

Superconducting fluctuation effects on the thermoelectric coefficient above the transition temperature

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(Received 6 April 1994)

The quantum kinetic-equation method is applied to calculate the response of a metal to a temperature gradient above the superconducting transition temperature T_c . It is shown that the fluctuation correction to the thermoelectric coefficient of a three-dimensional superconductor is nonsingular near T_c . The fluctuation correction is more important in low-dimensional systems: it diverges as $\ln(T - T_c)$ in a thin film and as $(T - T_c)^{1/2}$ in a filament. Applying the linear-response method, we confirm these results and prove microscopically the Onsager relation for this problem. We also demonstrate how more singular terms obtained in earlier papers are canceled out by other terms representing the corrections to the heat current operator. The universal relation, independent on the electron mean free path, between the electric and heat current operators for the fluctuating order parameter is obtained.

I. INTRODUCTION

The advent of high-temperature superconductivity has revived interest in the effect of superconducting fluctuations on the thermoelectric power. There have been a lot of experimental data¹⁻⁹ and a number of theoretical papers¹⁰⁻¹⁴ which have discussed this phenomenon. Let us recall the definition of the coefficients describing the thermoelectric effect. Using the Onsager relations the thermoelectric coefficient η may be expressed in terms of the electric and the heat currents (\mathbf{J}_e and \mathbf{J}_h) which arise due to an applied electric field \mathbf{E} and a temperature gradient ∇T :

$$\mathbf{J}_e = \sigma \mathbf{E} + \eta \nabla T, \quad (1)$$

$$\mathbf{J}_h = -\eta T \mathbf{E} + \kappa \nabla T, \quad (2)$$

where κ is the thermal conductivity and σ is the electrical conductivity.

The experimentally measurable quantity is the thermopower or the Seebeck coefficient $S = -\eta/\sigma$. Because both coefficients η and σ have corrections due to superconducting fluctuations above T_c , the total correction to the thermopower is given by

$$\Delta S_{fl} = -\frac{\eta_0}{\sigma_0} \left[-\frac{\Delta \sigma_{fl}}{\sigma_0} + \frac{\Delta \eta_{fl}}{\eta_0} \right], \quad (3)$$

where $\sigma_0 = (\frac{2}{3}\pi^2)e^2 p_F \epsilon_F \tau$ and $\eta_0 = -(\frac{2}{9})e p_F \tau T$ are the conductivity and the thermoelectric coefficient at the transition temperature without the fluctuation effects, τ is the momentum relaxation time due to electron-impurity scattering, p_F and ϵ_F are the Fermi momentum and energy, and e is the electron charge ($e < 0$).

Near the superconducting transition the fluctuation conductivity of ordinary superconductors is described by the Aslamazov-Larkin (AL) correction.¹⁵ The excess conductivity of high- T_c superconductors extracted from the experiments is also explained by AL theory if anisot-

ropy effects are included,^{5,9} while the present situation with the thermopower is rather confusing.

Most of the measurements of the temperature dependence of the thermopower above T_c demonstrate a wide maximum at 100–150 K. For high temperatures the thermopower decreases and even changes the sign.¹⁻⁵ Some authors^{1,2,14} interpreted these data as an indication of superconducting fluctuations. Note that nonmonotonic temperature dependence may be treated in many ways. The main difficulty is associated with the change of signs of the thermopower, while the type of carriers is the same. In Ref. 16 this behavior was explained on the basis of the renormalization of the thermopower due to the electron-phonon-impurity interference. In the context of the fluctuation effects it is more interesting that some groups^{3,4} found a very sharp peak just above T_c . This peak has the same temperature singularity as the fluctuation correction to the conductivity, but the sign of the effect is opposite to that which follows from the conductivity correction to the thermopower [see Eq. (3)]. Other groups^{6,7} did not observe this peak and considered it as an experimental artifact. Taking into consideration that in Refs. 3 and 4 different measurements were used, the experimental data seem to be more sensitive to the sample preparation than to the method of measurement.

Theoretical description of the fluctuation effects on the thermopower is also controversial. The results for the AL-type correction obtained in Refs. 10–14 demonstrate different temperature and electron mean-free-path dependencies. The problem of calculating the thermoelectric coefficient is very complicated, because one needs to take into account the interaction effects on the electron relaxation as well as a number of corrections to the heat current operator.

The main goal of our paper is to resolve the problem of the fluctuation correction to thermopower. In previous work¹⁷ we suggested a new approach to calculation of the thermopower, which was based on the quantum transport equation method. This method allows one to calculate

the electric current as a response of an electron system to the temperature gradient. In this way one can avoid all difficulties arising from interaction corrections to the heat current operator. In Sec. II we apply the quantum transport equation method to the problem of superconducting fluctuations. To compare our results with earlier papers,^{11,12,14} in Sec. III we also consider the linear-response method and demonstrate cancellation of the strong singular terms. Our conclusions also essentially differ from the results of Ref. 13, where the time-dependent Ginzburg-Landau equation is used. In Sec. IV we summarize our results and discuss the earlier papers in more detail.

