Critical Field and Specific Heat of Strong Coupling Superconductors*

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Expressions for thermal quantities such as the critical field, entropy, and specific heat are derived for strong coupling superconductors without making a quasiparticle approximation for electron motions. The contributions from the ion motions are also taken into account semiphenomenologically. Nambu's Green's-function formalism at finite temperature is used as well as a relation, derived by Chester, between the differences of the thermal averages of the total Hamiltonian and the ion kinetic energy between the normal and the superconducting phases. Assuming the simple isotope effect, where the transition temperature is proportional to the inverse square root of the ionic mass, the phase transition is shown to be of the second order. The thermal quantities are given in terms of a single function of the temperature and its derivatives, which can be obtained from the energy-gap function and the renormalization factor of the electron Green's function. These expressions lead to the BCS results in the appropriate limit. A new expression for the jump in specific heat is also derived. For strong coupling superconductors it is likely to give better agreement with experiments than the BCS expression. Present theory does not apply to superconductors with isotope effect not simple as above. A possible reason is discussed.

I. INTRODUCTION

EXPERIMENTAL results for superconductors with strong electron-phonon coupling, such as Pb and Hg, exhibit some deviations from the predictions of the BCS theory.[1] Schrieffer, Scalapino, and Wilkins[2] have shown that the experimental tunneling I-V characteristics for such superconductors can be predicted if the retardation of the effective electron interactions is correctly taken into account. We expect the same effect to be important in explaining the thermodynamic anomalies of the strong coupling superconductors. For instance, the ratio of the energy gap at zero temperature $2\Delta_0$ to κT_c, where κ is the Boltzmann constant and T_c is the transition temperature, has not been satisfactorily explained. Swihart[3,4] showed that this ratio is always less than the observed values, 4.1 for Pb and 4.6 for Hg, using a variety of nonretarded interactions. The retardation effect in interactions, especially, the accompanying damping of excitations is likely to explain this discrepancy.[5] Since the damping decreases the effective pairing interaction strength, the transition temperature as well as the energy gap at zero temperature are reduced. The former is reduced much more than the latter, because the damping rate is greater at higher temperatures. Thereby the ratio $2\Delta_0/\kappa T_c$ will increase. Actually, tentative calculations[6] for Pb including the effects of damping to the renormalization factor of the Green's function but neglecting the nonresonant processes, which do not conserve the energy at the intermediate states, resulted in even a larger ratio than the experimentally observed value. It should be possible to obtain the experimental ratio by a complete calculation, since the nonresonant effect, discarded in the above calculation, had been found to decrease the ratio.[5,6a]

The phonon-limited electronic thermal conductivity is another problem. Tewordt[7] concluded that the experimental temperature dependence of the ratio of the superconducting to normal thermal conductivity for Pb and Hg cannot be reproduced completely within the scope of the BCS model and the Boltzmann-equation approach. Ambegaokar and Tewordt[8] have derived a new expression for the above ratio using Kubo's formula[9] for the thermal conductivity and the method of thermodynamic Green's functions, taking into account retardation effects. Although full numerical results are not available yet, their result appears to improve agreement with experiment than the earlier results.

The temperature dependence of the critical field of Pb and Hg shows a deviation from the BCS theory. It deviates in the positive direction from a parabola given by the Gorter-Casimir two-fluid model, while the BCS theory gives a negative deviation. This problem has something in common with the above-mentioned discrepancies. It was shown that the positive deviation can be obtained even within the scope of the BCS model if the experimental value is used for the ratio of the energy gap at zero temperature to the transition temperature.[10]

Therefore, it is desirable to calculate the temperature dependence of the critical field within the framework of the retarded interaction theory.

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[2] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963).
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[6] Y. Wada, Rev. Mod. Phys. **36**, 253 (1964).
[6a] *Note added in proof.* Recently, D. J. Scalapino, J. C. Swihart, and the present author have solved the complete energy-gap equation at finite temperatures and obtained the value of $2\Delta_0/\kappa T_c$ close to the experimental one for Pb and Hg.
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[8] V. Ambegaokar and L. Tewordt, Phys. Rev. **134**, A805 (1964).
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Shiffman, Cochran, and Garber[11] have made a precise measurement of the temperature dependence of the specific heat of Pb and Hg near the transition temperature. The jump in the specific heat of Pb at the phase transition was observed to be $\Delta C=57.5\pm0.6$ mJ-mole^{-1} deg^{-1}. This value is larger by the factor 1.6 than the BCS result, but is in agreement with the value obtained by Decker, Mapother, and Shaw[12] from an analysis of the temperature dependence of the critical field. Using the expression for ΔC derived by Swihart[3] with nonretarded interactions, they concluded that the energy gap function must increase with energy for small energies.

The purpose of this paper is to derive new expressions for the critical field, the specific heat, and its jump at T_c, taking into account the retardation effects correctly. These quantities can be expressed in terms of the electron and phonon Green's functions in Gorkov-Nambu formalism.[13–16] It is possible to calculate the electron Green's function explicitly. However, the calculations of the phonon Green's function have some complications. Therefore it is desirable to derive the relations for the above quantities involving just the electron Green's function. This can be done if we take a semiphenomenological approach, using a relation derived by Chester.[17] It provides a way of expressing the difference of the thermal averages of the ionic kinetic energy in the normal and the superconducting phases in terms of the difference of the total energy in the two phases and the critical field. Chester's relation is based upon the fact that the ratio of the critical field H_c to its value at the zero temperature H_0 is given by a function of reduced temperature $t=T/T_c$, where T is the temperature, which is common to all isotopes of any one superconductor. The dependences on the isotopic mass M are assumed to be $H_0\propto M^{-\alpha}$ and $T_c\propto M^{-\alpha'}$. Assuming a simple isotope effect, $\alpha'=\frac{1}{2}$, it turns out that the critical field, the difference of the entropy between the two phases, and the specific heat are all given in terms of a single function of the temperature and its derivatives. This function can be written in terms of the energy-gap function and the renormalization factor of the electron Green's function. Our expressions reduce to the BCS results[1] if the energy-gap function is real and constant. Calculating the difference of the thermal average of the total energy between the two phases, one finds that the ionic kinetic-energy difference gives rise to a contribution which is equal to the total energy difference itself at $T\sim T_c$, thereby making it not obvious that the phase transition is not of the first order. The transition is shown to be not of the first order, making use of the defining equation for the renormalization factor of the Green's function. By means of similar discussions, the expression for the jump in specific heat ΔC is expressed in terms of the temperature derivative of the square of the energy-gap function. When the damping is neglected and the electron-phonon interaction is weak, our result reduces to that given by Swihart.[3] In the general case, it is expected to be larger than the BCS result and should, therefore, be in better agreement with experiment.

In Sec. II, the critical field, the difference of the total energy between the two phases, the entropy difference, and the specific heat are given in terms of a function $I(\beta)$, with $\beta=1/\kappa T$, which can be obtained from the electron Green's function. In Sec. III, the function $I(\beta)$ is transformed to a simple integral containing the energy-gap function and the renormalization factor. The phase transition is proved to be not of the first order and ΔC is rewritten in a simpler form. In Sec. IV, the expressions for the thermal quantities are shown to involve the BCS and Swihart results as special cases. The corrections to the BCS ΔC are examined and are likely to give a better agreement with experiments. Finally, validity of Chester's relation is discussed in Sec. V. Then a difficulty in applying the present theory to superconductors with more general isotope effect, $\alpha'\neq\frac{1}{2}$, is pointed out. A possible origin of this difficulty is discussed.

II. THERMAL QUANTITIES AND CHESTER'S RELATIONS

In this section, we shall first write the thermal average of the total Hamiltonian in terms of the Green's functions. The phonon Green's function is eliminated from the obtained relation, making use of Chester's relations. It gives expressions for the free-energy difference between the two phases, the critical field, entropy difference, and the specific-heat difference.

In terms of the second quantized (bare) operators, $c_{p\sigma}$ for the electron with quasimomentum p and spin σ, $a_{q\lambda}$ for the phonon with quasimomentum q and polarization λ, the Hamiltonian of the electron-ion system takes the form

$$K\equiv H-\mu N=K_0+H_1+H_2+E_0\,,$$

$$K_0=\sum_p \Psi_p{}^\dagger\epsilon_p\tau_3\Psi_p+\tfrac{1}{2}\sum_{q\lambda}\{\Pi_{q\lambda}{}^*\Pi_{q\lambda}+\omega_{q\lambda}{}^2Q_{q\lambda}{}^*Q_{q\lambda}\}\,,$$

$$H_1=\sum_{pqK\lambda}\frac{v_{q-K,\lambda}}{\sqrt{\Omega}}Q_{q\lambda}\Psi_{p+q-K}{}^\dagger\tau_3\Psi_p\,,$$

$$H_2=\tfrac{1}{2}\sum_{k_1k_2k_3k_4}V(k_1,k_2,k_3,k_4):\Psi_{k_1}\tau_3\Psi_{k_4}\Psi_{k_2}{}^\dagger\tau_3\Psi_{k_3}:\,.$$

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[11] C. A. Shiffman, J. F. Cochran, and M. Garber, Phys. Chem. Solids 24, 1369 (1963).
[12] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. 112, 1888 (1958).
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[14] Y. Nambu, Phys. Rev. 117, 648 (1960).
[15] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. 38, 966 (1960) [English transl.: Soviet Phys.—JETP 11, 696 (1960)].
[16] L. Tewordt, Phys. Rev. 128, 12 (1962).
[17] G. V. Chester, Phys. Rev. 103, 1693 (1956). The following procedure was used by Scalapino and Schrieffer to calculate the condensation energy of the superconducting phase at zero temperature (private communication).

Here we have subtracted μN, so that ϵ_p is the Bloch energy measured relative to the chemical potential μ. N is the total number of electrons and K_0 is the Hamiltonian of the system without interactions. We used Nambu's matrix notation,[14]

$$\Psi_p^\dagger=(c_{p\uparrow}^*,c_{-p\downarrow})\,,\quad \Psi_p=\begin{pmatrix} c_{p\uparrow} \\ c_{-p\downarrow}^* \end{pmatrix},$$

and τ_3 is the third component of the Pauli spin matrix. The phonon field operators are given by

$$\Pi_{q\lambda}=i(\omega_{q\lambda}/2)^{1/2}(a_{q\lambda}^*-a_{-q\lambda})\,,$$
$$Q_{q\lambda}=(2\omega_{q\lambda})^{-1/2}(a_{q\lambda}+a_{-q\lambda}^*)\,,$$

where $\omega_{q\lambda}$ is the bare phonon frequency. H_1 is the electron-phonon interaction Hamiltonian, $v_{q-K,\lambda}$ is the coupling matrix element which is assumed for simplicity to depend only on the electron-momentum transfer $q-K$ and the polarization of phonon λ.[18] K is any reciprocal lattice vector, and Ω the normalization volume. H_2 represents the Coulomb interactions among the electrons. $V(k_1,k_2,k_3,k_4)$ is the matrix element of the Coulomb interaction with the Bloch functions $\psi_k(r)$,

$$V(k_1,k_2,k_3,k_4)=\int \psi_{k_1}^*(r)\psi_{k_2}^*(r')\frac{e^2}{|r-r'|}\psi_{k_3}(r')\psi_{k_4}(r)drdr'\,,$$

which vanishes unless $k_1+k_2-k_3-k_4$ is equal to any reciprocal lattice vector K. The symbol $:\cdots:$ means the normal product with respect to $\Psi^\dagger$ and Ψ. The term E_0 involves the total numbers of the electrons with up spin and down spin as well as pure constants. Since these have nothing to do with the phase transition, we discard this term hereafter. It is worth remarking here that the kinetic energy of the ions

$$K_M=\sum_i(1/2M)P_i^2\,,$$

can be rewritten as

$$K_M=\tfrac{1}{2}\sum_{q\lambda}\Pi_{q\lambda}^*\Pi_{q\lambda}\,. \tag{2.1}$$

The operators at reciprocal temperature τ are defined by

$$\Psi_p(\tau)=e^{K\tau}\Psi_p e^{-K\tau}\,,$$

with the similar relations for $\Psi_p^\dagger(\tau)$, $\Pi_{q\lambda}(\tau)$ and $Q_{q\lambda}(\tau)$. The equations of motion take the forms

$$\frac{\partial\Psi_p}{\partial\tau}=[K,\Psi_p]=-\epsilon_p\tau_3\Psi_p-\sum_{qK\lambda}\frac{v_{q-K,\lambda}}{\sqrt{\Omega}}Q_{q\lambda}\tau_3\Psi_{p-q+K}$$
$$-\sum_{k_1k_2k_3}V(p,k_1,k_2,k_3):\tau_3\Psi_{k_3}\Psi_{k_1}^\dagger\tau_3\Psi_{k_2}:\,, \tag{2.2}$$

$$\partial Q_{q\lambda}/\partial\tau=-i\Pi_{-q\lambda}\,,$$

$$\frac{\partial\Pi_{-q\lambda}}{\partial\tau}=i\omega_{q\lambda}^2Q_{q\lambda}+i\sum_{pK}\frac{v_{-q-K,\lambda}}{\sqrt{\Omega}}\Psi_{p-q-K}^\dagger\tau_3\Psi_p\,. \tag{2.3}$$

