2=-i\Delta$ and $z_1=z_2=-i\Delta$. The corresponding ψ's are

$$\psi_N^R=1, \quad (2.34)$$

$$\psi_N^R=(\omega-i\Delta)/(\omega+i\Delta). \quad (2.35)$$

The high-temperature solution is also Eq. (2.34), and implies no scattering. The alternate low-temperature solution Eq. (2.35) predicts the maximum non-spin-flip scattering permitted by unitarity at the Fermi surface, and as pointed out by Fowler, no spin-flip scattering.[17]

We see that in this case, blind use of the integral representation Eq. (2.23) might have led us to overlook the zeros in Eq. (2.33) and hence the solution Eq. (2.35). However, examining the index told us of the existence of another solution below T_K. Because the formalism we have used takes care of zeros emerging from cuts automatically, as we have shown by example, we feel confident that nothing of this sort has been missed in our solution of Eq. (2.3).

III. SPECIFIC HEAT

The average internal energy of the metal-impurity system is

$$\langle E\rangle=-4\sum_k\int_{-\infty}^{\infty}\omega f(\omega)\ \mathrm{Im}G_{kk}^{R}(\omega)\,d\omega,\qquad(3.1)$$

which can be verified using the exact equation of motion (I2.5) and the general relation between Green's functions and thermal averages Eq. (I2.7). [Actually, Eq. (3.1) represents a free energy, since single particle energies are measured from the Fermi surface.]

Following the procedure used in I to derive the integral equation, we will evaluate the k sum in Eq. (3.1) using a Lorentzian density of states of width $2D$ at half-maximum. This leads to

$$\langle E-E_0\rangle=\frac{D}{\pi}\int_{-\infty}^{\infty}\frac{\omega d\omega}{(\omega+iD)^2}[f(\omega)-\tfrac{1}{2}][1-\psi^R(\omega)],\qquad(3.2)$$

where E_0 is the energy in the absence of the impurity. In deriving the integral equation, the function $(\omega+iD)^{-2}$ was replaced by its value at the origin and a cutoff. While we believe this procedure was adequate in that context, where the integrand also had a singular factor and fell off more rapidly, it is not adequate here. To illustrate this point, let us substitute Nagaoka's solution Eq. (2.35) in Eq. (3.2) and do the integral at $T=0$. We find

$$\langle E-E_0\rangle=-2\Delta/\pi+O(\Delta^2/D).\qquad(3.3)$$

Since Δ is of order T_{K}, the second term is extremely small compared to the first. If we had replaced $(\omega-iD)^{-2}$ by its value at $\omega=0$, however, we would have missed the large first term and found only the second. Close examination shows that the large contribution comes from the product of the imaginary parts of $(\omega-iD)^{-2}$ and ψ^R. In I, this large contribution to Eq. (3.2) was overlooked in calculating the specific heat, as it was in Nagaoka's first paper on this subject.[10] In a later paper, Nagaoka redid this calculation using a less direct expression than Eq. (3.1), and found exactly the large term in Eq. (3.3).[11] Since he used a square density of states, we see that the result is insensitive to details far from $\omega=0$, despite the fact that $\mathrm{Im}\psi^R$ at large ω makes the major contribution. This is extremely important; otherwise no result for ψ based simply on the Fermi surface anomaly could be consistently used in the energy calculation.

Next we must decide whether the imaginary part of our ψ contains a term which could lead to a temperature-dependent correlation energy of the expected magnitude. We will examine the form given in Eq. (2.29). For $T_{\mathrm{K}}\ll|\omega|<D$, the coefficient of the exponential is essentially unity since $\mathrm{Re}X$ is large. From Eq. (2.20), we see that $\ln|H(\omega)|$ is small, for the same reason, except perhaps for $\omega\sim T_{\mathrm{K}}$. Here it is still small for $T>T_{\mathrm{K}}$, but is of order unity for $T<T_{\mathrm{K}}$. For the present argument, let us replace it by

$$\ln|H(\omega)|\approx A(T)\theta(T_{\mathrm{K}}-|\omega|),\qquad(3.4)$$

where θ is the unit step function, and A is a function which is unity for $T=0$ and 0 for $T>T_{\mathrm{K}}$. Then Eq. (2.29) reduces to

$$\psi^R(\omega)\approx\exp(2\pi i)^{-1}A(T)\int_{-T_{\mathrm{K}}}^{T_{\mathrm{K}}}\frac{d\omega'}{\omega-\omega'+i\delta}.$$