II. QUANTUM TRANSPORT EQUATION METHOD

To calculate $\Delta\eta_{\text{fl}}$ we employ the quantum transport equation method. There are few modifications of this method (for a review see Ref. 18). We will follow the rigorous approach of Ref. 19, in which all nonequilibrium terms are taken into account without any phenomenological approximation. We have already applied this method in Refs. 17 and 20 to calculate the electron-phonon-impurity interference effects on the conductivity and the thermopower.

In the Keldysh diagrammatic technique for nonequilibrium processes the electron Green function G , the fluctuation propagator L describing the electron-electron interaction in the Cooper channel, the electron self-energy Σ , and the polarization operator P are represented by matrices

$$\hat{G} = \begin{pmatrix} 0 & G^A \\ G^R & G^C \end{pmatrix}, \quad \hat{L} = \begin{pmatrix} 0 & L^A \\ L^R & L^C \end{pmatrix}, \quad (4)$$

$$\hat{\Sigma} = \begin{pmatrix} \Sigma^C & \Sigma^R \\ \Sigma^A & 0 \end{pmatrix}, \quad \hat{P} = \begin{pmatrix} P^C & P^R \\ P^A & 0 \end{pmatrix}, \quad (5)$$

where A and R stand for advanced and retarded components of the matrix function and C corresponds to the kinetic component.

Without the electron-electron interaction the retarded and advanced electron Green functions averaged over impurity positions are

$$G_0^R(\mathbf{p}, \epsilon) = [G_0^A(\mathbf{p}, \epsilon)]^* \\ = \left[\epsilon - \xi_p + \frac{i}{2\tau} \right]^{-1}, \quad \xi_p = (p^2 - p_F^2)/2m, \quad (6)$$

where m is the electron mass and $[\dots]^*$ means the complex conjugation.

The interaction in the Cooper channel is conveniently described by the fluctuation propagator as it is shown in Fig. 1. In the thermodynamic equilibrium the fluctuation propagator has the form

$$L_0^R(q, \omega) = [L_0^A(q, \omega)]^* = [\lambda^{-1} - P_0^R(q, \omega)]^{-1}, \quad (7)$$

where λ is a constant of the electron-electron interaction and P is the polarization operator in the Cooper channel.

Because electrons and holes drifting in the temperature gradient give contributions to the electric current of op-

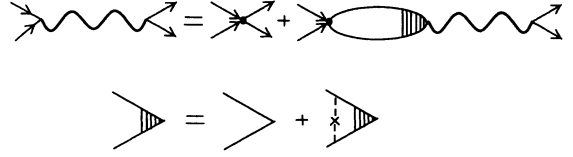


FIG. 1. Diagrammatic equation for the fluctuation propagator. The shaded triangles are the impurity vertex corrections. The dark spot is the constant of the electron-electron interaction λ .

posite signs, the thermoelectric phenomenon arises due to the difference between electron and hole states. The expression for $P_0(q, \omega)$ accounting for the electron-hole asymmetry is given by

$$P_0^R(q, \omega) = [P_0^A(q, \omega)]^* \\ = -\frac{\nu}{2} \left[\ln \frac{2\gamma\omega_D}{\pi T_c} - \alpha q^2 + \frac{i\pi\omega}{8T_c} \right. \\ \left. + \frac{\omega}{4\epsilon_F} \ln \frac{2\gamma\omega_D}{\pi T_c} \right], \quad (8)$$

where ν is the electron density of states at the Fermi energy, ω_D is the Debye frequency, and γ is the Euler constant. The electron-hole asymmetry is represented by the small correction term of the order of ω/ϵ_F , which is obtained due to expansion of the electron density of states near the Fermi surface.²¹ Note that without this term $P_0^R(q, \omega) = P_0^A(q, -\omega)$ and the combination $L_0^R(q, \omega)L_0^A(q, \omega)$ is an even function of ω .

For an arbitrary electron momentum relaxation time the coefficient α in Eq. (8) may be expressed as follows:

$$\alpha = -\frac{\nu_F^2}{3} \left\{ \tau^2 \left[\psi \left[\frac{1}{2} + \frac{1}{4\pi T_c \tau} \right] - \psi \left[\frac{1}{2} \right] \right] \right. \\ \left. - \frac{\tau}{4\pi T_c} \psi' \left[\frac{1}{2} \right] \right\}. \quad (9)$$

Here $\psi(x)$ is the logarithmic derivative of the γ function.

The functions G_0^C and L_0^C in the thermodynamic equilibrium are

$$G_0^C(q, \epsilon) = \tanh \left[\frac{\epsilon}{2T} \right] [G_0^R(q, \omega) - G_0^A(q, \epsilon)], \quad (10)$$

$$L_0^C(q, \omega) = \coth \left[\frac{\omega}{2T} \right] [L_0^R(q, \omega) - L_0^A(q, \omega)]. \quad (11)$$

The components of the matrix $\hat{P}(q, \omega)$ satisfy an equation similar to Eq. (11).

