Metastability in the BCS model

J Lauwers[1] **and A Verbeure**

Instituut voor Theoretische Fysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D,
B-3001 Leuven, Belgium

E-mail: joris.lauwers@fys.kuleuven.ac.be and andre.verbeure@fys.kuleuven.ac.be

Abstract

We discuss metastable states in the mean-field version of the strong-coupling
BCS model and study the evolution of a superconducting equilibrium state
subjected to a dynamical semigroup with Lindblad generator in detailed
balance w.r.t. another equilibrium state. The intermediate states are explicitly
constructed and their stability properties are derived. The notion of
metastability in this genuine quantum system is expressed by means of energy–
entropy balance inequalities and canonical coordinates of observables.

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1. Introduction

One of the best known phenomena in physics is metastability. Phenomena such as supercooled
water or hysteresis in magnetic systems are easily observed and identified with metastability.
However, in spite of its clear appearance, the development of a complete theory of metastability
is still a difficult and unresolved problem (for an overview, see e.g. [1]). The basic concept of
metastability could be formulated in the following way: a thermodynamic system is prepared
in a special initial state different from the equilibrium state. If the initial conditions are suitably
chosen, the system will not relax immediately to equilibrium, but it persists for a longer period
of time away from the equilibrium state, until some large fluctuation or an external disturbance
occurs driving the system to equilibrium. The key problem is to formulate an expression for
the size of the perturbation characterizing the metastable regime [1–4].

Metastability has intensively been studied for classical models, and interesting results are
obtained for the metastable relaxation in kinetic Ising models [1–4]; we will not try to give a full
overview of this field but refer to one of these papers for more references. It was conjectured
(see e.g. [1]) that the metastable evolution is governed by the growth of droplets of the stable
phase in a background of the (initial) metastable phase. Small droplets are likely to disappear
again, but bigger droplets tend to grow, ultimately driving the system to equilibrium. The

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[1] Bursaal KUL FLOF-10408.

lifetime of the metastable phase should then be linked to the probability of creating a droplet excitation of critical volume [3]. A rigorous result pointing in that direction was obtained in a paper by Schonmann and Shlosman [4], where they proved that the 'exit time' could be expressed as a function of the equilibrium surface tension of a Wulff droplet of unit volume. A Wulff droplet is a typical droplet excitation, for which the shape is found minimizing the surface terms in the free energy. This activity and success for classical models is in sharp contrast with the situation for quantum mechanical models, where little is known. In a recent paper [5], droplet states were constructed for the quantum mechanical *XXZ* Heisenberg model.

In this paper, we want to develop ideas of [4] in order to approach the phenomenon of metastability for quantum systems. We put forward that the underlying concept for exit times and the metastable evolution is situated in the behaviour of non-extensive terms such as fluctuations of relevant observables, as the non-extensive (equilibrium) surface tension of droplet excitations determines the metastable evolution in Ising models [4]. For the BCS model [6, 7] studied in this paper, we find a characterization for metastability and define exit times for different observables, expressed as a function of the equilibrium expectation values of the 'normal coordinates' of the observable under consideration. The metastable evolution at an arbitrary temperature between two extremal superconducting phases is studied. The evolution is driven by a semigroup with Lindblad generator [8, 9]. In fact we consider a detailed balance dynamics between two different fixed phase states and realize the evolution from one equilibrium state to another equilibrium state with a different phase. The intermediate states are explicitly constructed and their thermodynamic properties are derived. These states are not invariant under the Hamiltonian evolution, but the correlation inequalities (section 3) are satisfied for the normal coordinates of observables. We present a simple criterion to distinguish observables exhibiting monotonic relaxation or metastable relaxation, and in the latter case an expression for the exit time is given. The exit time is the time necessary to leave the initial state on the basis of having reached the maximum value of the observable under consideration. In the BCS model, the observables which are invariant under the gauge transformation group of the broken symmetry [10–12] come over as relevant observables. They all exhibit metastable relaxation and all have the same exit time.

2. The BCS model

The strong-coupling BCS model is described by the local Hamiltonians [6, 7]

$$H_N = -\frac{1}{N} \sum_{i \neq j=1}^{N} \sigma_i^+ \sigma_j^- + \epsilon \sum_{i=1}^{N} \sigma_i^z \qquad \epsilon > 0 \tag{1}$$

where σ^+, σ^- and $\sigma^z = \sigma^+\sigma^- - \sigma^-\sigma^+$ are the well known Pauli matrices. H_N acts on the Hilbert space $\bigotimes_{i=1}^{N} \mathbb{C}_i^2$.

