Spin glass versus superconductivity

V. M. Galitski$^1$ and A. I. Larkin$^{1,2}$

$^1$Theoretical Physics Institute, University of Minnesota, Minneapolis, MN 55455, USA
$^2$Landau Institute for Theoretical Physics, Kossiyan Str. 2, 117940, Moscow, Russia

A superconductor with interacting paramagnetic impurities is considered. The impurities are coupled via the Ruderman-Kittel-Kasuya-Yoshida interaction. At a temperature $T_g$, the system of magnetic impurities forms a spin-glass state. We study the effect of the spin-spin interactions on the superconducting transition point at $T < T_g$. We show that superconducting properties depend on the state of the spin system via spin-spin autocorrelation functions. With the help of the Keldysh technique, a general nonequilibrium Gor’kov equation is derived. Possible ageing effects in the superconducting transition point are discussed. The equilibrium superconducting transition point is found explicitly and shown to be shifted towards higher temperatures and impurity concentrations compared to the classical Abrikosov-Gor’kov’s curve. The corresponding shift of the superconducting quantum critical point is quite small (about 10%). A method of calculating spin-spin correlation function is suggested. The method combines the ideas of random mean-field method and virial expansion. We calculate analytically the first virial term for the spin-spin correlator for the quantum Heisenberg spin glass with the RKKY interactions in the quasiequilibrium regime.

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I. INTRODUCTION

The theory of superconducting alloys with paramagnetic impurities was developed long ago by Abrikosov and Gor’kov$^4$. They have shown that the superconducting transition temperature was suppressed by magnetic impurities. At some critical impurity concentration, the transition temperature was suppressed down to zero, which gives an example of a quantum critical point$^5$. The critical concentration can be determined from the condition: $\tau_s T_{c,0} = 2\gamma/\pi$, where $T_{c,0}$ is the superconducting transition temperature in a sample without impurities and $\tau_s$ is the spin-flip scattering time, which is inverse proportional to the concentration of magnetic impurities $n_s$. Let us note that the effect of magnetic impurities on superconductivity is, in many aspects, similar to the one of an external magnetic field$^7$.

In the Abrikosov-Gor’kov’s model, the magnetic impurities did not interact. Indeed, in any real system, one can not avoid having interactions between the impurities. Friedel oscillations in the electron density give rise to the similar oscillations in the spin-spin coupling which is well-known as Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction. The interaction may change the nature of the transition both qualitatively and quantitatively.

Interactions between impurities can significantly change the physical picture only if the typical energy of this interaction is of the order of temperature or higher. At a high temperature, one can take into account only those impurity clusters in which the typical distance between spins is small enough. The probability of having such a cluster containing three or more spins is small. Thus, virial expansion (or cluster expansion) coincides with the high-temperature expansion in the problem under discussion$^8$. The corresponding expansion parameter is $J_0 n_s / T$, where $J_0$ is the amplitude of the RKKY interaction.

Let us note that constant $J_0$ and spin-flip scattering time $\tau_s$ both follow from the same exchange Hamiltonian. Parametrically, they are of the same order. However, due to the numerical smallness of the two-particle statistical weight in the three-dimensional case, the amplitude of the RKKY interaction is numerically much smaller than the spin-flip scattering rate: $J_0 \tau_s n_s = 1/4 \pi^2 S (S + 1)$, where $S$ is the spin of a magnetic impurity.

The high-temperature corrections to the Abrikosov-Gor’kov’s result were derived in the paper of Larkin, Melnikov and Khmelnitskii$^6$. It was shown that the superconducting transition temperature was higher in the presence of the spin-spin interactions compared to the non-interacting case. However, the corresponding change was noticeable only at extremely low temperatures due to the small numerical factor mentioned above. Thus, in a very wide range of temperatures, the Abrikosov-Gor’kov’s theory was quantitatively correct. Let us mention that there have been a number of experiments in which deviations from the Abrikosov-Gor’kov’s picture were observed at low temperatures (see e.g. Ref.$^9$).

Since the RKKY interaction is random in sign, it introduces a frustration into the spin system. It may result in a spin glass transition at a low enough temperature $T_g \sim J_0 n_s$. This makes the physical picture much more puzzled compared to the high-temperature case. A widespread distribution of energy barriers exists in the glassy phase. The typical time of classical and quantum tunneling is comparable with the observation time in real experiments. Thus, the state of the system depends not only on the temperature and external magnetic field, but also on the history. Moreover, all physical quantities slowly
depend on time. In the present paper, we show that superconducting properties, transition temperature $T_c$, in particular, depend on the properties of the spin system. Thus, superconducting parameters are expected to depend on the history and real time if the spin system is in the ageing regime.

Although the dynamical properties of the spin glasses have been the subject of extensive studies in the recent years, the theoretical understanding of the effect is far from being impressive yet. However, it is clear that, in general, the dynamics of a glassy system consists of two parts: one is a fast quasiequilibrium dynamics and the other is a slow dynamics or ageing. One can expect that in the system under consideration different superconducting parameters should acquire similar behavior.