In the presence of an external disturbance the electron system becomes nonuniform. Deriving the quantum transport equation one makes the Fourier transformation from the coordinate representation, $X = (\mathbf{r}, t)$, to the momentum-energy representation (\mathbf{p}, ϵ) . Induced by the external disturbance the nonuniformity of the system leads to the correction terms in the Poisson brackets form:^{18,19}

$$A(X_1, X)B(X, X_2) \Rightarrow A(\mathbf{p}, \epsilon)B(\mathbf{p}, \epsilon) + \frac{i}{2} \{A(\mathbf{p}, \epsilon), B(\mathbf{p}, \epsilon)\}, \quad (12)$$

$$\{A, B\} = \left[\frac{\partial' A}{\partial \epsilon} \frac{\partial' B}{\partial t} - \frac{\partial' B}{\partial \epsilon} \frac{\partial' A}{\partial t} \right] - \left[\frac{\partial' A}{\partial \mathbf{p}} \frac{\partial' B}{\partial \mathbf{r}} - \frac{\partial' B}{\partial \mathbf{p}} \frac{\partial' A}{\partial \mathbf{r}} \right]. \quad (13)$$

The vector and scalar potentials (\mathbf{A} and Φ) of the external electromagnetic field are accounted for in the following way:

$$\frac{\partial'}{\partial t} = \frac{\partial}{\partial t} - \frac{e}{c} \frac{\partial \mathbf{A}}{\partial t} \frac{\partial}{\partial \mathbf{p}} - e \frac{\partial \Phi}{\partial t} \frac{\partial}{\partial \epsilon}, \quad (14)$$

$$\frac{\partial'}{\partial \mathbf{r}} = \frac{\partial}{\partial \mathbf{r}} - \frac{e}{c} \frac{\partial \mathbf{A}}{\partial r_i} \frac{\partial}{\partial p_i} - e \frac{\partial \Phi}{\partial \mathbf{r}} \frac{\partial}{\partial \epsilon}. \quad (15)$$

If the electron system is considered to be driven from equilibrium by the temperature gradient ∇T , Eqs. (13)–(15) result in

$$\{A, B\} = \nabla T \left[\frac{\partial A}{\partial T} \frac{\partial B}{\partial \mathbf{p}} - \frac{\partial B}{\partial T} \frac{\partial A}{\partial \mathbf{p}} \right]. \quad (16)$$

Note, that the response to the electric field is described by the Poisson brackets in the following way:

$$\{A, B\} = e\mathbf{E} \left[\frac{\partial A}{\partial \epsilon} \frac{\partial B}{\partial \mathbf{p}} - \frac{\partial B}{\partial \epsilon} \frac{\partial A}{\partial \mathbf{p}} \right]. \quad (17)$$

To the first order in nonuniformity it is convenient to look for a solution of the Dyson equation for the kinetic component of the electron Green function G^C in the form

$$G^C(\mathbf{p}, \epsilon) = S(\mathbf{p}, \epsilon)[G^A(\mathbf{p}, \epsilon) - G^R(\mathbf{p}, \epsilon)] + \delta G^C(\mathbf{p}, \epsilon), \quad (18)$$

where δG^C is the Poisson bracket correction

$$\delta G^C(\mathbf{p}, \epsilon) = \frac{i}{2} \{S(\mathbf{p}, \epsilon), G^A(\mathbf{p}, \epsilon) + G^R(\mathbf{p}, \epsilon)\}. \quad (19)$$

Here $S(\mathbf{p}, \epsilon)$ plays the role of the electron distribution function. In equilibrium $S = S_0 = -\tanh(\epsilon/T)$. In the presence of the temperature gradient the function S is determined from the following linearized quantum transport equation:

$$-(\mathbf{v} \cdot \nabla T) \frac{\epsilon}{T} \frac{\partial S_0}{\partial \epsilon} = I_{e\text{-imp}} + I_{e\text{-e}}, \quad (20)$$

where $I_{e\text{-imp}}$ and $I_{e\text{-e}}$ are the collision integrals which correspond to the electron-impurity interaction and the electron-electron interaction in the Cooper channel. They may be expressed in terms of the corresponding self-energies by the equation

$$I(S) = I^0(S) + \delta I(S), \quad I^0 = -i[\Sigma^C - S(\Sigma^A - \Sigma^R)], \quad (21)$$

$$\delta I = -i[\delta \Sigma^C - S_0(\delta \Sigma^A - \delta \Sigma^R)] + \frac{1}{2}[\Sigma^A + \Sigma^R, S_0],$$

where $\delta \Sigma$ is the Poisson bracket correction.