The thermodynamical Green's functions are defined by

$$G(p,\tau_1,\tau_2)=-\mathrm{Tr}Ue^{\beta(\Omega_0-K)}T(\Psi_p(\tau_1)\Psi_p^\dagger(\tau_2))\,,$$
$$D_\lambda(q,\tau_1,\tau_2)=-\mathrm{Tr}e^{\beta(\Omega_0-K)}T(Q_{q\lambda}(\tau_1)Q_{q\lambda}^\dagger(\tau_2))\,,$$

for electrons and phonons, respectively, where Tr means the thermodynamic trace operation and

$$e^{-\beta\Omega_0}=\mathrm{Tr}e^{-\beta K}\,,$$
$$\beta=1/\kappa T\,.$$

The operator U is given by

$$U=1+R+R^+$$

in terms of an operator R^+ which transforms a given state in an N-particle system into the corresponding state in the $N+2$-particle system[19,20]; thus for the ground states

$$R^+|0,N\rangle=|0,N+2\rangle\,.$$

and for the one-particle states

$$R^+|k,N\rangle=|k,\,N+2\rangle\,,$$

while

$$R|0,\,N+2\rangle=|0,N\rangle\,,\ \text{etc.}$$

The symbol T means the ordering operator with respect to τ_1 and τ_2. Due to the Umklapp processes, the quasi-momentum of one-electron state is not conserved. The electron Green's function becomes a matrix with respect to momentum suffices, too. Here we have defined the diagonal components which are relevant to the following discussions.

Because of the translational invariance and the periodicity in τ_1 and τ_2, the Green's functions can be expanded in the Fourier series[21]

$$G(p,\tau_1,\tau_2)=\frac{1}{\beta}\sum_{n=-\infty}^{\infty}\exp[-iE_n(\tau_1-\tau_2)]G(p,iE_n)\,, \tag{2.4}$$

$$D_\lambda(q,\tau_1,\tau_2)=\frac{1}{\beta}\sum_{n=-\infty}^{\infty}\exp[-i\nu_n(\tau_1-\tau_2)]D_\lambda(q,i\nu_n)\,, \tag{2.5}$$

where

$$E_n=(2n+1)\pi/\beta\,,$$
$$\nu_n=2n\pi/\beta\,,$$

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[19] L. P. Kadanoff and P. C. Martin, Phys. Rev. **124**, 670 (1961).
[20] J. R. Schrieffer, Lecture at the University of Pennsylvania, 1962 (unpublished).
[21] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

n being any integer. The inverse relations for (2.4) and (2.5) are

$$G(p,iE_n)=\frac{1}{\beta}\int_0^\beta\int_0^\beta d\tau_1 d\tau_2 \exp[iE_n(\tau_1-\tau_2)]G(p,\tau_1,\tau_2)\,,$$

$$D_\lambda(q,i\nu_n)=\frac{1}{\beta}\int_0^\beta\int_0^\beta d\tau_1 d\tau_2 \exp[i\nu_n(\tau_1-\tau_2)]D_\lambda(q,\tau_1,\tau_2)\,.$$

The thermal average of K_0 can be written in terms of the Green's functions.

$$\langle K_0\rangle \equiv \mathrm{Tr} e^{\beta(\Omega_0-K)}K_0 = \frac{1}{\beta}\sum_{pn}\mathrm{tr}\{G(p,iE_n)\epsilon_p\tau_3\}e^{iE_n0+} + \frac{1}{2\beta}\sum_{nq\lambda}\{(\nu_n{}^2-\omega_{q\lambda}{}^2)D_\lambda(q,i\nu_n)+1\}e^{i\nu_n0+}\,, \quad (2.6)$$

where the equation of motion for $Q_{q\lambda}$, (2.3), is used. Here, tr is the trace operation in the sense of Nambu's matrix notation.

Using the equation for Ψ_p, (2.2), one can get the equation of motion for the Green's function,

$$\frac{\partial G(p,\tau_1,\tau_2)}{\partial\tau_1}=-\delta(\tau_1-\tau_2)\cdot 1-\epsilon_p\tau_3 G(p,\tau_1,\tau_2)+\mathrm{Tr}Ue^{\beta(\Omega_0-K)}T\bigg\{\sum_{qK\lambda}\frac{v_{q-K,\lambda}}{\sqrt{\Omega}}Q_{q\lambda}(\tau_1)\tau_3\Psi_{p-q+K}(\tau_1) + \sum_{k_1k_2k_3}V(p,k_1,k_2,k_3):\tau_3\Psi_{k_3}(\tau_1)\Psi_{k_1}{}^\dagger(\tau_1)\tau_3\Psi_{k_2}(\tau_1):\,,\,\Psi_p{}^\dagger(\tau_2)\bigg\}\,,$$

which is transformed to

$$-iE_nG(p,iE_n)=-1-\epsilon_p\tau_3G(p,iE_n)+\frac{1}{\beta}\int_0^\beta\int_0^\beta d\tau_1d\tau_2\exp[iE_n(\tau_1-\tau_2)]\,\mathrm{Tr}Ue^{\beta(\Omega_0-K)} \times T\bigg\{\sum_{qK\lambda}\frac{v_{q-K,\lambda}}{\sqrt{\Omega}}Q_{q\lambda}(\tau_1)\tau_3\Psi_{p-q+K}(\tau_1)+\sum_{k_1k_2k_3}V(p,k_1,k_2,k_3):\tau_3\Psi_{k_3}(\tau_1)\Psi_{k_1}{}^\dagger(\tau_1)\tau_3\Psi_{k_2}(\tau_1):\,,\,\Psi_p{}^\dagger(\tau_2)\bigg\}\,. \quad (2.7)$$

The diagonal components of the electron Green's function with respect to the quasimomentum are known to satisfy the Dyson equation[14,15,19,20,22]

$$1/G(p,iE_n)=[1/G_0(p,iE_n)]-\Sigma(p,iE_n)\,, \quad (2.8)$$

if $\Sigma(p,iE_n)$ is defined as the contributions of all distinct self-energy diagrams diagonal with respect to the quasimomentum p and which cannot be separated into two parts by breaking a single particle line carrying the label p.[23] G_0 is the Green's function for a noninteracting system

$$G_0(p,iE_n)^{-1}=iE_n-\epsilon_p\tau_3\,.$$

Equation (2.7) gives an expression for the self-energy part,

$$\Sigma(p,iE_n)G(p,iE_n)=-\frac{1}{\beta}\int_0^\beta\int_0^\beta d\tau_1d\tau_2\exp[iE_n(\tau_1-\tau_2)]\,\mathrm{Tr}Ue^{\beta(\Omega_0-K)} \times T\bigg\{\sum_{qK\lambda}\frac{v_{q-K,\lambda}}{\sqrt{\Omega}}Q_{q\lambda}(\tau_1)\tau_3\Psi_{p-q+K}(\tau_1)+\sum_{k_1k_2k_3}V(p,k_1,k_2,k_3):\tau_3\Psi_{k_3}(\tau_1)\Psi_{k_1}{}^\dagger(\tau_1)\tau_3\Psi_{k_2}(\tau_1):\,,\,\Psi_p{}^\dagger(\tau_2)\bigg\}\,.$$

Transforming the expression back to the reciprocal temperature variable, one finally gets

$$\frac{1}{\beta}\sum_{pn}e^{iE_n0+}\,\mathrm{tr}(\Sigma(p,iE_n)G(p,iE_n)) =\mathrm{Tr}e^{\beta(\Omega_0-K)}\sum_p\bigg\{\sum_{qK\lambda}\frac{v_{q-K,\lambda}}{\sqrt{\Omega}}Q_{q\lambda}\Psi_p{}^\dagger\tau_3\Psi_{p-q+K}+\sum_{k_1k_2k_3}V(p,k_1,k_2k,_3):\Psi_p{}^\dagger\tau_3\Psi_{k_3}\Psi_{k_1}{}^\dagger\tau_3\Psi_{k_2}:\bigg\}=\langle H_1+2H_2\rangle\,. \quad (2.9)$$

By similar discussions, the equation for D_λ turns out to be

$$-\nu_n{}^2D_\lambda(q,i\nu_n)=1+\omega_{q\lambda}{}^2D_\lambda(q,i\nu_n)-\frac{1}{\beta}\int_0^\beta\int_0^\beta d\tau_1d\tau_2\exp[i\nu_n(\tau_1-\tau_2)]\,\mathrm{Tr}e^{\beta(\Omega_0-K)} \times T\bigg(\sum_{pK}\frac{v_{-q-K,\lambda}}{\sqrt{\Omega}}\Psi_{p-q-K}{}^\dagger(\tau_1)\tau_3\Psi_p(\tau_1)\,,\,Q_{q\lambda}{}^*(\tau_2)\bigg)\,.$$

[22] P. Nozieres, *Theory of Interacting Fermi Systems* (W. A. Benjamin, Inc., New York, 1964), Chap. 4.
[23] J. R. Schrieffer, Lecture at Argonne National Laboratory, 1962 (unpublished).

The self-energy part of the phonons Π_λ is defined by

$$1/D_\lambda(q,i\nu_n)=[1/D_{0\lambda}(q,i\nu_n)]-\Pi_\lambda(q,i\nu_n)\,, \tag{2.10}$$

where

$$D_{0\lambda}(q,i\nu_n)^{-1}=-(\nu_n^2+\omega_{q\lambda}^2)\,. \tag{2.11}$$

Then, one finds

$$\Pi_\lambda(q,i\nu_n)D_\lambda(q,i\nu_n)=-\frac{1}{\beta}\int_0^\beta\int_0^\beta d\tau_1 d\tau_2 \exp[i\nu_n(\tau_1-\tau_2)]\,\mathrm{Tr}e^{\beta(\Omega_0-K)}T\left(\sum_{pK}\frac{v_{-q-K,\lambda}}{\sqrt{\Omega}}\Psi_{p-q-K}^\dagger(\tau_1)\tau_3\Psi_p(\tau_1)\,,\,Q_{q\lambda}^*(\tau_2)\right),$$

and finally

$$\frac{1}{\beta}\sum_{nq\lambda} e^{i\nu_n0+}\Pi_\lambda(q,i\nu_n)D_\lambda(q,i\nu_n)=-\mathrm{Tr}e^{\beta(\Omega_0-K)}\sum_{pqK\lambda}\frac{v_{-q-K,\lambda}}{\sqrt{\Omega}}Q_{-q\lambda}\Psi_{p-q-K}^\dagger\tau_3\Psi_p=-\langle H_1\rangle\,. \tag{2.12}$$

The average of K_0, (2.6), and that of interaction energies, (2.9) and (2.12), give the thermal average of the total Hamiltonian,

$$\langle K\rangle=(1/\beta)\sum_{pn}\mathrm{tr}\{G(p,iE_n)\epsilon_p\tau_3+\tfrac{1}{2}\Sigma(p,iE_n)G(p,iE_n)\}e^{iE_n0+}$$
$$+(1/2\beta)\sum_{nq\lambda}\{(\nu_n^2-\omega_{q\lambda}^2)D_\lambda(q,i\nu_n)+1-\Pi_\lambda(q,i\nu_n)D_\lambda(q,i\nu_n)\}e^{i\nu_n0+}.$$