Now for $\omega\gg T_{\mathrm{K}}$, we can expand both the integrand and the exponential, obtaining

$$\mathrm{Im}\psi^R(\omega)\approx-T_{\mathrm{K}}A(T)/(\pi\omega).\qquad(3.5)$$

This result is similar in magnitude and form to the behavior of $\mathrm{Im}\psi_N$ at large ω. Instead of Nagaoka's $\Delta(T)$, however, we have $(2\pi)^{-1}T_{\mathrm{K}}A(T)$, which is $(4\pi)^{-1}$ times the zeroth moment of $\ln|H|$ in the approximation Eq. (3.4). The function H contains all the physics. Since only its value for $\omega\sim T_{\mathrm{K}}$ seems important in the correlation energy, we have established the consistency of our treatment. Finally, we note that the large contribution to the correlation energy comes completely from the factor correcting the solution found in I.

Having determined the sort of result we expect, let us develop a method to calculate it. Direct application of Eq. (3.2) is not easy. Neither is it advisable, since it involves ψ outside the range of the original approximation. The most expedient approximation is to let

$$\begin{aligned}(\omega+iD)^{-2}&\approx(\omega-iD)^2/D^4 &&|\omega|<D\\ &\approx 0 &&|\omega|>D.\end{aligned}\qquad(3.6)$$

This gives the same leading term as in Eq. (3.3) when applied to Nagaoka's solution. Nevertheless, making this approximation forces us to assume some degree of uncertainty in the numerical coefficient of the specific heat.

Inserting Eq. (3.6) in Eq. (3.2), and taking the complex conjugate in the integrand of this expression (which is real because of the symmetry of the integrand), we find

$$\langle E-E_0\rangle=\pi^{-1}D^{-3}\int_{-D}^{D}\omega(\omega+iD)^2[f(\omega)-\tfrac{1}{2}]\times[1-\psi^A(\omega)]d\omega.\qquad(3.7)$$

From Eq. (2.5), we see that the integrals

$$c_n=\int_{-D}^{D}\omega^{n-1}[f(\omega)-\tfrac{1}{2}]\psi^A(\omega)\,d\omega\qquad(3.8)$$

are just the coefficients in the asymptotic expansion of $\varphi_1(z)$ for $|z|\gg D$,

$$\varphi_1(z)\sim\sum_{n=1}^{\infty}\frac{c_n}{z^n}. \tag{3.9}$$

Since we intend to do exact mathematics from Eq. (3.7) on, there is nothing inconsistent about considering this asymptotic limit. The c_n are most easily found from Eq. (2.23). We can make an asymptotic expansion of the integral in the exponential,

$$\sum_{n=1}^{\infty}\frac{d_n}{z^n}\sim-(2\pi i)^{-1}\int_{-D}^{D}d\omega'\,\frac{\ln H(\omega')}{z-\omega'}, \tag{3.10}$$

where

$$d_n=-(2\pi i)^{-1}\int_{-D}^{D}\omega'^{n-1}\ln H(\omega')d\omega'. \tag{3.11}$$

Then we can write

$$a+\sum_{n=1}^{\infty}\frac{c_n}{z^n}=a\exp\sum_{n=1}^{\infty}\frac{d_n}{z^n}, \tag{3.12}$$

expand the exponential, and equate the coefficients of like powers of z. This gives [20]

$$\begin{aligned}c_1/a&=d_1,\\ c_2/a&=d_2+\tfrac{1}{2}d_1^2,\\ c_3/a&=d_3+d_1d_2+\tfrac{1}{6}d_1^3,\\ c_4/a&=d_4+d_1d_3+\tfrac{1}{2}d_2^2+\tfrac{1}{2}d_2d_1^2+(1/24)d_1^4.\end{aligned} \tag{3.13}$$

The part of Eq. (3.7) not involving ψ can be calculated essentially exactly. Our final expression for the correlation energy in terms of the c_n is

$$\begin{aligned}\langle E-E_0\rangle&=c_2/(\pi D)-2ic_3/(\pi D^2)-c_4/(\pi D^3)\\ &\quad+D/(4\pi)+7\pi^3T^4/(60D^3)-\pi T^2/(6D).\end{aligned} \tag{3.14}$$