Studying the out-of-equilibrium dynamics in a quantum system requires using a non-equilibrium formalism such as quantum transport equation or Keldysh technique. The Keldysh technique in superconductors was developed by Larkin and Ovchinnikov and by Feigel’man et al. and by Feigel’man et al. in the theory of quantum spin glasses. Keldysh formalism was recently used by Kennett et al. in the theory of classical spin glasses, Keldysh technique is replaced by so-called Doi-Peliti techniques, in which dynamics is generated via the Langevin noise introduced in the stochastic equation of motion. This kind of technique was used by Ioffe et al. who considered dynamics of a classical spin glass.

Our paper is structured as follows: In Section II, which is necessarily quite technical, we derive general equations on the superconducting Green functions taking into account a possible non-equilibrium dynamics in the spin system. The corresponding calculations are done with the help of the Keldysh technique. We reconsider the Abrikosov-Gor’kov’s theory, taking into account inelastic exchange electron scattering on magnetic impurities. Technically speaking, impurity lines, i.e. spin-spin correlators, carry frequency in this case. We show that all superconducting parameters, including the transition temperature, should depend on the properties of the spin system via the spin-spin autocorrelation function. In a non-equilibrium state, the spin system is described with the help of three correlators (retarded, advanced and Keldysh). In the quasiequilibrium case, these correlators are connected via the fluctuation-dissipation theorem. At the end of Sec. II, using analytical continuation on the discrete Matsubara frequencies, we rederive a relatively simple equation on the superconducting transition point in the quasiequilibrium case.

In Sec. III, we address the question of calculating spin-spin autocorrelation function in the spin-glass state. We propose a method which combines ideas of Thouless, Anderson, and Palmer (TAP) and virial expansion method. In the framework of this approximation, the $N$-spin problem is solved exactly while the other spins are replaced by a mean value, which plays the role of a random mean field. A distribution function for the random mean-field is derived analytically for the case of the three-dimensional Heisenberg model with the RKKY interactions. Let us note that despite the high-temperature asymptotics developed in Ref. in the glass phase, such an expansion does not contain any small parameter. One can expect, however, that at large enough $N$ this expansion gives a quantitatively correct result. At low $N$, we may expect to derive qualitatively acceptable results and get some insight into the complicated problem. To illustrate how the method works, we analytically derive the spin-spin autocorrelation function in the first virial approximation.

In Sec. IV, we derive a correction to the superconducting quantum critical point. We show that the shift of the Abrikosov-Gor’kov’s result is quite small (the critical concentration of magnetic impurities increases about 10% compared to the non-interacting case). We also discuss the back effect of the superconductivity on the spin system. The phase diagram for the system under consideration is given.

In Sec. V, we study a non-equilibrium or ageing dynamics in the superconducting transition point. We propose an experiment which should provide an explicit manifestation of the ageing dynamics in the superconducting quantum critical point. If an external magnetic field is switched off below $T_g$, the magnetization does not disappear immediately. Spins magnetize the electrons and this effect leads to a stronger suppression of superconductivity compared to the case of arbitrarily oriented spins. The remanent magnetization logarithmically slowly decreases and drives the system towards superconductivity.

II. NONEQUILIBRIUM GOR’KOV EQUATIONS

A. The model

The starting point for the problem is the following Abrikosov-Gor’kov’s Hamiltonian:

$$\mathcal{H}_{AG} = \mathcal{H}_{BCS} + \mathcal{H}_{es}.$$  (1)

where the first term is the usual BCS Hamiltonian:

$$\mathcal{H}_{BCS} = \int \left\{ \psi^\dagger \left( \frac{P^2}{2m} - \varepsilon_F \right) \psi - \lambda \psi^\dagger \lambda \psi^\dagger \lambda \psi \right\} d^3r$$  (2)

and the second one is the exchange interaction:

$$\mathcal{H}_{es} = \int \left\{ \psi^\dagger \sum_{\alpha} u(r - r_{\alpha}) \left( S_{\alpha} \sigma_{\alpha\beta} \right) \psi \right\} d^3r.$$  (3)

We neglect finite-size effects and consider the following form of the exchange potential:

$$u(r) = u_0 \delta(r).$$  (4)
The effective spin-spin interactions are described by the following Hamiltonian:

$$\mathcal{H}_{SS} = \frac{1}{2} \sum_{a \neq b} J (r_a - r_b) S_a S_b.$$  \hspace{1cm} (5)

In Eq. (5), $J(r)$ is the RKKY interaction:

$$J(r) = J_0 \frac{\cos(2\pi r)}{r^3}.$$  \hspace{1cm} (6)

The amplitude of this interaction reads:

$$J_0 = \frac{m_{PF}}{4\pi^3} v_0^2.$$  \hspace{1cm} (7)

This quantity is connected with the spin-flip scattering time as follows:

$$J_0 n_s \tau_s = \left[ 4\pi^2 S (S + 1) \right]^{-1}.$$  \hspace{1cm} (8)

Let us emphasize that the number in the right-hand side of Eq. (8) is very small.