The second term on the right-hand side is twice the average ionic kinetic energy, since it can be written as

$$(1/2\beta)\sum_{nq\lambda}\{(\nu_n^2-\omega_{q\lambda}^2)D_\lambda(q,i\nu_n)+1-\Pi_\lambda(q,i\nu_n)D_\lambda(q,i\nu_n)\}e^{i\nu_n0+}$$
$$=(1/2\beta)\sum_{nq\lambda}\left\{2\nu_n^2D_\lambda(q,i\nu_n)+2+\frac{1}{D_{0\lambda}(q,i\nu_n)}D_\lambda(q,i\nu_n)-1-\Pi_\lambda(q,i\nu_n)D_\lambda(q,i\nu_n)\right\}e^{i\nu_n0+}$$
$$=(1/\beta)\sum_{nq\lambda}\{\nu_n^2D_\lambda(q,i\nu_n)+1\}e^{i\nu_n0+}=\sum_{q\lambda}\langle\Pi_{q\lambda}^*\Pi_{q\lambda}\rangle=2\langle K_M\rangle,$$

where we have used the expression for $D_{0\lambda}$, (2.11), the equation for D_λ, (2.10), and the expression for K_M, (2.1). Thus $\langle K\rangle$ takes the form

$$\langle K\rangle=(1/\beta)\sum_{pn}\mathrm{tr}\{G(p,iE_n)\epsilon_p\tau_3+\tfrac{1}{2}\Sigma(p,iE_n)G(p,iE_n)\}e^{iE_n0+}+2\langle K_M\rangle. \tag{2.13}$$

Now, we will use the Chester's relation[17] in order to eliminate the ionic kinetic-energy term from (2.13). He pointed out that the quantities $\langle H\rangle$ and $\langle K_M\rangle$ can be given in terms of the free energy F as

$$\langle H\rangle=-T^2[\partial(F/T)/\partial T]_{\Omega,M}\,, \tag{2.14}$$

$$\langle K_M\rangle=-M[\partial F/\partial M]_{T,\Omega}. \tag{2.15}$$

If the difference in any quantity X between the normal and superconducting states is denoted by ΔX,

$$\Delta X=X_n-X_s\,,$$

then Eqs. (2.14) and (2.15) give

$$\Delta\langle H\rangle=-T^2[\partial(\Delta F/T)/\partial T]_{\Omega,M}\,,$$
$$\Delta\langle K_M\rangle=-M[\partial\Delta F/\partial M]_{T,\Omega}.$$

Substituting the expression

$$\Delta F=\Omega H_c^2/8\pi\,, \tag{2.16}$$

where H_c is the critical field, one obtains

$$\Delta\langle H\rangle=\frac{\Omega H_c}{4\pi}\left[-T\left(\frac{\partial H_c}{\partial T}\right)_{\Omega,M}+\frac{H_c}{2}\right],$$
$$\Delta\langle K_M\rangle=-\frac{\Omega H_c}{4\pi}\left[M\frac{\partial H_c}{\partial M}\right]_{T,\Omega}. \tag{2.17}$$

Following Chester, we assume the experimentally established fact that H_c can be written as

$$H_c=H_0h(t)\,,$$

where H_0 is the critical field at absolute zero, $h(t)$ is a function of $t=T/T_c$ which is identical for all the isotopes of any one superconductor satisfying $h(0)=1$, $h(1)=0$. We shall first assume a simple isotope effect

$$H_0\propto M^{-\alpha}\quad\text{and}\quad T_c\propto M^{-\alpha'},\quad \alpha'=\tfrac{1}{2}.$$

One will find a difficulty in more general cases, $\alpha'\neq\frac{1}{2}$, which will be discussed in Sec. V. Under the above approximation, Eqs. (2.17) turn out to be

$$\Delta\langle H\rangle=\Delta U_0h[h-2th']\,,$$
$$\Delta\langle K_M\rangle=\Delta U_0h[2\alpha h-th']\,, \tag{2.18}$$

where

$$\Delta U_0=\Omega H_0^2/8\pi\,,\quad h'=dh/dt.$$

Substituting (2.18) into the equation which can be obtained by taking the difference of $\langle K\rangle$, (2.13), between the two phases and using $\Delta\mu=0$ (see Appendix A), one gets the critical field and the total energy difference as

$$\Omega H_c^2/8\pi=\Delta U_0 h^2(t)=[1/(4\alpha-1)]N(0)I(\beta)\,, \tag{2.19}$$

$$\Delta\langle H\rangle=\frac{h-2th'}{(4\alpha-1)h}N(0)I(\beta)=\frac{N(0)}{4\alpha-1}\left[I(\beta)-t\frac{dI(\beta)}{dt}\right], \tag{2.20}$$

where

$$N(0)I(\beta)=-(1/\beta)\Delta\sum_{pn}\mathrm{tr}\{G(p,iE_n)\epsilon_p\tau_3+\tfrac{1}{2}\Sigma(p,iE_n)G(p,iE_n)\}e^{iE_n0+}, \tag{2.21}$$

and $N(0)$ is the density of Bloch states of one spin orientation per unit energy at the Fermi surface. Equation (2.19) is a direct generalization to finite temperatures of the calculation of condensation energy by Scalapino and Schrieffer.[17]

From the expression for ΔF in terms of $I(\beta)$, (2.16), and (2.19), the entropy difference is found to be

$$\Delta S=-\left(\frac{\partial\Delta F}{\partial T}\right)_\Omega=\frac{\kappa N(0)\beta^2}{4\alpha-1}\frac{\partial I(\beta)}{\partial\beta}. \tag{2.22}$$

It is now not obvious that the superconducting phase transition is of the second order. $\Delta\langle H\rangle$, (2.20), which is the energy difference between the normal and the superconducting phases is not manifestly zero at $T=T_c$, since it is not *a priori* clear that dI/dt vanishes at $t=1$. This comes from the fact that the difference of the ion kinetic energy is one-half of that of the total energy at $T\sim T_c$. This indicates the importance of ionic motions which are not present in the theories with nonretarded interactions. The illusory latent heat is

$$\Delta\langle H\rangle\bigg|_{t=1}=\frac{N(0)\beta_c}{4\alpha-1}\frac{dI}{d\beta_c}, \tag{2.23}$$

which must vanish in order to give the second-order transition.

The specific-heat difference is given by

$$\Delta C(t)=\frac{d\Delta\langle H\rangle}{dT}=-\frac{N(0)t}{(4\alpha-1)T_c}\frac{d^2I(\beta)}{dt^2}. \tag{2.24}$$

If we assume a second-order phase transition,

$$dI/d\beta_c=0\,,$$

Eq. (2.24) gives the jump in specific heat,

$$\Delta C=\Delta C(t)\bigg|_{t=1}=-\frac{\kappa N(0)\beta_c^3}{4\alpha-1}\frac{d^2I}{d\beta_c^2}. \tag{2.25}$$

III. SECOND-ORDER PHASE TRANSITION AND THE JUMP IN THE SPECIFIC HEAT

In order to facilitate the numerical calculations, the function $I(\beta)$, (2.21), will be rewritten in terms of the energy-gap function and the renormalization factor of the Green's function. By virtue of the result, the phase transition will be shown to be not of the first order and the jump in specific heat will be given in a simpler form.

According to Nambu[14,16] the electron self-energy part takes the form

$$\Sigma(p,iE_n)=\zeta_p(iE_n)iE_n+\chi_p(iE_n)\tau_3+\phi_p(iE_n)\tau_1\,, \tag{3.1}$$

where ζ_p, χ_p and ϕ_p are even functions of the complex variable iE_n, and the τ_i's are the Pauli's spin matrices. From the Dyson equation, (2.8), the electron Green's function is given by

$$G(p,iE_n)=\frac{zZ_p(z)+\bar\epsilon_p(z)\tau_3+\phi_p(z)\tau_1}{z^2Z_p^2(z)-E_p^2(z)}\bigg|_{z=iE_n}, \tag{3.2}$$

where

$$Z_p(iE_n)=1-\zeta_p(iE_n)\,,$$
$$\bar\epsilon_p(iE_n)=\epsilon_p+\chi_p(iE_n)\,,$$
$$E_p^2(iE_n)=\bar\epsilon_p^2(iE_n)+\phi_p^2(iE_n)\,.$$

Z_p is the renormalization factor of the electron Green's function.

Substituting (3.1) and (3.2) into the expression for $I(\beta)$, (2.21), we obtain

$$N(0)I(\beta)=-\frac{1}{\beta}\Delta\sum_{pn}\frac{z^2Z_p(z)+\epsilon_p\bar\epsilon_p(z)}{z^2Z_p^2(z)-E_p^2(z)}e^{z0+}\bigg|_{z=iE_n}=\frac{1}{2\pi i}\int_{c_1+c_2}\frac{dz}{1+e^{\beta z}}\Delta\sum_p\frac{z^2Z_p(z)+\epsilon_p\bar\epsilon_p(z)}{z^2Z_p^2(z)-E_p^2(z)}e^{z0+}, \tag{3.3}$$

where c_1 and c_2 are the contours illustrated in Fig. 1. Making use of the facts that the electron Green's function does not have any singularity on the first Riemannian sheet except along the real axis, and Z_p, χ_p,

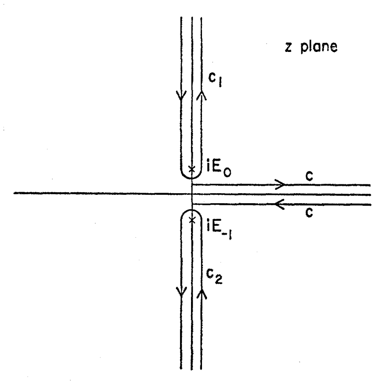

FIG. 1. The contours of integration in a complex z plane used in Eqs. (3.3) and (3.4).

and ϕ_p are even functions of z one can rewrite (3.3) as

$$N(0)I(\beta)=-\frac{1}{2\pi i}\Delta\sum_p\int_c dz\frac{z^2Z_p(z)+\epsilon_p\bar{\epsilon}_p(z)}{z^2Z_p^2(z)-E_p^2(z)}\tanh\frac{\beta z}{2}, \tag{3.4}$$

where the contour c is given in Fig. 1. Each of Z_p, ϕ_p, and χ_p satisfies a relation such as

$$Z_p(\omega+i\epsilon)=Z_p^*(\omega-i\epsilon), \tag{3.5}$$

for real ω due to the analytical property of the Green's function. If we use the notations

$$\lim_{\epsilon\to0+} Z_p(\omega+i\epsilon)=Z_p(\omega),$$

$$\lim_{\epsilon\to0+} \chi_p(\omega+i\epsilon)=\chi_p(\omega),$$

$$\lim_{\epsilon\to0+} \phi_p(\omega+i\epsilon)=\phi_p(\omega),$$

Eq. (3.4) takes the form

$$N(0)I(\beta)=-\frac{1}{\pi}\operatorname{Im}\sum_p\int_0^\infty d\omega\Delta \times\left[\frac{\omega^2Z_p(\omega)+\bar{\epsilon}_p^2(\omega)-\chi_p(\omega)\bar{\epsilon}_p(\omega)}{\omega^2Z_p^2(\omega)-E_p^2(\omega)}\right]\tanh\frac{\beta\omega}{2}. \tag{3.6}$$