These steps reduce the energy calculation to a straightforward numerical procedure, but it would be helpful conceptually to have a simpler expression. The function X is essentially constant over the overwhelming portion of the integration range in Eq. (3.11), and the significant temperature dependence of the integrand is concentrated in the region of small ω'. The moments d_1, d_2, d_3, and d_4 are successively less temperature-dependent since this region is weighted less and less heavily as the power of ω' in Eq. (3.11) increases. The odd moments d_2 and d_4 are calculated analytically in Appendix B and illustrate this point. The even moments d_1 and d_3 can be estimated by assuming X to be constant. These considerations indicate that a single term, the d_1d_2 term of the c_3 formula in Eq. (3.13), contributes all the important temperature dependence. Using the small γ limit

$$d_2\sim-\tfrac{1}{2}\gamma D^2, \tag{3.15}$$

we arrive at

$$\langle E-E_0\rangle\approx-(2\pi^2)^{-1}\int_{-D}^{D}d\omega\,\ln H(\omega)+c \tag{3.16}$$

where c is essentially a constant for temperatures of interest. This is exactly what one would obtain by making the identification suggested by Eq. (3.5) between the zeroth moment of $\ln H$ and Nagaoka's $\Delta(T)$ and substituting in Eq. (3.3). Therefore the crude argument in the beginning of this section is essentially correct.

A numerical computation was carried out based on Eqs. (2.20), (3.11), (3.13), (3.14) and (A8). In performing the numerical integration for the d_n, the choice of an evenly spaced mesh of points in the variable $\ln|\omega|$, with a lower limit of $\ln(0.01T)$, optimized computing efficiency. It was found impractical to study the correlation energy as a function of temperature directly because the individual terms in Eq. (3.14) are very large compared to the change sought. Instead, differentiation with respect to temperature was carried through the above-mentioned equations, and the specific heat was computed directly. The complete calculations confirm that Eq. (3.16) is a good approximation.

The specific heat was calculated for $S=\frac{1}{2}$ over a wide temperature range for three representative pairs

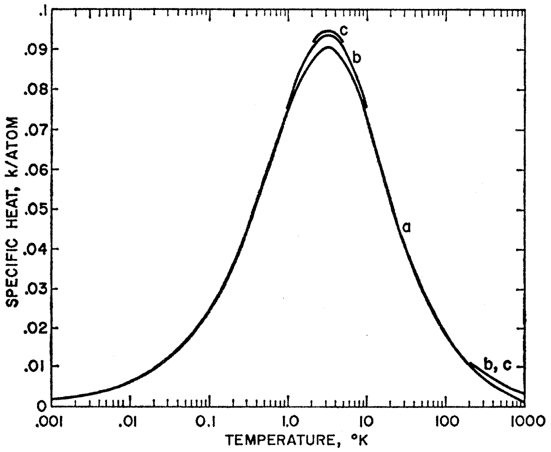

FIG. 2. The computed specific-heat results. For curve a, $T_K=10$°K, $D=2\times10^4$°K, and $\gamma=-0.125$. For curve b, $T_K=10$°K, $D=10^5$°K, and $\gamma=-0.105$. For curve c, $T_K=1$°K, $D=2\times10^4$°K, $\gamma=-0.097$, and the curve is shifted one decade to the right. The vertical scale is Boltzmann's constant per impurity.

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[20] M. Abramowitz, in *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover Publications, Inc., New York, 1965), p. 15, Eq. 3.6.23.

of values of the Kondo temperature and Fermi temperature. The results are shown in Fig. 2, plotted on a semilog scale for maximum clarity. The points from the three calculations fall essentially on a universal curve, depending only on T/T_K, except for the small deviations shown.

The C_v results have some interesting features. If they are plotted on log-log paper, the points from all three calculations form excellent straight lines from the lowest calculated T, $T/T_K=10^{-4}$, to nearly $T/T_K=10^{-1}$. The slope is 0.57, so this theory predicts

$$C_v \propto T^{0.57} \tag{3.17}$$

for T well below T_K. This is especially interesting because Anderson has recently calculated $C_v \propto T^{0.5}$ on the basis of the low-lying excitations of a new variational ground state for dilute alloys.[21] We may conjecture that our result of 0.57 will go asymptotically to 0.5 in some appropriate limit, like small γ. No such trend is evident among our computed values, but the actual range of γ is not large. Unfortunately, our computer programs are not capable of being pushed to the extreme ranges of the variables demanded by really small γ.