The equilibrium states ω_β studied here are elements of the set of (τ_t, β)-KMS states in the thermodynamic limit ($N \uparrow \infty$) of this model, i.e. the states satisfying the equilibrium conditions of Kubo, Martin and Schwinger [13]:

$$\omega_\beta(BA) = \omega_\beta(A\tau_{i\beta}B) \qquad \forall A, B \in \mathcal{B} \tag{2}$$

on the infinite tensor product algebra $\mathcal{B} = \bigotimes_{i=1}^{\infty} M_2$ at an inverse temperature β and with the reversible Heisenberg dynamics

$$\tau_t(\cdot) = w - \lim_{N \to \infty} = \mathrm{e}^{\mathrm{i}tH_N} \cdot \mathrm{e}^{-\mathrm{i}tH_N}.$$

The extremal points of the set of equilibrium states are given by the symmetric product states [14]:

$$\omega_\lambda(\cdot) = \prod_{i=1}^{\infty} \text{tr} \, \rho_\lambda \cdot \tag{3}$$

on the infinite tensor product algebra $\mathcal{B} = \bigotimes_{i=1}^{\infty} M_2$; ρ_λ is a 2×2 density matrix, given by the solutions of the gap equation:

$$\rho_\lambda = \frac{\exp[-\beta h_\lambda]}{\text{tr} \exp[-\beta h_\lambda]} \tag{4}$$

where

$$h_\lambda = \epsilon \sigma^z - \lambda \sigma^- - \bar{\lambda} \sigma^+ \tag{5}$$

and with order parameter λ, given by

$$\lambda = \text{tr} \, \rho_\lambda \sigma^+ = \omega_\lambda(\sigma^+). \tag{6}$$

This equation can be transformed into the equation

$$\lambda \left(1 - \frac{1}{2k} \tanh[\beta k] \right) = 0 \tag{7}$$

where $k = \sqrt{\epsilon^2 + |\lambda|^2}$; $\{-k, k\}$ is the spectrum of the effective Hamiltonians h_λ (5), which is independent of the phase of the order parameter $\lambda \in \mathbb{C}$. It can readily be seen that this equation (7) always has a solution $\lambda = 0$. This corresponds to the normal phase state. Solutions with $\lambda \neq 0$ exist if the following conditions are satisfied:

$$\epsilon < 1/2$$
$$\beta > \beta_c = \frac{1}{2\epsilon} \log \left(\frac{1 + 2\epsilon}{1 - 2\epsilon} \right). \tag{8}$$

These solutions $\lambda \neq 0$ are understood to describe the superconducting phase states. The inverse temperature $\beta > \beta_c$ fixes only $|\lambda|$, the norm of the order parameter. The phase of the order parameter ϕ, defined by $\lambda = |\lambda| e^{i\phi}$, $\phi \in [0, 2\pi]$, remains free to choose. This leads to an infinite degeneracy of the states in the superconductive regime and is due to spontaneous symmetry breaking [10, 11]. As this phase becomes important in the remainder of this paper, it will from now on explicitly be labelled, i.e. we denote the order parameter (6) as $\lambda e^{i\phi}$, with a phase $\phi \in [0, 2\pi]$, and norm $\lambda \in \mathbb{R}^+$. Furthermore, we fix now a certain subcritical temperature $\beta > \beta_c$, and hence the norm of the order parameter, which will now be labelled by $\lambda \in \mathbb{R}^+$. The superconducting pure phase states (4) are therefore from now on denoted by ω_ϕ instead of $\omega_{|\lambda| e^{i\phi}}$.