**B. Keldysh Green functions**

In order to find the superconducting transition point, we should first derive Gor’kov’s equation for the Green functions. To treat a possible non-equilibrium dynamics, we use the Keldysh technique. Below we recall the basic definitions and notations:

The electron Green functions are defined as follows:

$$\hat{G}^> (1, 2) = -i \left\langle \left( \psi^\dagger_1 \psi_2 \right) \left( \psi^\dagger_2 \psi_1 \right) \right\rangle$$  \hspace{1cm} (9)

and

$$\hat{G}^< (1, 2) = i \left\langle \left( \psi^\dagger_1 \psi_2 \right) \left( -\psi^\dagger_2 \psi_1 \right) \right\rangle.$$  \hspace{1cm} (10)

Retarded, advanced and Keldysh Green functions are then constructed in the following way:

$$\hat{G}^R (1, 2) = \theta(t_1 - t_2) \left[ \hat{G}^> (1, 2) - \hat{G}^< (1, 2) \right],$$  \hspace{1cm} (11)

$$\hat{G}^A (1, 2) = -\theta(t_2 - t_1) \left[ \hat{G}^> (1, 2) - \hat{G}^< (1, 2) \right],$$  \hspace{1cm} (12)

and

$$\hat{G}^K (1, 2) = \hat{G}^> (1, 2) + \hat{G}^< (1, 2).$$  \hspace{1cm} (13)

It is convenient to introduce a compact notation for the 4x4 matrix (here we use the Larkin-Ovchinnikov representation):

$$\hat{G}(1, 2) = \begin{pmatrix} \hat{G}^R (1, 2) & \hat{G}^K (1, 2) \\ 0 & \hat{G}^A (1, 2) \end{pmatrix}.$$  \hspace{1cm} (14)

The Green function satisfies the following matrix equation:

$$[G_0^{-1} - \Sigma] \hat{G} = 1.$$  \hspace{1cm} (15)

where $\hat{G}_0$ is the Green function of a normal metal without impurities and $\Sigma$ is the self-energy.

![FIG. 1. Electron self-energy in the leading approximation with respect to the magnetic impurity concentration. $\gamma$’s are the vertex matrices [see Eq. (21)].](image)

In the case under consideration, we have to find the self-energy associated with the scattering on magnetic impurities. In the leading approximation on the impurity concentration, the self-energy has the form shown on Fig. 1, where $\gamma$’s are the vertex matrices (see below). In this section, we will consider the case of zero-field cooling, so that there is no remanent magnetization in the spin system and no external magnetic field. In this case, we can average Green functions out over the spin degree of freedom. In the absence of the RKKY interaction, the electron scattering on magnetic impurities is elastic in the Born approximation. If we switch on the interactions between spins, self-energy $\Sigma$ becomes non-elastic and in some sense analogous to the self-energy due to the electron scattering off the phonons. As a result we obtain the following expression for the self-energy:

$$\hat{\Sigma}_{\mu\nu} = \frac{1}{4\pi S (S + 1)} \gamma^\lambda_{\mu\sigma} \left( \tau_z \hat{g} \tau_z \right)_{\sigma\rho} \hat{C}_{\lambda\eta} \gamma^\eta_{\rho\nu},$$  \hspace{1cm} (16)

where the Greek indexes label matrix elements in the Keldysh space. The structure of the self-energy in the Nambu-Gor’kov space is determined by the product $(\tau_z \hat{g} \tau_z)$ with

$$\tau_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$  \hspace{1cm} (17)

In Eq. (16), we have introduced quasiclassical Green function:

$$\hat{g}(t_1, t_2) = \frac{i}{\pi} \int_{-\infty}^{\infty} dp \hat{G}(p; t_1, t_2), \hspace{1cm} \xi_p = v_F (p - p_F),$$  \hspace{1cm} (18)

and the following spin-spin correlators:

$$C^>(t_1, t_2) = C^< (t_2, t_1) = -i \left\langle S(t_1) S(t_2) \right\rangle.$$  \hspace{1cm} (19)

The corresponding Keldysh matrix is defined as

$$\hat{C} = \begin{pmatrix} C^K & C^R \\ C^A & 0 \end{pmatrix},$$  \hspace{1cm} (20)
with \( C^R, C^A, \) and \( C^K \) defined via Eqs.\((13\)–\(15)\). Indeed, the spin-spin correlators are proportional to the unit matrix in the Nambu space. The vertex matrices have the following explicit form in the Larkin-Ovchinnikov representation:

\[
\gamma^1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad \gamma^2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.
\] (21)

C. Gor’kov equations

Since we are not interested in the momentum dependence of the Green function, it is convenient to integrate out the corresponding redundant degree of freedom. Using Eq.\((13)\), we obtain:

\[
\int d\xi_p \, \left\{ [\tilde{G}^{-1}_{0} - \tilde{\Sigma}] \tilde{G} - \tilde{G} [\tilde{G}^{-1}_{0} - \tilde{\Sigma}] \right\} = 0.
\]