The area under the curve in Fig. 2 gives the entropy change between low and high temperatures which we find to be $0.45k$ per impurity, where k is Boltzmann's constant. For a spin-$\frac{1}{2}$ impurity, one might expect an entropy change of $k \ln 2 = 0.69k$, on the basis that correlations remove one spin degree of freedom from the system at low T. We believe this discrepancy is simply a matter of the numerical coefficient of our approximate energy expression Eq. (3.7). Multiplying the right side of Eq. (3.7) by $\frac{3}{2}$ would make the entropy $k \ln 2$ within the numerical accuracy of the computation.

It is not possible to integrate the C_v function to produce a single number for the correlation energy change between $T \ll T_K$ and $T \gg T_K$. The deviations of the three calculations from a universal function at high T probably represent perturbation-theory terms, and produce deviations in the energy of the order of T_K, the expected anomalous part of the correlation energy.

The specific heat was not calculated for spins larger than $\frac{1}{2}$, since the susceptibility calculation in I indicated that the compensation of larger spins is not properly described by a model which permits only orbital s-wave scattering.

IV. CONCLUSIONS

We have shown that the integral equation based on the decoupled equations of motion for the s-d exchange model with a contact exchange interaction possesses a unique solution. This solution is in agreement with that of Suhl's scattering theory in all features that we consider essential.[15]

The exact solution modifies the approximate solution found in I by a factor which can be shown to contribute essentially all the specific heat. A particular part of this factor bears a strong resemblance to Nagaoka's low-temperature approximate solution to this same problem.[10] Thus despite the inability of his solution to predict correct temperature dependences through its exclusion of spin-flip scattering,[17] it correctly describes the net change of the anomalous part of the correlation energy (that proportional to T_K) between $T \gg T_K$ and $T=0$.

Our solution has led to a very reasonable looking curve of the specific heat as a function of T/T_K. We find that its magnitude would have to be increased by a factor of approximately $\frac{3}{2}$ to bring the calculated entropy into agreement with the value expected from the removal of one spin degree of freedom.

Agreement with the measured C_v of Cu(Fe) is found within the relevant uncertainties. The susceptibility data[5] indicate a spin of between $\frac{3}{2}$ and 2 per Fe atom at high temperatures. To treat this case properly, the model must be generalized to take account of the d-like character of the exchange potential. It has been suggested that as many d-wave scattering channels saturate as $T \to 0$ as there are unpaired electron spins on the impurity, and that the channels are approximately independent.[22] This indicates that the spin $\frac{1}{2}$ result times a factor of 3 or 4 should be compared with the measured C_v. Entropy considerations indicate a factor of 2 or 2.3. The observed peak value of C_v is 2.2 times our calculated result.[4]

The entropy associated with the measured C_v is estimated as near $k \ln 2$ per Fe atom in Ref. 4. Our results indicate that the falloff of C_v well away from the peak (both above and below) is less rapid than the extrapolations used to calculate this value. A correction in this direction will reduce the discrepancy between the entropy obtained from C_v and that expected from high-temperature susceptibility measurements.

Plotted on log-log paper, the lowest temperature measurements (0.4−1.1°K) form reasonably straight lines but with widely differing slopes that do not vary systematically with concentration.[4] Therefore Eq. (3.17) cannot be adequately checked. The feature of our calculated results which seems in best agreement with the Cu(Fe) data is the position of the C_v peak at $\frac{1}{3}T_K$, using the value of $T_K=16$°K for this system inferred from resistivity measurements.[5] To be fully consistent, the resistivity should be calculated from our exact solution and fit to the data to determine T_K, but we believe that we would find a value near the quoted one.

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[21] P. W. Anderson (to be published).

[22] J. R. Schrieffer, J. Appl. Phys. **38**, 1143 (1967).