By virtue of the equations satisfied by the three functions, one finds that the shift of χ_p between the normal and superconducting phases is small enough to neglect (Appendix B) so that $\bar{\epsilon}_p$'s are the same for the two phases. Moreover, the main effects of χ_p are the shifts in the chemical potential and the effective mass.[24] The $\chi_p\bar{\epsilon}_p$ term in the numerator of (3.6) gives a negligible contribution as shown in Appendix B. The energy region $\omega\leq\omega_c$, ω_c being a constant several times the Debye energy, gives the important contribution to ω integral in (3.6), since the difference between the two phases is small at $\omega>\omega_c$. Then the main contribution to the p integral comes from the region $|\bar{\epsilon}_p|\leq\omega_c$ where the p dependence of Z_p and ϕ_p are so small that we can replace them by their average values at the Fermi surface, Z and ϕ, respectively. The p integral is evaluated by changing the variable

$$\sum_p=N(0)\int d\bar{\epsilon}_p,$$

and extending the $\bar{\epsilon}_p$ integral from $-\infty$ to ∞. It gives

$$I(\beta)=\int_0^\infty d\omega\,\mathrm{Re}\left[(1+Z_n(\omega))\omega-\frac{\omega^2}{[\omega^2-\Delta^2(\omega)]^{1/2}}-Z_s(\omega)[\omega^2-\Delta^2(\omega)]^{1/2}\right]\tanh\frac{\beta\omega}{2}, \tag{3.7}$$

where Z_n and Z_s are the Z functions in the normal and superconducting phase, respectively. The energy-gap function is given by

$$\Delta(\omega)=\phi(\omega)/Z_s(\omega). \tag{3.8}$$

The square root is defined by the condition

$$\operatorname{Im}\{Z_s(\omega)[\omega^2-\Delta^2(\omega)]^{1/2}\}>0.$$

We shall calculate $dI/d\beta_c$ in order to show that the phase transition is of the second order. $dI/d\beta$ takes the form,

$$\frac{dI(\beta)}{d\beta}=\int_0^\infty d\omega\,\mathrm{Re}\left[\frac{\partial Z_n}{\partial\beta}\omega-\frac{\partial Z_s}{\partial\beta}(\omega^2-\Delta^2)^{1/2}-\left(\frac{\omega^2}{2(\omega^2-\Delta^2)^{3/2}}-\frac{Z_s}{2(\omega^2-\Delta^2)^{1/2}}\right)\frac{\partial\Delta^2}{\partial\beta}\right]\tanh\frac{\beta\omega}{2} +\int_0^\infty d\omega\,\mathrm{Re}\left[(1+Z_n)\omega-\frac{\omega^2}{(\omega^2-\Delta^2)^{1/2}}-Z_s(\omega^2-\Delta^2)^{1/2}\right]\frac{\omega/2}{\cosh^2(\beta\omega/2)}, \tag{3.9}$$

which gives

$$\frac{dI}{d\beta_c}=\int_0^\infty d\omega\,\mathrm{Re}\left[\left(\frac{\partial Z_n}{\partial\beta_c}-\frac{\partial Z_s}{\partial\beta_c}\right)\omega-\frac{1-Z_n}{2\omega}\frac{\partial\Delta^2}{\partial\beta_c}\right]\tanh\frac{\beta_c\omega}{2}. \tag{3.10}$$

Now we shall show the expression (3.10) which gives the illusory latent heat (2.23) actually vanishes. Due to the analytical property (3.5) and the evenness of Z and Δ, (3.10) can be rewritten

$$\frac{dI}{d\beta_c}=\frac{1}{2}\int_{-\infty}^\infty d\omega\left[\left(\frac{\partial Z_n}{\partial\beta_c}-\frac{\partial Z_s}{\partial\beta_c}\right)\omega-\frac{1-Z_n}{2\omega}\frac{\partial\Delta^2}{\partial\beta_c}\right]\tanh\frac{\beta_c\omega}{2}. \tag{3.11}$$

We can close the contour of the integration with a large semicircle in the upper ω plane along which the integral will turn out to vanish. In Appendix C, $\partial\Delta^2/\partial\beta_c$ is proved to be analytic in the upper half-plane as well as $\partial Z_n/\partial\beta_c$

[24] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins (private communication).

and $\partial Z_s/\partial\beta_c$. Therefore $dI/d\beta_c$ takes the form

$$\frac{dI}{d\beta_c}=\frac{2\pi i}{\beta_c}\sum_{m\geq 0}\left[\left(\frac{\partial Z_n}{\partial\beta_c}-\frac{\partial Z_s}{\partial\beta_c}\right)z-\frac{1-Z_n}{2z}\frac{\partial\Delta^2}{\partial\beta_c}\right]_{z=iE_m}. \tag{3.12}$$

On the other hand, the equation satisfied by $Z_s(\omega)$, (B5), gives the relation

$$\left(\frac{\partial Z_n}{\partial\beta_c}-\frac{\partial Z_s}{\partial\beta_c}\right)\omega=\sum_\lambda\int d\omega_q\alpha_\lambda{}^2(\omega_q)F_\lambda(\omega_q)\int_0^\infty\frac{d\omega'}{2\omega'^2}\operatorname{Re}\left(\frac{\partial\Delta^2(\omega')}{\partial\beta_c}\right)\cdot\Xi(\omega,\omega',\omega_q,\beta_c). \tag{3.13}$$

The relation derived in the Appendix D,

$$\int_0^\infty\frac{d\omega}{\omega^2}\operatorname{Re}\left(\frac{\partial\Delta^2}{\partial\beta_c}\right)=0, \tag{3.14}$$

tells that the quantity (3.13) vanishes more rapidly than $1/\omega$ when $|\omega|$ becomes large, thereby justifying the transformation from (3.11) to (3.12).

Transforming the ω' integral in (3.13) to that with a closed contour as in (3.11) we find

$$\sum_{m\geq 0}\left(\frac{\partial Z_n}{\partial\beta_c}-\frac{\partial Z_s}{\partial\beta_c}\right)z\bigg|_{z=iE_m}=\sum_\lambda\int d\omega_q\alpha_\lambda{}^2(\omega_q)F_\lambda(\omega_q)\sum_{m\geq 0}\int_{-\infty}^\infty\frac{d\omega'}{4\omega'^2}\frac{\partial\Delta^2(\omega')}{\partial\beta_c}\Xi(iE_m,\omega',\omega_q,\beta_c)$$

$$=\frac{\pi i}{2\beta_c}\sum_{\substack{m\geq 0\\ n\geq 0}}\frac{1}{(iE_n)^2}\frac{\partial\Delta^2(iE_n)}{\partial\beta_c}J(iE_m,iE_n), \tag{3.15}$$

where

$$J(iE_m,iE_n)=\sum_\lambda\int d\omega_q\alpha_\lambda{}^2(\omega_q)F_\lambda(\omega_q)\left\{\frac{1}{iE_n+iE_m+\omega_q}-\frac{1}{iE_n-iE_m+\omega_q}-\frac{1}{-iE_n+iE_m+\omega_q}+\frac{1}{-iE_n-iE_m+\omega_q}\right\}. \tag{3.16}$$

On the other hand, using Eq. (B5) one obtains

$$\sum_{m\geq 0}\frac{1-Z_n}{2z}\frac{\partial\Delta^2}{\partial\beta_c}\bigg|_{z=iE_m}=\sum_\lambda\int d\omega_q\alpha_\lambda{}^2(\omega_q)F_\lambda(\omega_q)\sum_{m\geq 0}\frac{1}{4(iE_m)^2}\frac{\partial\Delta^2(iE_m)}{\partial\beta_c}\int_{-\infty}^\infty d\omega'\Xi(iE_m,\omega',\omega_q,\beta_c)$$

$$=\frac{\pi i}{2\beta_c}\sum_{\substack{m\geq 0\\ n\geq 0}}\frac{1}{(iE_m)^2}\frac{\partial\Delta^2(iE_m)}{\partial\beta_c}J(iE_m,iE_n). \tag{3.17}$$

Combining (3.12), (3.15), and (3.17), we get

$$dI/d\beta_c=0. \tag{3.18}$$

Thus the transition is shown to be not of the first order. It is important to note that the above result (3.18) has been derived without recourse to the assumption about the isotope effect, particularly, the choice of the parameter α'.

We will turn to the calculation of $d^2I/d\beta_c{}^2$ to find the jump in specific heat ΔC. $d^2I/d\beta_c{}^2$ can be obtained by a direct differentiation of $dI/d\beta$, (3.9), and then setting $\beta=\beta_c$, since the gap function $\Delta(\omega)$ vanishes linearly at small ω by the damping effect as shown in the Appendix E. However, to get the expression which is also applicable to the approximate gap function which may be obtained without the damping, we make a partial integration and find

$$\frac{d^2I}{d\beta_c{}^2}=\int_0^\infty\frac{d\omega}{4\omega}\operatorname{Re}\frac{\partial}{\partial\omega}\left[\frac{-3+Z_n}{\omega}\cdot\left(\frac{\partial\Delta^2}{\partial\beta_c}\right)^2\tanh\frac{\beta_c\omega}{2}\right]+\int_0^\infty d\omega\operatorname{Re}\left[\left\{\frac{\partial^2Z_n}{\partial\beta_c{}^2}-\frac{\partial^2Z_s}{\partial\beta_c{}^2}\right\}\omega+\frac{1}{\omega}\frac{\partial Z_s}{\partial\beta_c}\frac{\partial\Delta^2}{\partial\beta_c}-\frac{1-Z_n}{2\omega}\frac{\partial^2\Delta^2}{\partial\beta_c{}^2}\right]\tanh\frac{\beta_c\omega}{2}$$

$$+\int_0^\infty d\omega\operatorname{Re}\left[\left\{\frac{\partial Z_n}{\partial\beta_c}-\frac{\partial Z_s}{\partial\beta_c}\right\}\omega-\frac{1-Z_n}{2\omega}\frac{\partial\Delta^2}{\partial\beta_c}\right]\frac{\omega}{\cosh^2(\beta_c\omega/2)}. \tag{3.19}$$

The right-hand side of (3.19) can be regarded as a sum of the terms which do not vanish when $Z_n=Z_s=1$ and other correction terms for which the same discussions can be applied as for $dI/d\beta_c$. The discussions are given in

Appendix F where we obtain

$$\frac{d^2I}{d\beta_c^2}=-\int_0^\infty\frac{d\omega}{2\omega}\mathrm{Re}\frac{\partial}{\partial\omega}\left[\frac{1}{\omega}\left(\frac{\partial\Delta^2}{\partial\beta_c}\right)^2\tanh\frac{\beta_c\omega}{2}\right]-\frac{\pi^2}{2\beta_c^2}\sum_{\substack{m\geq 0\\ n\geq 0}}\left[\frac{1}{(iE_n)^2}\frac{\partial\Delta^2(iE_n)}{\partial\beta_c}-\frac{1}{(iE_m)^2}\frac{\partial\Delta^2(iE_m)}{\partial\beta_c}\right]^2 J(iE_n,iE_m). \quad (3.20)$$

The quantity $\partial^2\Delta^2/\partial\beta_c^2$ in (3.19) is cancelled out so that we need only $\partial\Delta^2/\partial\beta_c$ to calculate ΔC. Finally, the expression (3.20) has to be rewritten in terms of $\partial\Delta^2/\partial\beta_c$ along the real axis. Since $\Delta(\omega)$ vanishes at $\omega=0$, we do not have to worry about the singularities from $1/(iE_n)^2$, etc., and the well-known procedure leads to

$$\frac{d^2I}{d\beta_c^2}=-\int_0^\infty\frac{d\omega}{2\omega}\mathrm{Re}\frac{\partial}{\partial\omega}\left[\frac{1}{\omega}\left(\frac{\partial\Delta^2}{\partial\beta_c}\right)^2\tanh\frac{\beta_c\omega}{2}\right]+\sum_\lambda\int d\omega_q\alpha_\lambda^2(\omega_q)F_\lambda(\omega_q)\left[\int_0^\infty d\omega\frac{1}{2\omega^4}\ln\left|\frac{\omega-\omega_q}{\omega+\omega_q}\right|\cdot\mathrm{Re}\left(\frac{\partial\Delta^2(\omega)}{\partial\beta_c}\right)^2\right.$$
$$\left.+\int_0^\infty d\omega\frac{\pi}{2(\omega+\omega_q)^4}\mathrm{Im}\left(\frac{\partial\Delta^2(\omega+\omega_q)}{\partial\beta_c}\right)^2-\int_0^\infty\int_0^\infty\frac{d\omega d\omega'}{\omega^2\omega'^2(\omega+\omega'+\omega_q)}\mathrm{Re}\left(\frac{\partial\Delta^2(\omega)}{\partial\beta_c}\right)\mathrm{Re}\left(\frac{\partial\Delta^2(\omega')}{\partial\beta_c}\right)\right], \quad (3.21)$$

as shown in Appendix G. The jump in specific heat is obtained by combining (3.21) with (2.25).

IV. CONNECTION WITH THE BCS AND SWIHART THEORIES

It is interesting to note that the present results reduce to the BCS expressions if we put

$$Z_n=Z_s=1,\quad \Delta=\text{a real constant},\quad 0\leq\omega\leq\omega_0$$
$$=\quad 0,\quad \omega_0<\omega,$$

and $\alpha=\frac{1}{2}$.