The mechanism of spontaneous symmetry breaking can be explicitly seen as follows: the Hamiltonian H_N (1) is invariant under the norm-continuous gauge transformation automorphism group $\mathcal{G} = \{\alpha_\psi \mid \psi \in [0, 2\pi]\}$ on $\mathcal{B}$, defined by the action

$$\alpha_\psi(\sigma_i^+) = e^{i\psi} \sigma_i^+. \tag{9}$$

On finite subsets $\Lambda \subset \mathbb{N}$, these transformations α_ψ are implemented by the unitaries

$$U_\Lambda^\psi = e^{i\psi Q_\Lambda / 2}$$

where Q_Λ is the (local) infinitesimal generator:

$$Q_\Lambda = \sum_{i \in \Lambda} \sigma_i^z.$$

Clearly $\alpha_\psi(H_N) = U_\Lambda^\psi H_N U_\Lambda^{\psi\,*} = H_N$ with $\{1, \ldots, N\} \subset \Lambda$, but this symmetry is broken in the equilibrium states of the superconducting phase; we have

$$\omega_\phi(\alpha_\psi(\sigma_i^+)) = \lambda e^{i(\phi+\psi)} \neq \lambda e^{i\phi} = \omega_\phi(\sigma_i^+). \tag{10}$$

In fact the gauge group $\mathcal{G}$ establishes a relation between the superconducting pure phase states with different phase factors:

$$\omega_\phi(\alpha_\psi(X)) = \omega_{\phi+\psi}(X) \qquad \forall X \in \mathcal{B} \qquad \text{and} \qquad \phi, \psi \in [0, 2\pi].$$

In the following we learn that the observables $X \in \mathcal{B}$ which are invariant under the gauge transformations, i.e. $\alpha_\psi(X) = X$, are relevant in order to determine the metastable evolution between two superconducting states.

We conclude this paragraph by remarking that a common method to single out an equilibrium state with fixed phase ϕ consists of adding a thermodynamically unimportant term to the local Hamiltonians (1), such as a vanishing external field:

$$-\frac{1}{N} \sum_{i=1}^N \sigma_i^+ e^{-i\phi} + \sigma_i^- e^{i\phi} \tag{11}$$

forcing the system into the limiting Gibbs state ω_ϕ (4) of the superconducting phase. This fixes the phase to ϕ.

3. Thermodynamic stability

An alternative way to characterize equilibrium states is given by the correlation inequalities [15]. These represent conditions which have been proven to be equivalent to the β-KMS condition (2), while their interpretation is related to the principle of minimum free energy. In other words, they are an expression for the thermodynamic stability of the KMS (equilibrium) states [13]:

Energy–entropy balance inequalities. *Let $\tau_t(\cdot) = \lim_N e^{itH_N} \cdot e^{-itH_N}$ be the Heisenberg dynamics (defined in a weak-limit sense) and β the inverse temperature. A state ω is a (τ_t, β)-KMS state if and only if for all $X \in \mathrm{Dom}(\delta)$*

$$-i\beta\omega(X^*\delta X) \geqslant \omega(X^*X) \log \frac{\omega(X^*X)}{\omega(XX^*)} \tag{12}$$

with $\delta(\cdot)$ the infinitesimal generator of the dynamics (τ_t).

In this paper we concentrate on the BCS model. Since this model is of mean-field type, we only need to consider product states (see section 2). For such states the correlation inequalities for operators $X \in \mathcal{B}$ of the form $X = X_1 \otimes X_2 \otimes \cdots \otimes X_n$ with $X_1, X_2, \ldots, X_n \in M_2$ follow from the correlation inequalities for $X_1, X_2, \ldots, X_n$. Therefore it is sufficient to consider only one-point operators, and (12) is reduced to the following.

Energy–entropy balance inequalities in the BCS model. *A product state ρ on $\mathcal{B} = \bigotimes_{i=1}^\infty M_2$ is a (τ_t, β)-KMS state for the BCS model (1) if and only if for every one-point operator $X \in M_2$ the following inequality holds:*

$$\beta\rho(X^*[h_\rho, X]) \geqslant \rho(X^*X) \log \frac{\rho(X^*X)}{\rho(XX^*)} \tag{13}$$

with h_ρ the effective Hamiltonian in this state, i.e. $h_\rho = \epsilon\sigma^z - \rho(\sigma^+)\sigma^- - \rho(\sigma^-)\sigma^+$.

The interpretation of these inequalities is the following: the lhs of (12) or (13) reflects the change in energy if we alter the state with a 'perturbation X'. The rhs of inequalities (12)

or (13) originates from the corresponding change in entropy $S(\rho) = -\operatorname{tr} \rho \log \rho$ under the 'perturbation X'. For example, if the criterion (13) is applied to unitaries $U \in M_2$, with $U^*U = \mathbf{1} = UU^*$, and we substitute U for X in (13), it is reduced to

$$\rho(U^*[h_\rho, U]) \geqslant 0.$$

This inequality expresses the fact that the local state $\operatorname{tr}(\rho \cdot)$ must have a lower internal energy than the perturbed states $\operatorname{tr}(U\rho U^* \cdot)$, while the entropy of these states remain unchanged: $S(\rho) = S(U\rho U^*)$.