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APPENDIX A

Here we derive an expression for $X^+(\omega)$ which is essentially exact. Let

$$x^+(\omega)=\int_{-D}^{D}\frac{f(\omega')-\frac{1}{2}}{\omega-\omega'+i\delta}\,d\omega'. \tag{A1}$$

Now consider

$$x(\omega+2\pi iT)=\int_{-D}^{D}\frac{[f(\omega')-\frac{1}{2}]\,d\omega'}{\omega-\omega'+2\pi iT+i\delta}. \tag{A2}$$

Let us change the variable of integration to $\omega''=\omega'-2\pi iT$. Utilizing the periodicity of the Fermi function in the imaginary direction, we find

$$x(\omega+2\pi iT)=\int_{-D-2\pi iT}^{D-2\pi iT}d\omega''\,\frac{f(\omega'')-\frac{1}{2}}{\omega-\omega''+i\delta}. \tag{A3}$$

Now let us deform the integration contour from that indicated in Eq. (A3) and shown by a dotted line in Fig. 3 to the solid line in Fig. 3. In doing so, we pick up a contribution from one of the poles of the Fermi function on the imaginary axis and obtain

$$x(\omega+2\pi iT)=x(\omega)-\frac{2\pi iT}{\omega+\pi iT}+\int_{-D-2\pi iT}^{-D}\frac{f(\omega'')-\frac{1}{2}}{\omega-\omega''+i\delta}\,d\omega''$$
$$+\int_{D}^{D-2\pi iT}d\omega''\,\frac{f(\omega'')-\frac{1}{2}}{\omega-\omega''+i\delta}. \tag{A4}$$

To evaluate the integrals over the two end pieces of the contour we assume $T\ll D$, replace $f-\frac{1}{2}$ by $\pm\frac{1}{2}$ in the first (second) integrand, and obtain

$$x(\omega+2\pi iT)=x(\omega)-\frac{2\pi iT}{\omega+\pi iT}+\tfrac{1}{2}\ln\frac{D^2-(\omega+2\pi iT)^2}{D^2-\omega^2}. \tag{A5}$$

Now the digamma function can be considered to be defined (within a constant) by the recurrence formula[23]

$$\psi(z+1)=\psi(z)+1/z. \tag{A6}$$

Equation (A5) is a similar recurrence formula:

$$\left[-x(\omega+2\pi iT)+\tfrac{1}{2}\ln\frac{(\omega+2\pi iT)^2-D^2}{(2\pi iT)^2}\right]$$
$$=\left[-x(\omega)+\tfrac{1}{2}\ln\frac{\omega^2-D^2}{(2\pi iT)^2}\right]+\left(\tfrac{1}{2}+\frac{\omega}{2\pi iT}\right)^{-1}. \tag{A7}$$

Upon examining (A6), (A7), and the asymptotic form[24] of $\psi[\frac{1}{2}+(\omega/2\pi iT)]$, one sees that we have chosen the constant of separation $(2\pi iT)^2$ so that each of the square brackets in (A7) is a digamma function; thus

$$x(\omega)=\tfrac{1}{2}\ln\frac{(\omega-D)(\omega+D)}{(2\pi iT)^2}-\psi\left(\tfrac{1}{2}+\frac{\omega}{2\pi iT}\right). \tag{A8}$$

It is clear that Eq. (A8) describes the end-point log singularities correctly within terms of order exp $(-D/T)$. A similar expression for this integral was given by Falk and Fowler,[13] but they neglect the end-point singularities.

Using Eq. (A8) in X^+, the Kondo temperature, defined as the temperature at which $X(0)=0$, is

$$T_K=D\exp(b+0.1256), \tag{A9}$$

where b is given by Eq. (2.15).

APPENDIX B

Here we prove Eq. (2.28). First, we will show that the function

$$X^2(z)+S(S+1)\pi^2 \tag{B1}$$

has no zeros. Following Eq. (2.26),

$$\mathrm{Re}[X^2(z)+S(S+1)\pi^2]\geq S(S+1)\pi^2-[\mathrm{Im}X(z)]^2. \tag{B2}$$

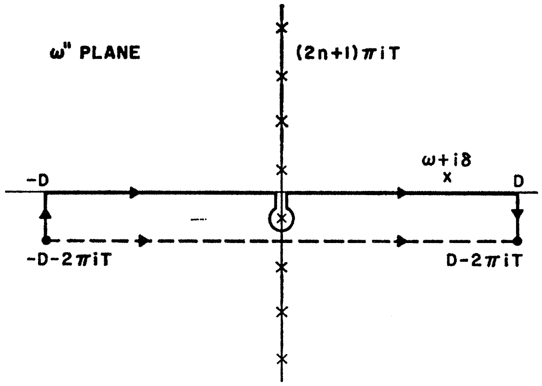

FIG. 3. The original contour of integration for Eq. (A3) and the deformed contour (solid) leading to Eq. (A4). The x's are the poles of the integrand.