For instance, the function $I(\beta)$, (3.7) is easily evaluated in this case and gives

$$I(\beta)=-\frac{\pi^2}{3\beta^2}+\omega_0^2\left[1-\left(1-\frac{\Delta^2}{\omega_0^2}\right)^{1/2}\right]+\int_0^\infty d\epsilon\frac{2(2\epsilon^2+\Delta^2)}{E(e^{\beta E}+1)}, \quad (4.1)$$

where

$$E=(\epsilon^2+\Delta^2)^{1/2}.$$

This gives the BCS critical field with (2.19). The entropy difference (2.22) can be rewritten, using the same approximations, as

$$\Delta S=\kappa N(0)\beta^2\left[\int_0^\infty d\epsilon\frac{\epsilon^2}{\cosh^2(\beta\epsilon/2)}+\frac{d\Delta^2}{d\beta}-\int_0^{\omega_0}d\epsilon\left\{\frac{\Delta^2}{2E^3}\tanh\frac{\beta E}{2}+\frac{\beta\Delta^2}{4E^2}\frac{1}{\cosh^2(\beta E/2)}\right\}\frac{d\Delta^2}{d\beta}\right.$$
$$\left.-\int_0^\infty d\epsilon\tfrac{1}{2}(E^2+\epsilon^2)\frac{1}{\cosh^2(\beta E/2)}-\int_0^{\omega_0}d\epsilon\frac{\beta\epsilon^2}{2E^2}\frac{1}{\cosh^2(\beta E/2)}\frac{d\Delta^2}{d\beta}\right]. \quad (4.2)$$

The last term in the parentheses can be transformed as

$$-\int_0^{\omega_0}d\epsilon\frac{\beta\epsilon^2}{2E^2}\frac{1}{\cosh^2(\beta E/2)}\frac{d\Delta^2}{d\beta}=-\int_0^{\omega_0}d\epsilon\frac{d\Delta^2}{d\beta}\frac{\epsilon}{E}\frac{d}{d\epsilon}\tanh\frac{\beta E}{2}=-\frac{d\Delta^2}{d\beta}+\frac{d\Delta^2}{d\beta}\int_0^{\omega_0}d\epsilon\frac{\Delta^2}{E^3}\tanh\frac{\beta E}{2}. \quad (4.3)$$

Substituting (4.3) into (4.2) and making use of the relation

$$\frac{d\Delta^2}{d\beta}\int_0^{\omega_0}\left[\frac{\tanh(\beta E/2)}{2E^3}-\frac{\beta}{4E^2}\cdot\frac{1}{\cosh^2(\beta E/2)}\right]d\epsilon=\int_0^{\omega_0}\frac{d\epsilon}{2\cosh^2(\beta E/2)},$$

which can be obtained by differentiating the BCS gap equation with respect to β, one finds

$$\Delta S=\frac{2\pi^2N(0)\kappa}{3\beta}-\kappa N(0)\beta^2\int_0^\infty\frac{\epsilon^2d\epsilon}{\cosh^2(\beta E/2)}=\gamma T-4\kappa N(0)\beta\int_0^\infty\frac{d\epsilon}{e^{\beta E}+1}\left(E+\frac{\epsilon^2}{E}\right),$$

where $\gamma=\frac{2}{3}\pi^2N(0)\kappa^2$. This agrees with BCS again. It is evident that we can get the BCS expression for $\Delta C(t)$ from (2.24).

It is possible to reduce the expression (2.25) for the specific heat jump to Swihart's formula[3] where the gap depends on the energy. His result can be rewritten as

$$\frac{\Delta C}{\gamma T_c}=-\frac{3\beta_c^4}{\pi^2}\int_0^\infty d\omega\frac{\partial\Delta^2(\omega)/\partial\beta_c}{[1+e^{\beta_c\omega}]^2}e^{\beta_c\omega}, \tag{4.4}$$

by virtue of the relation

$$\frac{\Delta(\omega,\beta_c)}{\Delta(\bar{\omega},\beta_c)}=\frac{\partial\Delta(\omega,\beta_c)}{\partial\beta_c}\bigg/\frac{\partial\Delta(\bar{\omega},\beta_c)}{\partial\beta_c}, \tag{4.5}$$

where $\bar{\omega}$ is a constant energy. To establish this relation, we divide the energy-gap equation (B6) by $\Delta(\bar{\omega},\beta)$ and take the limit $\beta\to\beta_c$ and find that the left-hand side of (4.5) satisfies a homogeneous linear equation obtained from (B6) by putting $\Delta(\omega')$ in the square root to be zero and replacing Z_s by Z_n. Then, after differentiating (B6) with respect to β, one applies the same discussion and finds that the right-hand side of (4.5) satisfies the same equation. In this way, the relation (4.5) is derived.

In Swihart's discussions the energy-gap equation,

$$\Delta(\omega)=-\frac{1}{2}\int d\omega' V(|\omega-\omega'|)\frac{\Delta(\omega')}{[\omega'^2+\Delta^2(\omega')]^{1/2}}\times\tanh\tfrac{1}{2}\beta[\omega'^2+\Delta^2(\omega')]^{1/2} \tag{4.6}$$

was used. Assuming this equation and putting $Z_n=Z_s=1$, Δ real, and $\alpha=\frac{1}{2}$, we shall derive his result for ΔC, (4.4), from the present result (2.25) in the case of weak electron-phonon coupling. Only the first term in the expression for $d^2I/d\beta_c^2$, (3.21), survives and turns out to be

$$\begin{aligned}\frac{d^2I}{d\beta_c^2}&=\int_0^\infty d\omega\left(\frac{\partial\Delta^2}{\partial\beta_c}\right)^2\left\{\frac{1}{2\omega^3}\tanh\frac{\beta_c\omega}{2}-\frac{\beta_c}{4\omega^2}\frac{1}{\cosh^2(\beta_c\omega/2)}\right\}-\int_0^\infty\frac{d\omega}{2\omega^2}\frac{\partial}{\partial\omega}\left(\frac{\partial\Delta^2}{\partial\beta_c}\right)^2\cdot\tanh\frac{\beta_c\omega}{2}\\&=\int_0^\infty d\omega\frac{1}{2}\frac{\partial\Delta^2}{\partial\beta_c}\frac{1}{\cosh^2(\beta_c\omega/2)}-\int_0^\infty d\omega\frac{\partial\Delta^2}{\partial\beta_c}\cdot\frac{\partial}{\partial\beta}\left\{\frac{1}{(\omega^2+\Delta^2)^{1/2}}\tanh\frac{\beta(\omega^2+\Delta^2)^{1/2}}{2}\right\}_{\beta=\beta_c}\\&\quad-\int_0^\infty\frac{d\omega}{2\omega^2}\frac{\partial}{\partial\omega}\left(\frac{\partial\Delta^2}{\partial\beta_c}\right)^2\tanh\frac{\beta_c\omega}{2}.\end{aligned} \tag{4.7}$$

The second term on the right-hand side can be shown to vanish. We find from (4.5)

$$\begin{aligned}&\int_0^\infty d\omega\frac{\partial\Delta^2}{\partial\beta_c}\cdot\frac{\partial}{\partial\beta}\left\{\frac{1}{(\omega^2+\Delta^2)^{1/2}}\tanh\frac{\beta(\omega^2+\Delta^2)^{1/2}}{2}\right\}_{\beta=\beta_c}\propto\int_0^\infty d\omega\Delta^2\frac{\partial}{\partial\beta}\left\{\frac{1}{(\omega^2+\Delta^2)^{1/2}}\tanh\frac{\beta(\omega^2+\Delta^2)^{1/2}}{2}\right\}_{\beta=\beta_c}\\&=-\frac{1}{2}\int_0^\infty\int_0^\infty d\omega d\omega'\left[\frac{\partial}{\partial\beta}\left\{\frac{\Delta(\omega)}{(\omega^2+\Delta^2)^{1/2}}\tanh\frac{\beta(\omega^2+\Delta^2)^{1/2}}{2}\right\}_{\beta=\beta_c}-\frac{\partial\Delta(\omega)}{\partial\beta_c}\cdot\frac{\tanh\beta_c\omega/2}{\omega}\right]\cdot V(|\omega-\omega'|)\frac{\Delta(\omega')}{\omega'}\tanh\frac{\beta_c\omega'}{2}\\&=\int_0^\infty d\omega'\frac{\partial\Delta(\omega')}{\partial\beta_c}\cdot\frac{\Delta(\omega')}{\omega'}\tanh\frac{\beta_c\omega'}{2}-\int_0^\infty d\omega\frac{\partial\Delta(\omega)}{\partial\beta_c}\cdot\frac{\Delta(\omega)}{\omega}\tanh\frac{\beta_c\omega}{2}=0.\end{aligned} \tag{4.8}$$

Combining the relation between ΔC and $d^2I/d\beta_c^2$, (2.25), with (4.7) and (4.8), one obtains

$$\Delta C=-\kappa N(0)\beta_c^3\left[\frac{1}{2}\int_0^\infty d\omega\frac{\partial\Delta^2/\partial\beta_c}{\cosh^2(\beta_c\omega/2)}-\int_0^\infty\frac{d\omega}{2\omega^2}\frac{\partial}{\partial\omega}\left(\frac{\partial\Delta^2}{\partial\beta_c}\right)^2\cdot\tanh\frac{\beta_c\omega}{2}\right]. \tag{4.9}$$

The first term in the parentheses gives Swihart's result (4.4). The relative order of magnitude of the second term to the first may be estimated by assuming a constant $\partial\Delta^2/\partial\beta_c$ at $0<\omega<\omega_0$ and zero elsewhere. It turns out to be

$$\frac{\beta_c}{2\omega_0^2}\frac{\partial\Delta^2}{\partial\beta_c}\approx\frac{1}{2}\left(\frac{\pi}{\omega_0\beta_c}\right)^2.$$

This is small in the weak coupling limit $\omega_0\beta\gg1$. Therefore, ΔC reduces to (4.4).

The new expression (2.25) and (3.21) for ΔC is different from the BCS result in three respects. First of all, $\partial\Delta^2/\partial\beta_c$ in the first term of (4.9) increases with energy for small energies[2,25] thereby increasing $|\Delta C|$. The low-energy behavior is essential in this term because of the rapidly increasing denominator $\cosh^2(\beta_c\omega/2)$. This difference was already pointed out by Shiffman, Cochran, and Garber.[11] The second difference is the last term in

[25] P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).

(4.9). Since this term does not have such a rapidly increasing denominator as the first term, we might expect that the main contribution comes from the sharp drop in $\Delta(\omega)$ at the average phonon energy ω_0 although $\Delta(\omega)$ has many other structures in its ω dependence. Thus the second term might give rise to a further increase in $|\Delta C|$. The last difference between the present and the BCS results is the effects of $Z\neq 1$ and complex Δ. Unfortunately this is difficult to estimate without the detailed solution of the gap equations.

In this way, we may conclude that the present theory is likely to predict a larger jump in specific heat and give a better agreement with the experimental results for the strong coupling superconductors than the BCS results.

Shiffman, Cochran, and Garber pointed out that mercury remains an anomalous case.[11] The jump in its specific heat can be explained with a constant energy gap. We believe this is due to the fact that the typical phonon energy ω_0 in Hg is large in comparison with Pb. $\partial\Delta^2(\omega)/\partial\beta_c$ has the first maximum at $\omega\simeq\omega_0$. If $\beta_c\omega_0$ is large enough, the structure in $\partial\Delta^2(\omega)/\partial\beta_c$ does not give any contribution for ΔC, (4.4), which is presumably the main term. $\beta_c\omega_0$ is about 7 for Pb, and 22 for Hg.[26] Therefore, the retarded interaction theory might be able to account for Hg, too.