Assuming that the electron-impurity scattering is a dominant momentum relaxation process, one can solve the transport equation [Eq. (20)] by iteration: $S = S_0 + \phi_0 + \phi_1$, where ϕ_0 is the nonequilibrium correction to the distribution function S_0 determined by electron-impurity scattering

$$\phi_0(\mathbf{p}, \epsilon) = \tau(\mathbf{v} \cdot \nabla T) \frac{\epsilon}{T} \frac{\partial S_0(\epsilon)}{\partial \epsilon}. \quad (22)$$

The correction ϕ_1 includes the effects of the electron-electron interaction

$$\phi_1(\mathbf{p}, \epsilon) = \tau[I_{e\text{-e}}(S_0 + \phi_0)]. \quad (23)$$

Our aim is to calculate the electric current which is initiated by the temperature gradient

$$\mathbf{J}_e = \eta \nabla T = 2e \int \frac{d\mathbf{p} d\epsilon}{(2\pi)^4} \mathbf{v} [S(\mathbf{p}, \epsilon) \text{Im} G^A(\mathbf{p}, \epsilon) + \frac{1}{2} \{S(\mathbf{p}, \epsilon), \text{Re} G^A(\mathbf{p}, \epsilon)\}]. \quad (24)$$

It is clear from Eq. (24), that the fluctuation corrections to the thermoelectric coefficient $\Delta \eta_{\text{fl}}$ may originate from the correction to the distribution function as well as from various corrections to $\text{Im} G^A$, which may be treated as corrections to the electron density of states.

Near T_c the most singular contribution to η_{fl} is determined by the AL correction. In the transport equation method this term corresponds to the following nonequilibrium correction to $\text{Im} G^A$:

$$\delta G^A = (G_0^A)^2 \delta \Sigma_{\text{AL}}^A, \quad (25)$$

where $\delta \Sigma_{\text{AL}}^A$ is the nonequilibrium correction to the electron self-energy in the form of the Poisson bracket.

The Aslamazov-Larkin self-energy diagram Σ_{AL} is shown in Fig. 2. The corresponding equation has the form

$$\Sigma_{\text{AL}}^A = \frac{i}{2} \int \frac{d\mathbf{q} d\omega}{(2\pi)^4} \frac{1}{[1 - \zeta(q, \omega)]^2} G^R(\mathbf{q} - \mathbf{p}, \omega - \epsilon) L^C(\mathbf{q}, \omega), \quad (26)$$

where

$$\zeta(q, \omega) = \frac{1}{\pi v \tau} \int \frac{d\mathbf{p} d\epsilon}{(2\pi)^4} G^A(\mathbf{p}, \epsilon) G^R(\mathbf{q} - \mathbf{p}, \omega - \epsilon). \quad (27)$$

The nonequilibrium correction in Eq. (26) originates from the composite fluctuation propagator shown in Fig. 2: $L^C = L_{\text{eqv}}^C + \delta L^C$. Without the Poisson bracket, the equilibrium term is given by

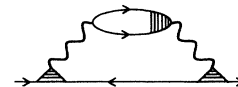


FIG. 2. The electron self-energy Σ_{AL} corresponding to the Aslamazov-Larkin correction.

$$L_{\text{eqv}}^C(q, \omega) = L_0^R(q, \omega) P_0^C(q, \omega) L_0^A(q, \omega), \quad (28)$$

and Eq. (28) reduces to Eq. (11). In accordance with Eq. (12), the Poisson bracket correction to Eq. (28) is given by

$$\delta L^C = \frac{i}{2} (\{L_0^R, P_0^C\} L_0^A + L_0^R \{P_0^C, L_0^A\} + P_0^C \{L_0^R, L_0^A\}). \quad (29)$$

Recalling that P_0^C satisfies an equation analogous to Eq. (11), we rewrite Eq. (29) in the following way:

$$\delta L^C = \frac{i}{2} (P_0^A - P_0^R) \left[L_0^R \left\{ \coth \frac{\omega}{2T}, L_0^A \right\} + \left\{ L_0^R, \coth \frac{\omega}{2T} \right\} L_0^A \right]. \quad (30)$$

As we mentioned before, the main contribution to the electric current originates from the nonequilibrium correction to $\text{Im}G^A$, which according to Eqs. (25), (26), and (30), is

$$\begin{aligned} \mathbf{J}_e &= 2e \int \frac{d\mathbf{p} d\epsilon}{(2\pi)^4} \mathbf{v} S_0(\epsilon) \delta G^A(\mathbf{p}, \epsilon) \\ &= -2e \int \frac{d\mathbf{q} d\omega}{(2\pi)^3} \frac{\partial P_0^R(\mathbf{q}, 0)}{\partial \mathbf{q}} \\ &\quad \times \left\{ \coth \frac{\omega}{2T}, P_0^R(\mathbf{q}, 0) \right\} L_0^R(\mathbf{q}, \omega) L_0^A(\mathbf{q}, \omega). \end{aligned} \quad (31)$$

Integration over electron variables in Eq. (31) corresponds to that in the electric current block of electron Green functions \mathbf{B}_e in the linear-response method [see Eq. (40) of the following section].