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[23] Reference 20, p. 258, Eq. (6.3.5).

[24] Reference 20, p. 259, Eq. (6.3.18).

Let $z=\omega+i\tau$. Then

$$\begin{aligned} |\operatorname{Im}X(z)| &= \left| \int_{-D}^{D} \frac{-\tau}{(\omega-\omega')^2+\tau^2} [f(\omega')-\tfrac{1}{2}] d\omega' \right| \\ &\leq \int_{-D}^{D} \frac{\tau}{(\omega-\omega')^2+\tau^2} |f(\omega')-\tfrac{1}{2}| \, d\omega' \\ &\leq \frac{1}{2}\int_{-D}^{D} \frac{\tau}{(\omega-\omega')^2+\tau^2} d\omega' \\ &\leq \frac{1}{2}\int_{-\infty}^{\infty} \frac{\tau}{(\omega-\omega')^2+\tau^2} d\omega' \\ &= \frac{1}{2}\int_{-\infty}^{\infty} \frac{\tau}{\omega'^2+\tau^2} d\omega' \\ &= \tfrac{1}{2}\pi. \end{aligned} \tag{B3}$$

Therefore substituting in Eq. (B2),

$$\begin{aligned} \operatorname{Re}[X^2(z)+S(S+1)\pi^2] &\geq \tfrac{1}{2}\pi^2 \\ &> 1. \end{aligned} \tag{B4}$$

From Eq. (B4), we see that the function

$$\ln\{[X^2(z)+S(S+1)\pi^2]/a^2\} \tag{B5}$$

has no singularities except the cut of $X(z)$, no zeros in the finite z plane, and goes to zero at infinity. Therefore it can be represented by a Cauchy integral along the cut,

$$\begin{aligned} &\ln\{[X^2(z)+S(S+1)\pi^2]/a^2\} \\ &\quad = \frac{-1}{2\pi i}\int_{-D}^{D} (z-\omega')^{-1} \ln \frac{[X^+(\omega')]^2+S(S+1)\pi^2}{[X^-(\omega')]^2+S(S+1)\pi^2} d\omega'. \end{aligned} \tag{B6}$$

From Eq. (2.20) and the relation $X^+=(X^-)^*$, we see that Eq. (B6) can be rewritten

$$\begin{aligned} &\tfrac{1}{2}\ln\{[X^2(z)+S(S+1)\pi^2]/a^2\} \\ &\quad = \frac{-1}{2\pi}\int_{-D}^{D} d\omega' \frac{\operatorname{Im}\ln H(\omega')}{z-\omega'}. \end{aligned} \tag{B7}$$

Exponentiating Eq. (B7) gives Eq. (2.28). Note that Eq. (B4) also proves that the function $[X^2(z)+S(S+1)\pi^2]^{1/2}$ is SH.

Since Im ln$H$ is an odd function of ω', the asymptotic expansion of Eq. ($B7$) as $z\rightarrow\infty$ contains even powers of $(1/z)$ only.

The coefficients of this expansion are the d_n defined in Eq. (3.10), with n even. Carrying out the expansion of Eq. (B7) using Eqs. (A8), (2.4), (2.15), (2.19) and the asymptotic series for the digamma function[24] yields

$$\begin{aligned} d_2 &= -D^2 b g_2/(2a^2), \\ d_4 &= -D^4\{b g_4+[(b^2/a^2)-\tfrac{1}{2}]g_2^2\}/(4a^2), \end{aligned} \tag{B8}$$

where

$$\begin{aligned} g_2 &= 1-(\tfrac{1}{3})(\pi T/D)^2, \\ g_4 &= 1-(\tfrac{7}{15})(\pi T/D)^4. \end{aligned} \tag{B9}$$