As a result, we obtain the following equation which involves quasiclassical Green function only:\(\tilde{\Sigma}\):

\[
\begin{align*}
\left[ \frac{\partial}{\partial t_1} - i \tilde{\alpha} \frac{\partial}{\partial t_2} \right] \beta_{\mu\nu}(t_1, t_2) &+ i \left[ (t_1) + (t_2) \right] \alpha_{\mu\nu}(t_1, t_2) \\
&= - \frac{i}{4\tau_\alpha S(S+1)} \left\{ \gamma^\lambda_{\sigma\rho}, \rho_\delta, \rho_\rho, \lambda_{\sigma\rho}, \rho_\delta, \lambda_{\sigma\rho} \right\} (t_1, t_2) + \left[ \alpha_{\lambda\delta}, \beta_{\lambda\mu}, \beta_{\lambda\nu}, \alpha_{\lambda\delta} \right] (t_1, t_2) + \left[ \alpha_{\lambda\delta}, \beta_{\lambda\mu}, \beta_{\lambda\nu}, \alpha_{\lambda\delta} \right] (t_1, t_2) \gamma^\lambda_{\sigma\rho}, \rho_\delta, \lambda_{\sigma\rho}, \rho_\rho, \lambda_{\sigma\rho} \right\} (t_1, t_2)  \\
&= \hat{g} = \begin{pmatrix} \alpha & \beta_1 \\ -\beta_1 & -\alpha \end{pmatrix},
\end{align*}
\] (23)

where symbol \(\bullet\) means convolution with respect to the time variable.

Note that each element of \(\hat{g}\) is a 2x2 matrix in the Nambu space:

\[
\hat{g} = \begin{pmatrix} \alpha & \beta_1 \\ -\beta_1 & -\alpha \end{pmatrix}.
\] (24)

with \(\hat{\alpha}\) and \(\hat{\beta}\) being matrices in the Keldysh space. Since we are looking for the transition point, we should first derive equation linear on the superconducting Green function \(\hat{\beta}\). Thus, form \((23)\) is more convenient for our purposes. Using the notations introduced above, the order parameter \(\Delta\) can be written as

\[
\Delta(t) = \pi |\lambda| \nu \beta^K (t, t+0),
\] (25)

where \(\nu\) is the density of states per spin at the Fermi surface. In the matrix notations, the order parameter takes on the form:

\[
\Delta(t) = \begin{pmatrix} 0 & \Delta(t) \\ -\Delta^*(t) & 0 \end{pmatrix}.
\] (26)

In the Keldysh space, \(\Delta\) is proportional to the unit matrix (we neglect superconducting fluctuations).

To find the superconducting transition point we have first to extract the equation on the Gor’kov Green function \(\hat{\beta}\). After some algebra, we obtain:

\[
\hat{\beta} = \frac{1}{4\tau_\alpha S(S+1)} \int_{-\infty}^{+\infty} d\omega \, \hat{C}(\omega, t) e^{-i\omega(t_1-t_2)}.
\] (28)

In Eq.\((28)\), parameter \(t = (t_1 + t_2)/2\) describes slow dynamics and, in some sense, is similar to the waiting time. From Eqs.\((13)–(15)\), we obtain the following equations:

\[
\varepsilon \beta^R(\varepsilon) - \left[ \Delta(t) \alpha^R(\varepsilon) + \frac{1}{4} \Delta''(t) \frac{\partial^2 \alpha^R(\varepsilon)}{\partial \varepsilon^2} + \ldots \right] = \frac{1}{4\tau_\alpha S(S+1)} \int_{-\infty}^{+\infty} d\omega \, \hat{C}(\omega, t) e^{-i\omega(t_1-t_2)}.
\] (29)

and
The corresponding Keldysh function reads:

\[ \beta^K(\varepsilon) = [\beta^R(\varepsilon) - \beta^A(\varepsilon)] \tanh \left( \frac{\varepsilon}{2T} \right). \]  

Note, that all quantities in Eqs. (29, 30) weakly depend on the “waiting time.” Together with Eq. (25), Eqs. (29, 30) form a closed equation system, which contains all the information about the superconducting properties of the physical system under consideration. The spin system is completely described by the three functions: \( C^K, C^A, \) and \( C^K \). These functions are not necessarily connected with each other in an out-of-equilibrium state and depend upon the details of the state and history.

At the superconducting transition point, Eqs. (29, 30) can be simplified with the aid of the following relations:

\[ \alpha^R(\varepsilon) = -\alpha^A(\varepsilon) = 1 \]  
\[ \alpha^K(\varepsilon) = 2 \tanh \left( \frac{\varepsilon}{2T} \right). \]

D. Quasiequilibrium regime

Let us consider a regime when the dynamics of the spin glass state has two well separated time scales: The first one is “waiting time” \( \overline{t} \), which is comparable with the typical time of an experiment. At these time scales, large energy barriers change. The second typical time is \( \hbar/T_p \). At these time scales, a quasiequilibrium state is reached within the large energy barriers. Tunneling processes through the large barriers are supposed to be very rare at such a time-scale. In this approximation, the waiting time can be considered as an independent external parameter and equilibrium techniques can be used. In this equilibrium regime the fluctuation-dissipation theorem holds and it significantly simplifies the calculation.

In the equilibrium, Keldysh, retarded and advanced spin-spin correlators are not independent functions anymore. They are connected via the fluctuation-dissipation theorem, which follows directly from the Gibbs’s distribution and in our language can be formulated as follows:

\[ C^K(\omega) = [C^R(\omega) - C^A(\omega)] \coth \left( \frac{\omega}{2T} \right) \]  
\[ - 2\pi i \delta(\omega) \left( \sum_k e^{-\frac{\omega}{2T}} \right)^{-1} \sum_{\varepsilon_k = \varepsilon_j} |\langle k|S|j\rangle|^2 e^{-\frac{\omega}{2T}}, \]

where \( |k\rangle \) is a quantum state in the spin system and \( \varepsilon_k \) is the corresponding energy level. Note, that for spin correlators, the last “static” term in Eq. (14) does not vanish.