Calculating the electric current as a response of a system to the electric field and taking the Poisson brackets in the form of Eq. (17), we obtain from Eq. (31) the well-known Aslamazov-Larkin correction to the conductivity. Considering a response to the temperature gradient and

taking the Poisson brackets in the form of Eq. (16), we get the thermoelectric coefficient $\Delta\eta_{\text{fl}}$,

$$\begin{aligned} \Delta\eta_{\text{fl}} &= e \int \frac{d\mathbf{q} d\omega}{(2\pi)^3} \left[\frac{\partial P_0^R(\mathbf{q}, 0)}{\partial \mathbf{q}} \right]^2 \frac{\omega}{T^2} \left[\sinh \frac{\omega}{2T} \right]^{-2} \\ &\quad \times L_0^R(\mathbf{q}, \omega) L_0^A(\mathbf{q}, \omega). \end{aligned} \quad (32)$$

Without the electron-hole asymmetry the combination $L_0^R L_0^A$ is an even function of ω , therefore the integrand in Eq. (32) is an odd function. The only way to get a nonzero result is to take into consideration the electron-hole asymmetry in the fluctuation propagators $L_0^{R,A}$. Bearing in mind Eq. (8), we get

$$\begin{aligned} L_0^R(\mathbf{q}, \omega) &= -\frac{2}{v} \left[\frac{T - T_c}{T_c} + \alpha q^2 - \frac{i\pi\omega}{8T_c} \right. \\ &\quad \left. - \frac{\omega}{4\epsilon_F} \ln \frac{2\gamma\omega_D}{\pi T_c} \right]^{-1}. \end{aligned} \quad (33)$$

Expanding $L_0^R L_0^A$ over ω/ϵ_F we get the odd part of $L_0^R L_0^A$

$$\begin{aligned} L_0^R L_0^A &= \frac{2\omega}{4\epsilon_F v^2} \ln \frac{2\gamma\omega_D}{\pi T_c} \\ &\quad \times \text{Re} \left[\left[\frac{T - T_c}{T_c} + \alpha q^2 - \frac{i\pi\omega}{8T_c} \right]^{-2} \right. \\ &\quad \left. \times \left[\frac{T - T_c}{T_c} + \alpha q^2 + \frac{i\pi\omega}{8T_c} \right]^{-1} \right]. \end{aligned} \quad (34)$$

Substituting Eq. (34) into Eq. (32) and performing the integration, we find that there is no singularity in the temperature dependence of the thermoelectric coefficient in a three-dimensional superconductor. The fluctuation corrections to η for a two-dimensional film of thickness d and for a one-dimensional filament with the cross section d^2 are presented in Table I. The dimensional crossover takes place for critical dimension $d \sim v_F / [T_c (T - T_c)]^{1/2}$ for the pure case and $d \sim [v_F l / (T - T_c)]^{1/2}$ for the im-

TABLE I. Fluctuation corrections to the thermoelectric coefficient and the conductivity (Ref. 15) in different dimensions.

		$\frac{\Delta\eta_{\text{fl}}}{\eta_0}$	$\frac{\Delta\sigma_{\text{fl}}}{\sigma_0}$
Two dimensional	General	$-\frac{1.8}{p_F^2 l d} \ln \left[\frac{2\gamma\omega_D}{\pi T_c} \right] \ln \left[\frac{T_c}{T - T_c} \right]$	$\frac{1.84}{p_F^2 l d} \left[\frac{T_c}{T - T_c} \right]$
One dimensional	Impure	$-\frac{2.1}{(\tau T_c)^{1/2} (p_F d)^2} \ln \left[\frac{2\gamma\omega_D}{\pi T_c} \right] \left[\frac{T_c}{T - T_c} \right]^{1/2}$	$\frac{5.4}{(\tau T_c)^{1/2} (p_F d)^2} \left[\frac{T_c}{T - T_c} \right]^{3/2}$
	$T_c \tau < 1$		
One dimensional	Pure	$-\frac{0.54}{\tau T_c (p_F d)^2} \ln \left[\frac{2\gamma\omega_D}{\pi T_c} \right] \left[\frac{T_c}{T - T_c} \right]^{1/2}$	$\frac{0.39}{\tau T_c (p_F d)^2} \left[\frac{T_c}{T - T_c} \right]^{3/2}$
	$T_c \tau > 1$		

pure one. It is seen that in all cases the fluctuation corrections to the thermoelectric coefficient are less singular near T_c than the AL corrections to the conductivity.

It may be shown that unlike the conductivity, the Maki-Thompson correction to the thermoelectric coefficient is not singular close to T_c in all dimensions even if the electron-hole asymmetry is taken into account in the fluctuation propagator.

III. LINEAR-RESPONSE METHOD

In the linear-response method the thermoelectric coefficient is given by

$$\eta = \frac{1}{\Omega T} \text{Im}[Q_{e-h}^R(\Omega)], \quad (35)$$

where $Q_{e-h}^R(\Omega)$ is the Fourier representation of the retarded correlation function of the heat and charge currents

$$Q_{e-h}^R(X-X') = -\Theta(t-t') \langle [\tilde{J}_h(X), \tilde{J}_e(X')] \rangle, \quad (36)$$

$\tilde{J}_e(X)$ and $\tilde{J}_h(XZ)$ are operators in the Heisenberg representation, $X=(\mathbf{r}, t)$ and $\langle \dots \rangle$ represents both the thermodynamic averaging and position averaging over random impurity sites.