V. CONCLUDING REMARKS

Expressions for temperature dependence of critical field, entropy, specific heat, and its jump at T_c are obtained for strong coupling superconductors without making a quasiparticle approximation for electron motions. The contribution from the ion motions are taken into account semiphenomenologically, assuming H_c/H_0 is the same function h of the reduced temperature $t=T/T_c$ for all the isotopes of any one superconductor,

$$H_c=H_0h(t). \tag{5.1}$$

Isotopic mass dependences are assumed as

$$H_0\propto M^{-\alpha},\quad T_c\propto M^{-\alpha'},\quad \alpha'=\tfrac{1}{2}.$$

According to the experiment,[27] α and α' for Pb are observed to be

$$\alpha\simeq\alpha'=0.478\pm0.014$$

and the deviation from the "similarity principle" for the critical field, (5.1), is given by

$$\frac{1}{h(0)}\frac{\partial h(t)}{\partial M}<5\times10^{-4}\text{ per amu}. \tag{5.2}$$

If this value were taken literally, the expression for $\Delta\langle K_M\rangle$, (2.18), would be modified to

$$\Delta\langle K_M\rangle=2\Delta U_0h[\alpha h-\alpha' th'-M(\partial h/\partial M)], \tag{5.3}$$

and we would have a correction term whose magnitude is

$$M(\partial h/\partial M)<\tfrac{1}{10}h(0),$$

since $M\simeq207$ amu for Pb. This upper limit would give rise to 40% correction to the condensation energy at zero temperature. However, the similarity principle is quite well satisfied experimentally at the high-temperature region, $T\sim T_c$, where we can expect a smaller upper limit than (5.2), presumably, by a factor of about 10. We hope a further experimental study will give a smaller upper limit in the lower temperature region, too.

In the former sections, the isotope effect of T_c was always assumed to be $\alpha'=\frac{1}{2}$. Otherwise, an inconsistency occurs. Substituting the expression for $\Delta\langle H\rangle$, (2.18) and $\Delta\langle K_M\rangle$, (5.3), [$M(\partial h/\partial M)$ term being neglected] into the equation obtained by taking the difference of the thermal average of $\langle K\rangle$, (2.13), between the two phases and using $\Delta\mu=0$, one obtains

$$N(0)I(\beta)=\Delta U_0h\{(4\alpha-1)h-(4\alpha'-2)th'\}. \tag{5.4}$$

$dI/d\beta$ was shown to vanish at $\beta=\beta_c$ at (3.18) irrespective of α and α'. However, Eq. (5.4) gives

$$N(0)(dI/d\beta_c)=(\Delta U_0/\beta_c)(4\alpha'-2)h'(1)^2. \tag{5.5}$$

Making use of experimental results for Pb

$$(\partial H_c/\partial T)_{T=T_c}=-238.4\text{ G/°K},$$
$$H_0\sim800\text{ G},$$

one estimates the right-hand side of (5.5),

$$N(0)(dI/d\beta_c)=-0.4(\Delta U_0/\beta_c),$$

which is too large to be accounted for by the corrections of $I(\beta)$. The corrections are supposed to be small by the electron-ionic mass ratio $(m/M)^{1/2}$.

At present, the origin of this inconsistency is not clear. We can only make the following conjecture. The physical origin of the nonsimple isotope effect is the existence of Coulomb interactions among electrons.[25,28] The (screened) Coulomb interactions do not decrease rapidly for the large energy transfer as is the case for the phonon interaction. Accordingly the energy-gap function $\Delta(\omega)$ is not negligibly small even at $\omega\geq\omega_c$. For this reason the ω integral in the expression for $I(\beta)$, (3.6), may not be limited to the region $|\omega|<\omega_c$ and the trick of integrating first with respect to the 3-momentum may not work in a straightforward way. Since we do not know a method to get rid of this difficulty, the present paper is confined to the superconductors with $\alpha'=\frac{1}{2}$.

The expression for the jump in specific heat, (3.21), involves the quantity $\partial\Delta^2(\omega)/\partial\beta_c$. By virtue of the rela-

[26] Tunneling data give $\omega_0\approx7.8$ meV for Hg. D. M. Ginsberg (private communication).

[27] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **121**, 86 (1961).

[28] J. C. Swihart, Phys. Rev. **116**, 45 (1959); J. W. Garland (private communication).

tion between $\Delta(\omega,\beta_c)$ and $\partial\Delta(\omega,\beta_c)/\partial\beta_c$, (4.5), one finds

$$\frac{\partial\Delta^2(\omega)}{\partial\beta_c}\propto\left[\frac{\Delta(\omega,\beta_c)}{\Delta(\bar{\omega},\beta_c)}\right]^2.$$

Therefore, the knowledge for $\partial\Delta^2/\partial\beta_c$ at only one energy value is sufficient to know it all over the energy. This will be discussed in a separate paper with the results of numerical calculation.

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APPENDIX A: SHIFT IN CHEMICAL POTENTIAL DUE TO THE PHASE TRANSITION

The purpose of this appendix is to show that the shift in chemical potential due to the phase transition $\Delta\mu$ is quite small in comparison with the energy gap. Self-consistent discussions will be used, assuming a small change in the function χ_p. Thus, we assume the modified Bloch energy $\bar{\epsilon}_p$ does not change by the phase transition.

The chemical potential is determined in terms of average electron density ρ:

$$\rho=\frac{\langle N\rangle}{\Omega}=\frac{2}{\Omega}\lim_{\tau_2\to\tau_1+0}\sum_p G_{11}(p,\tau_1,\tau_2)\equiv\rho(\mu).\qquad\text{(A1)}$$

Denoting the function $\rho(\mu)$ in the superconducting and normal phases by the suffices s and n, respectively, and putting

$$\mu_n-\mu_s=\Delta\mu,$$

one obtains

$$\rho=\rho_s(\mu_s)=\rho_n(\mu_n)=\rho_n(\mu_s)+\Delta\mu(d\rho_n/d\mu_s)+\cdots,\qquad\text{(A2)}$$

$$\Delta\mu=[\rho_s(\mu_s)-\rho_n(\mu_s)]/(d\rho_n/d\mu_s).$$

Since ρ_n is given by

$$\rho_n(\mu_n)=(2m^*\mu_n)^{3/2}/3\pi^2,$$

with the effective electron mass m^*, $d\rho_n/d\mu_s$ is roughly equal to

$$d\rho_n/d\mu_s\approx(m^*/\pi^2)k_F,\qquad\text{(A3)}$$

where k_F is the Fermi momentum. Making use of the expression for $\rho(\mu)$, (A1), the numerator in (A2) can be rewritten

$$\begin{aligned}\rho_s(\mu_s)-\rho_n(\mu_s)&=-\frac{2}{\beta\Omega}\Delta\sum_{pn}\frac{zZ_p+\bar{\epsilon}_p}{z^2Z_p^2-E_p^2}e^{z0+}\Big|_{z=iE_n}\\&=\frac{2}{\pi\Omega}\operatorname{Im}\sum_p\int_0^\infty d\omega\Delta\frac{1}{\omega^2Z_p^2-E_p^2}\left\{\omega Z_p-\bar{\epsilon}_p\tanh\frac{\beta\omega}{2}\right\}\\&=-\frac{2}{\pi\Omega}\operatorname{Im}\sum_p\int_0^\infty d\omega\Delta\frac{\bar{\epsilon}_p}{\omega^2Z_p^2-E_p^2}\tanh\frac{\beta\omega}{2}.\qquad\text{(A4)}\end{aligned}$$

Here the same arguments are used as those which simplified the expression for $I(\beta)$ from (2.21) to (3.6) as well as a sum rule (D1). The main contributions to (A4) are expected from $|\bar{\epsilon}_p|$, $\omega\leq\omega_c$ as in the case of $I(\beta)$. However, the integrand is an odd function with respect to $\bar{\epsilon}_p$ at that region, thereby cancelling the main contributions. In order to estimate the order of magnitude of (A4), we take into account the momentum dependence of the electron density of states in normal metal, putting

$$\sum_p=N(0)\int\frac{p}{k_F}d\bar{\epsilon}_p\approx N(0)\int\left(1+\frac{m\bar{\epsilon}_p}{k_F^2}\right)d\bar{\epsilon}_p,$$

where m is the (bare) electron mass. Substituting this into (A4), one obtains

$$\rho_s(\mu_s)-\rho_n(\mu_s)=-\frac{2N(0)m}{\pi\Omega k_F^2}\operatorname{Im}\int d\bar{\epsilon}_p\times\int_0^\infty d\omega\Delta\frac{\bar{\epsilon}_p^2}{\omega^2Z_p^2-E_p^2}\tanh\frac{\beta\omega}{2}\qquad\text{(A5)}$$

$$\approx\frac{m^2}{\pi^2k_F}I(\beta).\qquad\text{(A6)}$$

Here, we used the fact that the integral in (A5) has the same order of magnitude with $I(\beta)$, (3.6). The magnitude of $I(\beta)$ is $\Delta^2/2$, as seen from (4.1) at zero temperature. Substituting (A3) and (A6) into the expression for $\Delta\mu$, (A2), one finally obtains

$$\Delta\mu\approx\Delta^2/4\mu_n.\qquad\text{(A7)}$$

The ratio between $\Delta\mu$ and the energy gap 2Δ turns out to be

$$\Delta/8\mu_n\sim10^{-4},$$

so that $\Delta\mu$ can always be neglected.

One might think that the shift (A7) would be essential for the condensation energy since it is multiplied by the total electron number in the relation

$$\Delta\langle H\rangle=\Delta\langle K\rangle+N\Delta\mu.\qquad\text{(A8)}$$

However, it is not the case, since $N\Delta\mu$ in (A8) must cancel the corresponding term in $\Delta\langle K_0\rangle$ which we calculated assuming $\Delta\mu=0$. Therefore, it is consistent to neglect the last term in (A8). Actually, Scalapino[29] has shown that the shift $\Delta\mu$ does not give rise to any change for the condensation energy in the case of the BCS model.

APPENDIX B: EQUATIONS FOR Z_p, χ_p, AND ϕ_p

In order to derive the equations satisfied by Z_p, χ_p, and ϕ_p,[8] we calculate the electron self-energy part Σ, (3.1), under the following approximations. First of all, the corrections to the electron-phonon vertex part are down by the electron-ion mass ratio and can be neglected.[30] Secondly, we might have to take into account the contribution from such diagrams shown in Fig. 2 where the solid lines correspond to the electron Green's functions and the dotted lines mean the interactions, that is, the phonon Green's function and the screened Coulomb interaction. We can discard these

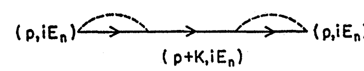

FIG. 2. One of the diagrams of the electron self-energy part Σ which are neglected in (B1). The electron momentum $p+K$ in the intermediate one-electron state is different from the incident momentum p, because of the umklapp processes. The intermediate momentum $p+K$ is usually far from the Fermi surface when p is on the surface.

diagrams. Since $|p+K|$ is generally far from the Fermi momentum k_F while $p\sim k_F$, the summation with respect to n in the expression for $I(\beta)$, (2.21), gives rise to a large energy denominator for such terms in Σ. For some special p's, we might have $|p+K|\sim k_F$. However, the measure of such p's is very small since the reciprocal lattice vector K can have only discrete values. Therefore, the lowest order diagram is sufficient for Σ which gives

$$\Sigma(p,iE_n)=-(1/\beta\Omega)\sum_{qK\lambda m}\bar{v}_{q+K,\lambda}\bar{v}_{-q-K,\lambda}\tau_3G(p-q-K,\,iE_n-iE_m)\tau_3D_\lambda(q,iE_m)$$
$$-(1/\beta\Omega)\sum_{qm}V_c(p,q,iE_m)\tau_3G(q,iE_n-iE_m)\tau_3\,, \quad \text{(B1)}$$

where $\bar{v}$ is the screened electron-phonon coupling matrix element and V_c the screened Coulomb interactions. Substituting Nambu's expressions for Σ and G, (3.1) and (3.2), into (B1), we obtain

$$[1-Z_p(iE_n)]iE_n=-\frac{1}{\beta\Omega}\sum_{qm}U(p,\,q,\,iE_n-iE_m)\frac{iE_mZ_q(iE_m)}{\{iE_mZ_q(iE_m)\}^2-E_q{}^2(iE_m)}\,,$$
$$\chi_p(iE_n)=-\frac{1}{\beta\Omega}\sum_{qm}U(p,\,q,\,iE_n-iE_m)\frac{\bar{\epsilon}_q(iE_m)}{\{iE_mZ_q(iE_m)\}^2-E_q{}^2(iE_m)}\,, \quad \text{(B2)}$$
$$\phi_p(iE_n)=\frac{1}{\beta\Omega}\sum_{qm}U(p,\,q,\,iE_n-iE_m)\frac{\phi_q(iE_m)}{\{iE_mZ_q(iE_m)\}^2-E_q{}^2(iE_m)}\,,$$

where

$$U(p,\,q,\,iE_n-iE_m)=\sum_{K\lambda}\bar{v}_{p-q,\lambda}\bar{v}_{-p+q,\lambda}D_\lambda(p-q-K,\,iE_n-iE_m)+V_c(p,\,q,\,iE_n-iE_m)\,. \quad \text{(B3)}$$