In the equilibrium, it is convenient to introduce Matubara Green functions \( \beta(\varepsilon_n) \) and \( \alpha(\varepsilon_n) \) which depend on the fermion frequency \( \varepsilon_n = \pi(2n + 1)T \) and the Matubara spin-spin correlator:

\[ C(\omega_m) = \int_0^{1/T} d\tau \langle T_\tau [S(\tau)S(0)] \rangle e^{-i\omega_m \tau}, \]

where

\[ S(\tau) = e^{-\mathcal{H}_\tau}S(0)e^{\mathcal{H}_\tau} \]

and \( \omega_m = 2\pi m T \) is the bosonic Matubara frequency.

![Contour in the complex plane \( \omega \) used to perform analytical continuation on discrete Matsubara frequencies for \( \varepsilon_n > 0 \).](image)
As an example, let us consider the first and third terms in the right-hand side of Eq. (36). After analytical continuation on discrete Matsubara frequencies $\varepsilon_n > 0$, we get for these terms:

\[
\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left\{ \beta R(i\varepsilon_n - \omega) \left[ \tilde{C}^R(\omega) - \tilde{C}^A(\omega) \right] \coth \left[ \frac{\omega}{2T} \right] + \tilde{C}^R(\omega) \left[ \beta R(i\varepsilon_n - \omega) - \beta A(i\varepsilon_n - \omega) \right] \tanh \left[ \frac{i\varepsilon_n - \omega}{2T} \right] \right\}
\]

where the averaging over the random spin-spin interaction and over spin orientations is implied. For the RKKY interaction (4), averaging means:

\[
\langle f(J) \rangle_j = \frac{1}{V} \int d^3r \int_0^{2\pi} \frac{d\phi}{2\pi} f \left( \frac{J_0 \cos \phi}{r^3} \right),
\]

where $V$ is the volume of the system and $f$ is an arbitrary function.

Performing averaging over the spin orientations and evaluating the corresponding elementary integral we get the distribution function for the random mean field:

\[
P[h] = \frac{1}{a} \left( 1 - \frac{4\pi J_0}{3V} \right) \frac{a}{a^2 + h^2}, \quad a = \frac{2\pi}{3} J_0 n_s S,
\]

where $n_s$ is the concentration of magnetic impurities and $S$ is their spin.

Let us note that for a different model of spin-spin interactions the distribution function (38) would be different. For example, if we start with the Gaussian distribution of spin-spin couplings in the Sherrington-Kirkpatrick model, the distribution function of the mean field is necessarily Gaussian as well.

In the non-equilibrium case, the simple calculation presented above is not valid. The distribution function of the mean-field should depend on time and on the type of the non-equilibrium state. For example, if we study a non-equilibrium dynamics due to a slowly decaying remanent magnetization, one should modify the definition of the distribution function as follows:

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\]
\[ P[h, t] = \delta \left( h - \sum_a J_{ab} S_a \right) \times \delta \left( m(t) - \sum_a S_a \right) \] ,

where \( m(t) \) is the remanent magnetization.

**B. Virial expansion**

Now, let us consider the following set of Hamiltonians:

\[ \mathcal{H}_1 = S h, \] \hspace{1cm} (44)

\[ \mathcal{H}_2 = J_{12} S_1 S_2 + S_1 h_1 + S_2 h_2, \] \hspace{1cm} (45)

\[ \cdots, \]

\[ \mathcal{H}^{(k)} = \frac{1}{2} \sum_{a,b} J_{ab} S_a S_b + \sum_a S_a h_a, \] \hspace{1cm} (46)

where both \( J \)’s and \( h \)’s are random and distributed according to Eq.(41) and Eq.(22), correspondingly.

In principal, one can calculate any quantity using Hamiltonians (44) (one spin), (45) (cluster of two spins), etc. and than average out the quantities of interest using Eq.(40) and distribution (42). This procedure generates a series which can be called virial or cluster expansion. It is well known that the corresponding solution is not stable. The usual parameter in the replica symmetric case. It is well known that the corresponding solution is not stable. The usual parameter at low temperatures, one can try to calculate the equilibration regime only. For the Matsubara correlator, we obtain:

\[ C(\omega_m, h) = \left[ \sum_k e^{-\beta \epsilon_k} \right]^{-1} \sum_{k_1, k_2} |\langle k_1 | S(0) | k_2 \rangle|^2 \times \frac{\epsilon_{k_2} - \epsilon_{k_1}}{\omega_m^2 + (\epsilon_{k_2} - \epsilon_{k_1})^2} [e^{-\beta \epsilon_{k_1}} - e^{-\beta \epsilon_{k_2}}]. \] \hspace{1cm} (47)