The heat current operator may be defined in terms of the energy current operator J_ϵ if the electron energy is measured with respect to the chemical potential μ ,

$$J_h = J_\epsilon - \frac{\mu}{e} J_e. \quad (37)$$

The energy current operator for interacting electrons may be obtained from the equation of motion for the electron field operators²² or from the energy-momentum tensor.²³ Both methods result in the same expression

$$\begin{aligned} J_h = & \sum_{\mathbf{p}} \frac{\mathbf{p}}{m} \xi_{\mathbf{p}} a_{\mathbf{p}}^+ a_{\mathbf{p}} - \frac{\lambda}{2} \sum_{\mathbf{p}, \mathbf{p}', \mathbf{p}'', \mathbf{p}'''} \frac{(\mathbf{p} + \mathbf{p}')}{2m} a_{\mathbf{p}'''}^+ a_{\mathbf{p}''}^+ a_{\mathbf{p}'} a_{\mathbf{p}} \\ & \times \delta(\mathbf{p} + \mathbf{p}' - \mathbf{p}'' - \mathbf{p}''') \\ & + \sum_{\mathbf{p}, \mathbf{p}', R_i} \frac{(\mathbf{p} + \mathbf{p}')}{2m} U_{e\text{-imp}} e^{i(\mathbf{p} + \mathbf{p}')R_i} a_{\mathbf{p}}^+ a_{\mathbf{p}'}, \end{aligned} \quad (38)$$

where $a_{\mathbf{p}}^+$ and $a_{\mathbf{p}}$ are the electron creation and annihilation operators, $U_{e\text{-imp}}$ is the electron-impurity potential, and R_i is the impurity position.

The first term of the Eq. (38) describes the heat flux of noninteracting electrons. The second term represents the additional heat current due to the electron-electron interaction and the third one is due to the electron-impurity interaction. Diagrammatically the vertices of the heat current operator are shown in Fig. 3.

As we discussed in the previous section, the main contribution to the thermoelectric coefficient comes from the Aslamazov-Larkin diagram, which is shown in Fig. 4. The right block of electron Green functions B_e is connected with the electric current operator. The left block of the electron Green function B_h originates from the heat current vertices of Fig. 3. Therefore, this block is presented by the sum of the diagrams shown in Fig. 4, $B_h = \sum_i B_h^i$. One can obtain the second block B_h^2 from

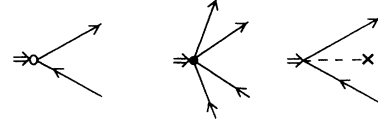


FIG. 3. The heat current operator vertices corresponding to Eq. (37).

the second vertex of Fig. 3. Here the constant of the electron-electron interaction of the heat current vertex is included in one of the fluctuation propagators. The analytical expression corresponding to the diagram of the thermoelectric coefficient shown in Fig. 4 has the form

$$\begin{aligned} \Delta\eta_{fl} = & \frac{4}{\Omega T} \int \frac{d\mathbf{q} d\omega}{(2\pi)^4} \left[\frac{1}{\sqrt{2}} \right]^6 B_h(\mathbf{q}, \omega) B_e(\mathbf{q}, \omega) \\ & \times [L^C(\mathbf{q}, \omega + \Omega) L^A(\mathbf{q}, \omega) \\ & + L^R(\mathbf{q}, \omega + \Omega) L^C(\mathbf{q}, \omega)], \end{aligned} \quad (39)$$

where numerical factor 4 has spin origin and factors $1/\sqrt{2}$ appear due to the Keldysh vertex representation (see Ref. 18). The block B_e was calculated in Ref. 15. For an arbitrary electron mean free path it may be expressed as follows:

$$B_e(\mathbf{q}, \omega) = -2e \frac{\partial P_0^R(\mathbf{q}, 0)}{\partial \mathbf{q}}, \quad (40)$$

where $P_0^R(\mathbf{q}, \omega)$ is determined by Eq. (8).

As we emphasized, to obtain a nonzero thermoelectric coefficient, the electron-hole asymmetry must be taken into account. Let us begin with the first block