U is a symmetric function with respect to the interchange of p and q as well as n and m. The phonon Green's function $D_\lambda(q,i\nu_n)$ takes the form

$$D_\lambda(q,i\nu_n)^{-1}=-(\nu_n{}^2+\bar{\omega}_{q\lambda}{}^2)\,, \quad \text{(B4)}$$

in terms of the dressed phonon frequency $\bar{\omega}_{q\lambda}$. Substituting (B3) and (B4) into (B2) one can derive the equations for the analytically continued $Z_p(\omega)$ and $\phi_p(\omega)$ by applying Schrieffer, Scalapino, and Wilkins's discussion[20,24] used in the case of zero temperature. The results are given by

$$[1-Z_s(\omega)]\omega=\int_0^\infty d\omega'\,\mathrm{Re}\left\{\frac{\omega'}{[\omega'^2-\Delta^2(\omega')]^{1/2}}\right\}\sum_\lambda\int d\omega_q\alpha_\lambda{}^2(\omega_q)\cdot F_\lambda(\omega_q)\Xi(\omega,\omega',\omega_q,\beta)\,, \quad \text{(B5)}$$

$$\Delta(\omega)=\frac{1}{Z_s(\omega)}\int_0^{\omega_c}d\omega'\,\mathrm{Re}\left\{\frac{\Delta(\omega')}{[\omega'^2-\Delta^2(\omega')]^{1/2}}\right\}\left[\sum_\lambda\int d\omega_q\alpha_\lambda{}^2(\omega_q)\cdot F_\lambda(\omega_q)\Xi_0(\omega,\omega',\omega_q,\beta)-U\tanh\frac{\beta\omega'}{2}\right], \quad \text{(B6)}$$

[29] D. J. Scalapino (private communication).
[30] A. B. Migdal, Zh. Eksperim. i Teor. Fiz. 34, 1438 (1958) [English transl.: Soviet Phys.—JETP 7, 996 (1958)].

where

$$\Xi(\omega,\omega',\omega_q,\beta)=\left\{\frac{1}{e^{\beta\omega_q}-1}+\frac{1}{e^{-\beta\omega'}+1}\right\}\left\{\frac{1}{\omega'+\omega+\omega_q+i\epsilon}-\frac{1}{\omega'-\omega+\omega_q-i\epsilon}\right\}$$
$$+\left\{\frac{1}{e^{\beta\omega_q}-1}+\frac{1}{e^{\beta\omega'}+1}\right\}\left\{\frac{1}{-\omega'+\omega+\omega_q+i\epsilon}-\frac{1}{-\omega'-\omega+\omega_q-i\epsilon}\right\},$$

$$\Xi_0(\omega,\omega',\omega_q,\beta)=\left\{\frac{1}{e^{\beta\omega_q}-1}-\frac{1}{e^{-\beta\omega'}+1}\right\}\left\{\frac{1}{\omega'+\omega+\omega_q+i\epsilon}+\frac{1}{\omega'-\omega+\omega_q-i\epsilon}\right\}$$
$$-\left\{\frac{1}{e^{\beta\omega_q}-1}+\frac{1}{e^{\beta\omega'}+1}\right\}\left\{\frac{1}{-\omega'+\omega+\omega_q+i\epsilon}+\frac{1}{-\omega'-\omega+\omega_q-i\epsilon}\right\}.$$

$F_\lambda(\omega_q)$ is a phonon frequency distribution function and $\alpha_\lambda(\omega_q)$ is an interaction strength which are defined by

$$\alpha_\lambda^2(\omega)F_\lambda(\omega)=\frac{1}{(2\pi)^3}\int_{q<q_m}\delta(\bar{\omega}_{q\lambda}-\omega)d^3q\sum_K\frac{\bar{v}_{q+K,\lambda}\bar{v}_{-q-K,\lambda}}{2\bar{\omega}_{q\lambda}}\cdot\frac{m}{2k_F|q+K|}\theta(2k_F>|q+K|),$$

q_m is the Debye momentum, k_F the Fermi momentum and θ is the step function which is unity if the condition is satisfied and vanishes otherwise. The screened Coulomb interaction is replaced by a pseudopotential U defined to include interactions between electrons outside a band of energies $|\omega|<\omega_c$. The same discussion is applied for $\Delta\chi_p$, the difference of χ_p between the two phases, and shows $\Delta\chi_p$ is negligible since the integrand in (B2) is essentially an odd function of $\bar{\epsilon}_g$, as was the case for $\Delta\mu$, (A4).

Making use of this fact, we can show that the $\chi_p\bar{\epsilon}_p$ term in the expression for $I(\beta)$, (3.6), does not give the contribution. The term can be rewritten as

$$\frac{1}{\pi}\operatorname{Im}\sum_p\int_0^\infty d\omega\Delta\frac{\chi_p\bar{\epsilon}_p}{\omega^2Z_p^2-E_p^2}\tanh\frac{\beta\omega}{2}=-\frac{4}{\beta}\sum_{pn}\Delta\frac{\chi_p\bar{\epsilon}_p}{(iE_nZ_p)^2-E_p^2}. \tag{B7}$$

Denoting the superconducting and normal χ_p by $\chi_p{}^s$ and $\chi_p{}^n$ respectively, we can derive a relation

$$\sum_{pn}\frac{\chi_p{}^n(iE_n)\bar{\epsilon}_p(iE_n)}{(iE_nZ_{sp})^2-E_p{}^2(iE_n)}=-\frac{1}{\beta\Omega}\sum_{\substack{pq\\nm}}\frac{\bar{\epsilon}_p(iE_n)}{(iE_nZ_{sp})^2-E_p{}^2(iE_n)}U(p,q,iE_n-iE_m)$$
$$\times\frac{\bar{\epsilon}_q(iE_m)}{(iE_mZ_{nq})^2-\bar{\epsilon}_q{}^2(iE_m)}=\sum_{qm}\frac{\chi_q{}^s(iE_m)\bar{\epsilon}_q(iE_m)}{(iE_mZ_{nq})^2-\bar{\epsilon}_q{}^2(iE_m)},$$

where the equation for χ_p, (B2), is used. Since $\chi^n=\chi^s$, this means the quantity (B7) vanishes.

APPENDIX C: THE ANALYTICITY OF $\partial\Delta^2/\partial\beta_c$

The quantity,

$$\frac{\partial\Delta^2(\omega)}{\partial\beta_c}=\frac{1}{Z_n{}^2(\omega)}\frac{\partial\phi^2(\omega)}{\partial\beta_c},$$

obtained from the definition of $\Delta(\omega)$, Eq. (3.8), is analytic in the upper half ω plane if $Z_n(\omega)$ does not have any zeros there. Suppose $\omega=z_0$ is such a zero, and calculate the imaginary part of the equation continued analytically from the equation for $[1-Z_n(\omega)]\omega$, (B5), ($\Delta=0$) at that point. The left-hand side gives $\operatorname{Im}z_0$, while the right-hand side is proportional to $\operatorname{Im}z_0{}^*$, including the sign. Therefore, there are no such zeros of $Z_n(\omega)$.

APPENDIX D: THE DERIVATION OF EQ. (3.14)

Writing the τ_i dependence of the Green's function $G(p,\tau_1,\tau_2)$ explicitly in terms of the eigenstates $|n\rangle$ and the corresponding eigenvalues E_n of the Hamiltonian K,

$$K|n\rangle=E_n|n\rangle,$$

one finds

$$G_{11}(p,\omega+iO)=\sum_{nm}u_n\left\{\frac{|\langle m|c_{p\uparrow}{}^*|n\rangle|^2}{\omega+E_n-E_m+i\epsilon}+\frac{|\langle m|c_{p\uparrow}|n\rangle|^2}{\omega+E_m-E_n+i\epsilon}\right\},$$

where

$$u_n = e^{-\beta E_n} / \sum_m e^{-\beta E_m}.$$

This gives

$$\int_{-\infty}^{\infty} \mathrm{Im} G_{11}(p, \omega + i0) d\omega = -\pi.$$

Substituting the expression for G_{11}, (3.2), we obtain

$$\mathrm{Im} \int_0^{\infty} \frac{\omega Z_s(\omega)}{\omega^2 Z_s^2(\omega) - E_p^2(\omega)} d\omega = -\frac{\pi}{2}. \tag{D1}$$

Taking the difference of (D1) between the two phases, integrating with respect to d^3p, it is found that

$$\mathrm{Re} \int_0^{\infty} d\omega \left[1 - \frac{\omega}{[\omega^2 - \Delta^2(\omega)]^{1/2}} \right] = 0,$$

which gives Eq. (3.14).

APPENDIX E: THE GAP FUNCTION $\Delta(\omega)$ AT SMALL ω

From the equation for $[1 - Z_s(\omega)]\omega$, (B5), it is easily found that

$$\mathrm{Re}[1 - Z_s(\omega)]\omega = -a\omega \ln|\omega| + (1-b)\omega + O(\omega^3), \quad \mathrm{Im}\,\omega Z_s(\omega) = \Gamma + O(\omega^2).$$

Here a, b, and Γ are constants and $\Gamma > 0$, if $T > 0$. These relations give

$$\frac{1}{Z_s(\omega)} = \frac{\omega}{b\omega + a\omega \ln|\omega| + i\Gamma + O(\omega^2)}. \tag{E1}$$

By virtue of the equation satisfied by $\Delta(\omega)$, (B6), we obtain

$$\mathrm{Re} Z_s(\omega)\Delta(\omega) = A + O(\omega^2), \quad \mathrm{Im} Z_s(\omega)\Delta(\omega) = C\omega + O(\omega^3), \tag{E2}$$

where A and C are constants. Combining (E1) and (E2), we find

$$\Delta(\omega) = \frac{\omega[A + iC\omega + O(\omega^2)]}{i\Gamma + a\omega \ln|\omega| + b\omega + O(\omega^2)} \approx \frac{A\omega}{i\Gamma}, \tag{E3}$$

indicating the fact that $\Delta(\omega)$ vanishes linearly with ω. The density of states of the quasiparticles may be modified in the small ω region. The size of this modification will depend on the magnitude of the damping rate Γ as seen from (E3).

APPENDIX F: THE DERIVATION OF EQ. (3.20)

The transformations of the integration contour as in (3.12) allow us to rewrite (3.19) as

$$\frac{d^2 I}{d\beta_c^2} + \int_0^{\infty} \frac{d\omega}{2\omega} \mathrm{Re} \frac{\partial}{\partial \omega} \left[\frac{1}{\omega} \left(\frac{\partial \Delta^2}{\partial \beta_c} \right)^2 \tanh \frac{\beta_c \omega}{2} \right] = \frac{2\pi i}{\beta_c} \sum_{m \geq 0} \left[\frac{Z_n - 1}{4z^2} \left(\frac{\partial \Delta^2}{\partial \beta_c} \right)^2 + \left(\frac{\partial^2 Z_n}{\partial \beta_c^2} - \frac{\partial^2 Z_s}{\partial \beta_c^2} \right) z + \frac{1}{z} \frac{\partial Z_s}{\partial \beta_c} \frac{\partial \Delta^2}{\partial \beta_c} - \frac{1 - Z_n}{2z} \frac{\partial^2 \Delta^2}{\partial \beta_c^2} \right.$$
$$\left. - 2 \left(\frac{\partial^2 Z_n}{\partial \beta_c \partial z} - \frac{\partial^2 Z_s}{\partial \beta_c \partial z} \right) \frac{z^2}{\beta_c} - \frac{2(1 - Z_n)}{\beta_c z} \frac{\partial \Delta^2}{\partial \beta_c} - \frac{1}{\beta_c} \frac{\partial Z_n}{\partial z} \frac{\partial \Delta^2}{\partial \beta_c} - \frac{Z_n - 1}{\beta_c} \frac{\partial^2 \Delta^2}{\partial \beta_c \partial z} \right]_{z = iE_m}, \tag{F1}$$