For spin \( S = 1/2 \), in the first virial approximation, we get:

\[ C(\omega_m, h) = \frac{1}{4T} \delta_{\omega_m, 0} + \frac{h}{\omega_m^2 + h^2} \tanh \left[ \frac{h}{2T} \right]. \] \hspace{1cm} (48)

Note, that for an arbitrary spin value \( S \), the tangent factor is replaced by the corresponding Brillouin function. We have to average out quantity (48) with respect to the distribution function (42):

\[ \overline{C}(\omega_m) = \int d^3 h \ P[h] \ C(\omega_m, h). \] \hspace{1cm} (49)

Evaluating the corresponding integral, we obtain

\[ \overline{C}(\omega_m) = \frac{1}{4T} \delta_{\omega_m, 0} + \overline{C}(\omega_m), \] \hspace{1cm} (50)

where

\[ \overline{C}(\omega_m) = 4ai \left[ \frac{\text{res}}{z = a} + \frac{\text{res}}{z = i|\omega_m|} \right] g(z) + \frac{2a}{\pi} \left[ I(a, \omega_m) + 2a \frac{\partial I(a, \omega_m)}{\partial a} \right], \] \hspace{1cm} (51)

with

\[ g(z) = \frac{z^3}{(z^2 + \omega^2)(z^2 + a^2)^2} \tanh \left[ \frac{z}{2T} \right] \]

and

\[ I(a, \omega_m) = \frac{1}{\omega_m^2 - a^2} \text{Re} \left[ \psi \left( \frac{1}{2} + i \omega_m \right) - \psi \left( \frac{1}{2} + i a \right) \right]. \]

At a low temperature \( T \ll a \sim T_g \), Eq.(51) can be simplified and we obtain the following zero-temperature result:

\[ \overline{C}(\omega) = \frac{2a}{\pi} \frac{a^2 - \omega^2 + \omega^2 \ln \left( \frac{\omega}{a} \right)^2}{(\omega^2 - a^2)^2}. \] \hspace{1cm} (52)
Let us emphasize the following property of correlators (50) and (52):

$$\lim_{a \to 0} \overline{\mathcal{C}}(\omega_m) = \frac{1}{T} S (S+1) \delta_{\omega_m 0}, \quad (53)$$

which can be verified by a straightforward calculation. This property means that if we switch off the interactions between the spins, the corresponding autocorrelation function turns into the time-independent correlation function of a free spin.

In the second virial approximation we should calculate correlator (47) using eigenfunctions of Hamiltonian (45). There are four quantum states possible in this case. Even at zero temperature, finding the ground state energy requires solving spectral problem which turns out to be an equation of the fourth order. Moreover we should average out correlator (47) over the random fields and coupling constant:

$$\overline{\mathcal{C}}(\omega_m) = \int d\mathbf{h}_1 d\mathbf{h}_2 P[\mathbf{h}_1] P[\mathbf{h}_2] \langle C(\omega_m; J, \mathbf{h}_1, \mathbf{h}_2) \rangle_j$$

This is hard to handle this analytically. Numerical work is required in this case.

IV. SUPERCONDUCTING TRANSITION POINT

A. Quantum critical point. Equilibrium case.

To find the superconducting transition point, we have to solve Eqs. (29, 30) or Eq. (37) in the quasiequilibrium regime. Let us first consider the latter case. At a finite temperature, Eq. (27) is an infinite system of coupled equations corresponding to different Matsubara frequencies. As temperature goes to zero, the picture is simplified and Eq. (37) turns into an integral equation:

$$\frac{1}{\pi \nu |\lambda|} - \int \frac{d\varepsilon}{2\pi} \frac{\beta(0)(\varepsilon)}{\varepsilon} = - \frac{1}{2\tau_s S (S+1)} \times \int \frac{d\omega}{2\pi} \left[ \overline{\mathcal{C}}(\omega) - S (S+1) \delta(\omega) \right] \times \int \frac{d\varepsilon}{2\pi} [\beta(\varepsilon + \omega) + \beta(\varepsilon) \text{sgn} \varepsilon \text{sgn} (\varepsilon + \omega)] \beta(0)(\varepsilon). \quad (57)$$

As it will be shown below, this equation can be solved using the perturbation theory. Due to numerical reasons, the term in the right-hand side can be treated as a small perturbation. Thus, one can use expression (53) for the Green functions in Eq. (57). In this case, the integral over $\varepsilon$ in the right-hand side of (57) can be easily evaluated and we get the following expression for the integral:

$$2\tau_s I(\omega \tau_s) = 2\tau_s \left\{ \frac{1}{1 + |\omega| \tau_s} + \frac{1 + |\omega| \tau_s}{|\omega| \tau_s (1 + |\omega| \tau_s/2)} \ln (1 + |\omega| \tau_s) \right\}. \quad (58)$$

Correlator $\overline{\mathcal{C}}$ follows from Hamiltonian (1) and distribution function defined by relation (10). There is only one dimensional parameter upon which it can depend: $a \sim J_0 n_s$. Thus, in the equilibrium, the correlator is bound to have the following form:

$$\overline{\mathcal{C}}(\omega) = \frac{1}{a} \tilde{C} \left( \frac{\omega}{a} \right)$$