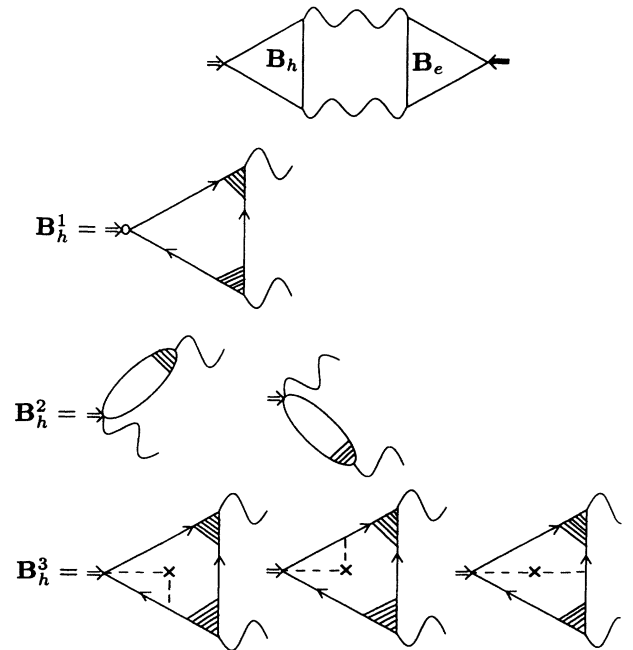


FIG. 4. The Aslamazov-Larkin diagram for the thermoelectric coefficient in the linear-response method and blocks of electron Green function B_h^i obtained from the three vertices of the heat current operator.

$$\begin{aligned} \mathbf{B}_h^1(\mathbf{q}, \omega) = & -2 \operatorname{Im} \int \frac{d\mathbf{p} d\epsilon}{(2\pi)^4} \mathbf{n} \frac{\mathbf{p}}{m} \xi_p \frac{1}{[1 - \xi(q, \omega)]^2} \\ & \times [G^A(\mathbf{p}, \epsilon)]^2 G^R(\mathbf{q} - \mathbf{p}, \omega - \epsilon) \\ & \times \tanh \left[\frac{\epsilon}{2T} \right], \end{aligned} \quad (41)$$

where \mathbf{n} is the unit vector directed along the temperature gradient. Expanding the electron velocity and density of states in powers of ξ_p/ϵ_F and then integrating over ξ_p we find that ξ_p^2 may be transformed to $(i/\tau)^2$ or ϵ^2 or ω^2 . The analysis shows that $\epsilon^2 \sim T^2$ and $\omega^2 \sim (T - T_c)^2$. The $(T - T_c)^2$ term does not give a singularity near the transition temperature, while the τ^{-2} and T^2 terms result in more singular corrections to the thermoelectric coefficient than the corrections obtained in Sec. II. However, we will show below that these corrections are canceled out by the second and third blocks.

Let us consider the T^2 term, which we denote as $(\mathbf{B}_h^1)'$. It may be shown that for both the pure and impure cases this term has the same form

$$(\mathbf{B}_h^1)' = -\mathbf{q} \ln \left[\frac{2\gamma\omega_D}{\pi T_c} \right] \frac{1}{6} \frac{\partial(vv^2)}{\partial\epsilon} \Big|_{\epsilon=\epsilon_F}. \quad (42)$$

For a pure superconductor Eq. (42) was obtained in Ref. 11, where the fluctuation correction to the thermoelectric coefficient from the T^2 term was found to be $\Delta\eta_{fl} \sim (T^2/\epsilon_F)\Delta\sigma_{AL}$.

In the block \mathbf{B}_h^2 the difference between the electron and hole states has already been accounted for in the heat current vertex (without electron-hole asymmetry it is equal to zero). Thus, the block \mathbf{B}_h^2 contributes to the thermoelectric coefficient without additional expansion of electron parameters near the Fermi surface. As seen from Fig. 4, the expression for the second block is

$$\mathbf{B}_h^2(q, \omega) = \frac{\mathbf{q}}{m} \operatorname{Re} P_0^R(q, \omega). \quad (43)$$

Comparing Eqs. (42) and (43) we see that $(\mathbf{B}_h^1)' = -\mathbf{B}_h^2$ and the T^2 term of the first block is canceled out.

The τ^{-2} term of the first block is

$$(\mathbf{B}_h^1)'' = -\mathbf{q} \frac{\pi}{24} \frac{1}{T_c \tau} \frac{\partial(vv^2)}{\partial\epsilon} \Big|_{\epsilon=\epsilon_F}, \quad (44)$$

and gives the strong singular contribution $\Delta\eta_{fl} \sim (\tau^2\epsilon_F)^{-1}\Delta\sigma_{AL}$. However, it may be shown that $(\mathbf{B}_h^1)''$ is canceled by the block \mathbf{B}_h^3 .

Therefore, to get a nonzero contribution to thermoelectric coefficient, it is necessary to take into account the electron-hole asymmetry in the fluctuation propagators in Eq. (39) [see Eq. (33)], while the block \mathbf{B}_h^1 is taken without any expansion and is expressed through the block $\mathbf{B}_e(q, \omega)$ in the following way:

$$\mathbf{B}_h(q, \omega) = \frac{\omega}{e} \mathbf{B}_e(q, \omega). \quad (45)$$

We note that Eq. (45) holds for an arbitrary electron mean free path.

Finally, substituting Eq. (45) into Eq. (39) we determine

the fluctuation correction to the thermoelectric coefficient. As we could have anticipated, the results coincide with the conclusions, obtained by the quantum transport equation.