where (3.12) and (3.18) have been used. Making use of the relations

$$\sum_\lambda \int d\omega_q \alpha_\lambda^2(\omega_q) F_\lambda(\omega_q) \int_{-\infty}^{\infty} d\omega' \psi(\omega') \Xi(iE_m, \omega', \omega_q, \beta) = \frac{2\pi i}{\beta} \sum_{n \geq 0} \psi(iE_n) J(iE_m, iE_n),$$

$$\sum_\lambda \int d\omega_q \alpha_\lambda^2(\omega_q) F_\lambda(\omega_q) \int_{-\infty}^{\infty} d\omega' \psi(\omega') \frac{\partial \Xi(iE_m, \omega', \omega_q, \beta)}{\partial \beta}$$
$$= -\frac{2\pi i}{\beta^2} \sum_{n \geq 0} \frac{\partial}{\partial z} [z \psi(z) J(iE_m, z)]_{z = iE_n} + 2\pi i \sum_\lambda \int d\omega_q \alpha_\lambda^2(\omega_q) F_\lambda(\omega_q) \frac{iE_m e^{\beta \omega_q}}{(e^{\beta \omega_q} - 1)^2} \{\psi(iE_m - \omega_q) - \psi(iE_m + \omega_q)\},$$

$$\sum_\lambda \int d\omega_q \alpha_\lambda{}^2(\omega_q) F_\lambda(\omega_q) \int_{-\infty}^{\infty} d\omega' \psi(\omega') \frac{\partial \Xi(z,\omega',\omega_q,\beta)}{\partial z}\bigg|_{z=iE_m}$$

$$= \frac{2\pi i}{\beta} \sum_{n\geq 0} \psi(iE_n) \frac{\partial J(iE_n,z)}{\partial z}\bigg|_{z=iE_m} + 2\pi i\beta \sum_\lambda \int d\omega_q \alpha_\lambda{}^2(\omega_q) F_\lambda(\omega_q) \frac{e^{\beta\omega_q}}{(e^{\beta\omega_q}-1)^2} \{\psi(iE_m-\omega_q)-\psi(iE_m+\omega_q)\},$$

where ψ is any analytic function on the upper half-plane, we obtain

$$\sum_{m\geq 0} \frac{Z_n-1}{4z^3}\left(\frac{\partial\Delta^2}{\partial\beta_c}\right)^2\bigg|_{z=iE_m} = -\frac{\pi i}{4\beta_c} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{(iE_m)^4}\left(\frac{\partial\Delta^2(iE_m)}{\partial\beta_c}\right)^2 J(iE_m,iE_n),$$

$$\sum_{m\geq 0}\left(\frac{\partial^2 Z_n}{\partial\beta_c{}^2}-\frac{\partial^2 Z_s}{\partial\beta_c{}^2}\right) z\bigg|_{z=iE_m}$$

$$= \frac{\pi i}{2\beta_c} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{(iE_n)^2} \frac{\partial^2\Delta^2(iE_n)}{\partial\beta_c{}^2} J(iE_n,iE_m)$$

$$+\frac{3\pi i}{4\beta_c} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{(iE_m)^4}\left(\frac{\partial\Delta^2(iE_m)}{\partial\beta_c}\right)^2 J(iE_m,iE_n) - \frac{\pi i}{\beta_c{}^2} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{\partial}{\partial z}\left[\frac{1}{z}\frac{\partial\Delta^2(z)}{\partial\beta_c} J(iE_m,z)\right]_{z=iE_n}$$

$$+\pi i \sum_{\substack{\lambda\\ m\geq 0}} \int d\omega_q \alpha_\lambda{}^2(\omega_q) F_\lambda(\omega_q) \frac{iE_m e^{\beta\omega_q}}{(e^{\beta\omega_q}-1)^2}\left\{\frac{1}{(iE_m-\omega_q)^2}\frac{\partial\Delta^2(iE_m-\omega_q)}{\partial\beta_c} - \frac{1}{(iE_m+\omega_q)^2}\frac{\partial\Delta^2(iE_m+\omega_q)}{\partial\beta_c}\right\},$$

$$\sum_{m\geq 0} \frac{1}{z}\frac{\partial Z_s}{\partial\beta_c}\frac{\partial\Delta^2}{\partial\beta_c}\bigg|_{z=iE_m} = -\frac{\pi i}{2\beta_c} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{(iE_m)^2(iE_n)^2}\frac{\partial\Delta^2(iE_m)}{\partial\beta_c}\frac{\partial\Delta^2(iE_n)}{\partial\beta_c} J(iE_m,iE_n)$$

$$+\frac{\pi i}{\beta_c{}^2} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{(iE_m)^2}\frac{\partial\Delta^2(iE_m)}{\partial\beta_c}\frac{\partial}{\partial z}[zJ(iE_m,z)]_{z=iE_n},$$

$$\sum_{m\geq 0} \frac{Z_n-1}{2z}\frac{\partial^2\Delta^2}{\partial\beta_c{}^2}\bigg|_{z=iE_m} = -\frac{\pi i}{2\beta_c} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{(iE_m)^2}\frac{\partial^2\Delta^2(iE_m)}{\partial\beta_c{}^2} J(iE_n,iE_m),$$

$$\sum_{m\geq 0}\left\{-2\left(\frac{\partial^2 Z_n}{\partial\beta_c\partial z}-\frac{\partial^2 Z_s}{\partial\beta_c\partial z}\right)\frac{z^2}{\beta_c} - \frac{2(1-Z_n)}{\beta_c z}\frac{\partial\Delta^2}{\partial\beta_c}\right\}_{z=iE_m}$$

$$= -\frac{\pi i}{\beta_c{}^2} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{(iE_m)^2}\frac{\partial\Delta^2(iE_m)}{\partial\beta_c} J(iE_m,iE_n) - \frac{\pi i}{\beta_c{}^2} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{iE_m}{(iE_n)^2}\frac{\partial\Delta^2(iE_n)}{\partial\beta_c}\frac{\partial}{\partial z} J(iE_n,z)\bigg|_{z=iE_m}$$

$$-\pi i \sum_{\substack{m\geq 0\\ \lambda}} \int d\omega_q \alpha_\lambda{}^2(\omega_q) F_\lambda(\omega_\lambda) \frac{iE_m e^{\beta\omega_q}}{(e^{\beta\omega_q}-1)^2}\left\{\frac{1}{(iE_m-\omega_q)^2}\frac{\partial\Delta^2(iE_m-\omega_q)}{\partial\beta_c} - \frac{1}{(iE_m+\omega_q)^2}\frac{\partial\Delta^2(iE_m+\omega_q)}{\partial\beta_c}\right\},$$

$$\sum_{m\geq 0}\left\{-\frac{1}{\beta_c}\frac{\partial Z_n}{\partial z}\frac{\partial\Delta^2}{\partial\beta_c}\right\}_{z=iE_m} = \frac{\pi i}{\beta_c{}^2} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{iE_m}\frac{\partial\Delta^2(iE_m)}{\partial\beta_c}\frac{\partial}{\partial z} J(iE_n,z)\bigg|_{z=iE_m} - \frac{\pi i}{\beta_c{}^2} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{(iE_m)^2}\frac{\partial\Delta^2(iE_m)}{\partial\beta_c} J(iE_n,iE_m),$$

$$\sum_{m\geq 0}\left\{-\frac{Z_n-1}{\beta_c}\frac{\partial^2\Delta^2}{\partial\beta_c\partial z}\right\}_{z=iE_m} = \frac{\pi i}{\beta_c{}^2} \sum_{\substack{m\geq 0\\ n\geq 0}} \frac{1}{iE_m}\frac{\partial^2\Delta^2}{\partial\beta_c\partial z}\bigg|_{z=iE_m} J(iE_n,iE_m).$$

Adding up all of the above equations, one rewrites the right-hand side of (F1) and gets (3.20).

APPENDIX G: THE DERIVATION OF EQ. (3.21)

Suppose a function $\psi(z)$ is analytic on the upper half z plane and bounded at $|z|\to\infty$. Then the series $\sum_{m\geq 0}\psi(iE_m)J(iE_n,iE_m)$ is calculated as follows:

$$\sum_{m\geq 0}\psi(iE_m)J(iE_n,iE_m)=\frac{\beta}{2\pi i}\sum_{\lambda}\int d\omega_q\alpha_\lambda^2(\omega_q)F_\lambda(\omega_q)\int_{c1}dz\psi(z)$$
$$\times\left\{\left(\frac{1}{iE_n+z+\omega_q}-\frac{1}{-iE_n+z+\omega_q}\right)\frac{1}{e^{-\beta z}+1}+\left(\frac{1}{iE_n-z+\omega_q}-\frac{1}{-iE_n-z+\omega_q}\right)\frac{1}{e^{\beta z}+1}\right\}$$
$$=\frac{\beta}{2\pi i}\sum_{\lambda}\int d\omega_q\alpha_\lambda^2(\omega_q)F_\lambda(\omega_q)\int_0^\infty d\omega\{\psi(\omega)+\psi(-\omega)\}\left\{\frac{1}{iE_n+\omega+\omega_q}-\frac{1}{-iE_n+\omega+\omega_q}\right.$$
$$\left.+\left(\frac{1}{iE_n-\omega+\omega_q}-\frac{1}{-iE_n-\omega+\omega_q}-\frac{1}{iE_n+\omega+\omega_q}+\frac{1}{-iE_n+\omega+\omega_q}\right)\frac{1}{e^{\beta\omega}+1}\right\}$$
$$-\beta\sum_{\lambda}\int d\omega_q\frac{\alpha_\lambda^2(\omega_q)F_\lambda(\omega_q)}{e^{\beta\omega_q}-1}\{\psi(iE_n-\omega_q)+\psi(iE_n+\omega_q)\}. \quad \text{(G1)}$$

The last term in the first integral, which has the factor $1/(e^{\beta\omega}+1)$, is presumably small in comparison with the first term, since the contribution to ω integral from the region $\omega>1/\beta$ is small due to the factor $1/(e^{\beta\omega}+1)$ and the contribution from $\omega<1/\beta$ is also small because of the other factor. We can neglect the last term in (G1), too, since $\beta\omega_q\geq 7$ for the typical phonon frequency in Pb.

With another analytic function $\varphi(z)$ which vanishes at $|z|\to\infty$ as $1/|z|^\gamma$, $\gamma>1$, one finds

$$\sum_{\substack{m\geq 0\\ n\geq 0}}\varphi(iE_n)\psi(iE_m)J(iE_n,iE_m)$$
$$=-\frac{\beta^2}{8\pi^2}\sum_{\lambda}\int d\omega_q\alpha_\lambda^2F_\lambda\int_{c1}dz\varphi(z)\tanh\frac{\beta z}{2}\int_0^\infty d\omega\{\psi(\omega)+\psi(-\omega)\}\left[\frac{1}{z+\omega+\omega_q}-\frac{1}{-z+\omega+\omega_q}\right]$$
$$=-\frac{\beta^2}{8\pi^2}\sum_{\lambda}\int d\omega_q\alpha_\lambda^2F_\lambda\left[\int_0^\infty d\omega'\{\varphi(\omega')+\varphi(-\omega')\}\int_0^\infty d\omega\{\psi(\omega)+\psi(-\omega)\}\left[\frac{1}{\omega+\omega'+\omega_q}-\frac{P}{\omega-\omega'+\omega_q}\right]\right.$$
$$\left.-i\pi\int_0^\infty d\omega\{\psi(\omega)+\psi(-\omega)\}\{\varphi(\omega+\omega_q)-\varphi(-\omega-\omega_q)\}\right]. \quad \text{(G2)}$$

Here small terms are neglected as done for (G1). If the function $\psi(z)$ becomes small at $|z|\to\infty$ as $\varphi(z)$, the relation (G2) takes a simple form

$$\sum_{\substack{m\geq 0\\ n\geq 0}}\varphi(iE_n)\psi(iE_m)J(iE_n,iE_m)=-\frac{\beta^2}{4\pi^2}\sum_{\lambda}\int d\omega_q\alpha_\lambda^2(\omega_q)F_\lambda(\omega_q)\int_0^\infty\int_0^\infty d\omega d\omega'\frac{\{\psi(\omega)+\psi(-\omega)\}\{\varphi(\omega')+\varphi(-\omega')\}}{\omega+\omega'+\omega_q}. \quad \text{(G3)}$$

Applying the relations (G2) and (G3) to the expression for $d^2I/d\beta_c^2$, (3.20), we easily obtain the result (3.21).