This statement is true both in the high-temperature and low-temperature regions. Let us make the following change of variables in the integral over $\omega$ in Eq. (57): $\omega \rightarrow x = \omega / a$. Then, this equation can be rewritten as follows:

$$\ln \left[ \frac{\pi T c_0 \tau_s}{2\gamma} \right] = \frac{1}{4\pi S (S+1)} \times \int_{-\infty}^{\infty} dx \left[ \tilde{C}(x) - S (S+1) \delta(x) \right] I(\sigma x), \quad (59)$$

where function $I(x)$ is defined in (58) and $\sigma = a \tau_s$. The latter quantity is just a number. From, Eq. (11) and Eq. (12), we find

$$\sigma = \frac{1}{6\pi (S+1)} \ll 1.$$

One can see that this number is very small. If, formally, we put $\sigma = 0$, we will get zero in the right-hand side of Eq. (59) [see also (53)] and recover the Abrikosov-Gor’kov’s formula for the quantum critical point:

$$T_{c0}^{(AG)} = \frac{2\gamma}{\pi} \approx 1.13.$$
If we keep \( \sigma \) finite, the right-hand side term in Eq.(59) will give a correction to the quantum critical point due to the spin-spin interactions. For example, we can use correlator (62) calculated in the previous section. Evaluating the corresponding integral numerically we get correction to the critical concentration of magnetic impurities concentration:

\[
\frac{\delta n_{s0}^{(1)}}{n_{s0}^{(AG)}} = 0.073.
\]

Similarly, we can obtain the shift corresponding to the second virial approximation (54). This has been done numerically. The corresponding result is

\[
\frac{\delta n_{s0}^{(2)}}{n_{s0}^{(AG)}} = 0.085.
\]

We see that these corrections are quite small. This smallness is connected with the parameter \( T_g\tau_s \) present in the theory and should exist in any order of the virial expansion. Thus, we conclude that the shift of the Abrikosov-Gor’kov quantum critical point is about 10%.

**B. Equilibrium phase diagram**

Another interesting question which is worth discussing is the effect of the superconductivity on the effective spin-spin interactions. This question has been addressed long ago by Abrikosov. Recently it was revisited by Aristov et al. The effective spin-spin coupling is determined by the following expression:

\[
J(r) = 2u_0^2 T \sum_{\varepsilon_n} \left[ \alpha(\varepsilon_n, r) \right]^2 + \beta(\varepsilon_n, r)^2 ,
\]

where \( \alpha(\varepsilon_n, r) \) and \( \beta(\varepsilon_n, r) \) are Green functions in the real space. A straightforward calculation yields the following form of the effective RKKY interaction below the superconducting transition point:

\[
J(r) = \left[ J_0 \cos \left( \frac{2k_F r}{\xi} \right) + \frac{1}{r^2} J_{AF} \right] e^{-2r/\xi},
\]

where \( \xi = v_F/\Delta \) and antiferromagnetic contribution \( J_{AF} \times \Delta/\xi \) is quite small.

At the transition line, \( \xi = \infty \) and \( \Delta = 0 \), so we recover the usual RKKY formula. However, well below the transition the interaction becomes screened. This fact has a very transparent physical explanation. The RKKY interactions appears due to the fact that a spin polarizes the normal electrons around it. The Friedel’s oscillations in the electron density lead to the Ruderman-Kittel oscillations in the spin-spin coupling. In a superconductor, the spins are not polarized in the ground state. Thus at the distances larger than Cooper pair size \( \xi \), the indirect spin-spin coupling must be suppressed.

**V. Ageing in the Superconducting Quantum Critical Point**

Let us study the following experiment. Consider a superconductor at a low temperature with the concentration of magnetic impurities \( n_s < n_{s0} \), where \( n_{s0} \) is the equilibrium critical concentration found in the previous section. Now, let us switch on a large magnetic field. This field polarizes the magnetic impurities and electrons and destroys superconductivity. Then, we switch off the magnetic field. The electron system equilibrate very quickly. However, in the system of magnetic impurities, one finds a remanent magnetization which decays very slowly with time. This magnetization acts on the electrons as an external magnetic field, which affects only the spin degree of freedom but not the orbital one. In some sense the effect due to the remanent magnetization on the electron system is equivalent to the effect of an external magnetic field applied parallel to a two-dimensional superconducting sample. This leads to the
further suppression of superconductivity. Thus, even after the external magnetic field is switched off, the superconductivity may be absent in such an experiment due to the ageing effects in the system of magnetic impurities.

To get some qualitative insight into the non-equilibrium case, let us consider a small enough remanent magnetization and neglect corrections to the Abrikosov-Gor’kov form of the spin-spin correlator. In this case, we obtain the following set of equations which describes the superconducting transition and determines the order parameter:

\[
[\varepsilon - i\delta \mu] \beta(\varepsilon) = \Delta \alpha(\varepsilon) - \frac{1}{\tau_s} \alpha(\varepsilon) \beta(\varepsilon),
\]

(62)

where \(\alpha(\varepsilon)\) and \(\beta(\varepsilon)\) are superconducting Green functions subject to the following constraint:

\[
\alpha^2(\varepsilon) + |\beta(\varepsilon)|^2 = 1
\]

(63)

and the order parameter is defined as usual:

\[
\Delta = \pi \nu |\lambda| T \sum_{\varepsilon_n} \beta(\varepsilon_n).
\]

(64)

In Eq. (62), we have introduced the splitting of the Fermi-surface due to the remanent magnetization:

\[
\delta \mu = u_0 m(t),
\]

(65)

where \(u_0\) is the integral over the exchange potential [see Eq. (3)] and \(m(t) = n_s (S)\) is the remanent magnetization which slowly depends on time. Let us note, that upon \(m(t)\), all superconducting quantities in Eq. (62) acquire similar slow time-dependence.