IV. CONCLUSIONS

Employing both the quantum transport equation and the linear-response methods we have calculated the thermoelectric coefficient of a superconductor above the transition temperature. The main results are presented in Table I. We found that the fluctuation correction to the thermoelectric coefficient for a three-dimensional superconductor is nonsingular near T_c , while it diverges as $\ln[T_c/(T - T_c)]$ and as $(T_c - T)^{-1/2}$ in two- and one-dimensional systems, respectively. In all cases this correction has the same dependence on the electron mean free path as the corresponding AL correction to the conductivity. According to Eq. (3), both the fluctuation correction to the thermoelectric coefficient and the AL correction to the conductivity contribute to the thermopower. As seen from Table I, $\Delta\sigma_{fl}/\sigma_0$ is more singular than $\Delta\eta_{fl}/\eta_0$. Furthermore $\Delta\eta_{fl}/\eta_0$ has a negative sign, and both $\Delta\sigma_{fl}$ and $\Delta\eta_{fl}$ corrections result in a decrease of the thermopower near the superconducting transition. Thus a sharp peak in the thermopower observed in Refs. 3 and 4 cannot be explained by the fluctuation effects.

Now we compare our calculations with the previous papers.¹⁰⁻¹⁴ We found that the temperature singularity of the thermoelectric coefficient η coincides only with that obtained by Maki.^{10,13} However, Maki's results are opposite by sign to ours and he actually found a peak in the temperature dependence of η . We predict a monotonous decrease of an absolute value of η with decreasing the temperature ($\eta=0$ in the superconducting state). The discrepancy stems from a sign of the term, which describes the electron-hole asymmetry in the fluctuation propagator [see Eq. (34)]. An erroneous sign originally obtained in Ref. 21 was quoted in Refs. 10 and 13. Besides the sign of the effect, our results for a pure superconductor differ by a factor of $T_c\tau$ from the corresponding ones of Ref. 13. The reason for the discrepancy is as follows. We found the universal relation, independent on the electron mean free path, between the blocks of electron Green functions connected with the heat and electric current operators: $\beta = e\mathbf{B}_h(\mathbf{q}, \omega)/\mathbf{B}_e(\mathbf{q}, \omega) = \omega$ [see Eq. (45)], and according to Eq. (39), ω is of order $T - T_c$. Following Refs. 10, 13, and 24 such an equation may be treated as the relation between the electric and heat current operators associated with the fluctuating order parameter, and further calculation of the thermoelectric coefficient may be carried out by the time-dependent Ginzburg-Landau equation.^{10,13} In Ref. 13 the equation $\beta \simeq T_c\tau\omega$ was used, which is wrong as we discussed above.

More singular terms than ours were obtained in Refs. 11, 12, and 14, using the linear-response method. The relation between the heat and electric current operators was found to be $\beta \simeq T_c$ in Ref. 11. Electron scattering by paramagnetic impurities with the characteristic time τ_s was considered in Ref. 12 that results in $\beta \simeq \tau_s^{-1}$. In Ref.

14 the effect was calculated in the frame of the marginal Fermi-liquid hypothesis, the equation for β had the form $\beta = \Sigma^{-1}$, where Σ is the electron self-energy. Note that these anomalously large terms in the heat current block B_h originate from the heat current operator for noninteracting electrons and also from the corrections to the heat current operator, which arise due to the electron-electron interaction in the Cooper channel as well as due to any other interaction taken into consideration. However, our direct calculations for a system with the electron-electron and electron-impurity interactions (Sec. III) have demonstrated that all such terms are canceled out, therefore the results of Refs. 11, 12, and 14 are wrong. To show the cancellation we use the method of nearly free electrons. The problem seems to be complex in the case of an arbitrary electron spectrum, because the modification of the electron spectrum results from the electron-ion interaction, which also contributes to the heat current operator.

To avoid all difficulties associated with the heat current operator we use the quantum transport equation method and calculate the electric current as a response to the temperature gradient. This method provides a convenient framework for a description of the thermoelectric phenomena, because the anomalously large terms corresponding to the interaction effects on the heat current do not appear at all. In particular, using the quantum transport equation we did not find strong singular terms due to the spin-spin interaction, which were obtained in Ref. 12 by the linear-response method.

We also show that in the quantum transport equation method the AL corrections to the thermoelectric coefficient and to the conductivity are described by the terms in the form of the Poisson bracket. The relation between the Poisson brackets for the electric field and the temperature gradient [see Eqs. (16) and (17)] confirms the universal relation between the electric and the heat current operators for the fluctuating order parameter.

Note that a starting point of the linear-response method is the Kubo formula [Eq. (35)]. This relation can be proved only for a response of an electron system to the electric field. It is still unclear how to formulate the linear-response method for a nonmechanical disturbance such as the temperature gradient. The advantage of the quantum transport equation method is that it allows the temperature gradient to be incorporated in a natural way. Here we demonstrate that both methods lead to the same results, therefore we confirm microscopically the validity of the Onsager relation for this problem.

ACKNOWLEDGMENTS

The authors are very grateful to J. Wilkins for valuable advice and to A. G. Aronov, A. A. Varlamov, and V. D. Livanov for discussion of various aspects of the fluctuation thermopower in the early stage of this work. The work was supported by U.S. Office of Naval Research.

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