From Eqs. (62–64), it follows that for large enough values of remanent magnetization \(\delta \mu \sim \tau_s^{-1}\), the superconducting transition becomes of the first order. The order parameter jumps from the zero value up to a finite value. Let us consider smaller values of the magnetization and find the corresponding second-order superconducting transition point. From Eqs. (62–64), we get:

\[
1 = \pi \nu |\lambda| T \sum_{\varepsilon} \frac{1}{|\varepsilon - i (\delta \mu) \text{sgn} \varepsilon + \tau_s^{-1}}.
\]

(66)

At zero temperature, the corresponding integral can be easily evaluated and we get:

\[
1 = \ln \left[ \frac{\pi}{2\gamma} \frac{T_{c0}}{\sqrt{\delta \mu^2 + \tau_s^{-2}}} \right].
\]

Finally, we obtain the following time-dependent critical concentration:

\[
n_s(t) = \sqrt{n_{s0}^2 - cm^2(t)},
\]

(67)

where constant \(c\) has the form:

\[
c = \left[ \frac{\pi}{S (S + 1)} \frac{u_0^2}{v \text{mpf}} \right]^2.
\]

(68)

The dynamics of the remanent magnetization in the spin-glass state can be usually well-fitted via the following formula:

\[
m(t) = m_0 - v \ln t.
\]

Where \(m_0\) is of the order of the remanent magnetization just after the magnetic field is turned off and quantity \(v\) is called magnetic viscosity. Thus, the superconducting critical point is slowly flowing towards its equilibrium value:

\[
n_s(t) = n_{s0} - \frac{c}{2} [m_0 - v \ln t]^2.
\]

(69)

We see that after some time, which can be macroscopically large, the superconductivity should appear again.

Let us note that non-equilibrium effects at the superconducting transition point does not necessarily have to be connected with the dynamics of remanent magnetization. Another possible experiment could be done as follows. Let us consider a superconductor with the concentration of magnetic impurities such as \(n_{s0}^{(AG)} < n_s < n_{s0}\), where again \(n_{s0}^{(AG)}\) is the Abrikosov-Gor’kov’s critical concentration at zero temperature and \(n_{s0}\) is the real critical concentration at zero temperature with the account of interactions. Consider large enough initial temperature so that no superconductivity is present at the beginning. Then, let us cool a sample down very quickly at zero field. One should expect that superconductivity appears only some time after the sample was cooled down due to the slow relaxation processes in the spin subsystem.

**VI. CONCLUSION**

We have considered a superconductor with interacting magnetic impurities. The central result of this paper is the dependence of the superconducting properties in such a system upon the spin-spin autocorrelation function. At low temperatures, one can expect to observe ageing effects in the superconducting transition point. The limiting manifestation of the ageing would be the observation of the spontaneous appearance of superconductivity after some macroscopic waiting time due to a slow change in the remanent magnetization in the spin subsystem.

In the equilibrium, we predict that the Abrikosov-Gor’kov’s critical line shifts towards higher temperatures and impurity concentrations due to the spin-spin interactions. Let us note that the high-temperature expansion diverges as \(T \rightarrow 0\) and, formally, predicts very large shift of the critical point. The two asymptotics match at a temperature \(T^* \approx 2J_0 n_s\). This gives a good estimate for the temperature of the spin-glass transition \(T_g\). At \(T = T_g\), a crossover from the high-temperature (paramagnetic) asymptotics to the low-temperature (spin-glass)
one takes place. We have shown that the actual shift of the superconducting transition due to the RKKY interactions is small at any temperatures. This is connected with the small parameter $T_g \tau_s$ which exists in the theory.

Let us also mention that our calculations are valid only for temperatures $T \gg T_K$, where $T_K$ is the Kondo temperature. In this case we can neglect higher order processes in the electron scattering off the impurities. At $T \sim T_K$ the magnetic impurities become screened, which presumably should lead to the further enhancement of superconductivity.

Let us note that some deviations from the Abrikosov-Gor’kov’s curve have been observed experimentally. The measurements showed some increase in the critical concentration at low temperatures. Except the effects discussed in the present paper, this increase can also be connected with the phenomena similar to the ones discussed in Refs. [1,2]. Namely, optimal fluctuations in the distribution of magnetic impurities may lead to the formation of superconducting islands coupled via the Josephson effect. This effect may also lead to some increase in the critical concentration. However, we do not expect this increase to be very large due to the suppression of the Josephson coupling by quantum fluctuations. To identify which effect is dominant at low temperatures, additional experiments are highly desirable. In either case, we expect that some interesting non-equilibrium phenomena (hysteresis, ageing, etc.) should reveal themselves at low temperatures.

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