If a state ω satisfies condition (12) for an operator X, we say that ω is stable under the 'perturbation X'.

4. The perturbed states

In classical kinetic models [1–4] the metastable evolution is introduced by a dynamical semigroup of dissipative maps (e.g. Glauber dynamics), satisfying the detailed balance conditions w.r.t. the asymptotic equilibrium measure. The notion of detailed balance and dissipative evolutions are generalized for quantum systems [8, 9]. The quantum dynamical semigroups as well as the classical Glauber dynamics do share the same physical background, in the sense that they can be constructed as the result of a weak coupling of the system with a temperature reservoir system [16].

A continuous one-parameter group $\{\gamma(t) \mid t \geqslant 0\}$ of linear maps $\gamma(t)$ on the algebra $\mathcal{B} = \bigotimes_{i=1}^{\infty} M_2$ is called a dynamical semigroup if for every $t \geqslant 0$ $\gamma(t)$ is a completely positive, unity preserving map on $\mathcal{B}$ and $\gamma(0)$ is the identity map.

Let L be the (densely defined) infinitesimal generator of such a dynamical semigroup, i.e.

$$\gamma(t) = e^{tL} \qquad \forall t \geqslant 0.$$

The dynamical semigroup is then called dissipative if the generator L is self-adjoint, i.e. $L(A^*) = L(A)^* \ \forall A \in \mathcal{B}$, and satisfies the following inequalities:

$$L(A^*A) \geqslant A^*L(A) + L(A^*)A \qquad \forall A \in \mathcal{B}. \tag{14}$$

Let ω be a state on $\mathcal{B}$; the dynamical semigroup $(\gamma(t))_{t \geqslant 0}$ is said to satisfy the detailed balance conditions w.r.t. the state ω if the following duality property holds:

$$\omega(XL(Y)) = \omega(L(X)Y) \qquad \forall X, Y \in \mathcal{B}.$$

Consider now one of the extremal superconducting phase states ω_ϕ (4); we can construct a dynamical semigroup $\{\gamma_\phi(t) \mid t \geqslant 0\}$ with generator L_ϕ, satisfying the condition of detailed balance w.r.t. this state. Because we are dealing with product states, the generator L_ϕ of $(\gamma_\phi(t))$ is globally defined if it is defined on the local sites, i.e.

$$L_\phi : M_2 \to M_2.$$

It is given by [8, 9]:

$$L_\phi(\cdot) = \sum_{i,j} \exp[-\beta(\epsilon_i - \epsilon_j)/2](E_{ij}^*[\cdot, E_{ij}] + [E_{ij}^*, \cdot]E_{ij}) \tag{15}$$

where $E_{ij} = |\psi_i\rangle\langle\psi_j|$ stands for the matrix units in the base of eigenvectors $\{|\psi_i\rangle \mid i \in \{-, +\}\}$ of h_ϕ, the effective Hamiltonian (5) of the (τ_t, β)-KMS state ω_ϕ (4); $|\psi_i\rangle$ is the eigenvector corresponding to the eigenvalue ϵ_i of h_ϕ. It is immediately checked that L_ϕ is dissipative (14) and satisfies the detailed balance conditions in the state ω_ϕ with fixed phase ϕ, i.e.

$$\omega_\phi(XL_\phi(Y)) = \omega_\phi(L_\phi(X)Y) \qquad \forall X, Y \in M_2. \tag{16}$$

The action of this generator (15) is naturally extended to operators $X \in \mathcal{B}$ of the form $X = X_1 \otimes X_2 \otimes \cdots \otimes X_n$ with $X_1, X_2, \ldots, X_n \in M_2$ by

$$L_\phi(X_1 \otimes X_2 \otimes \cdots \otimes X_n) = \sum_{i=1}^{n} X_1 \otimes \cdots \otimes L_\phi(X_i) \otimes \cdots \otimes X_n.$$

Since ω_ϕ is a symmetric product state (3), the dissipativity and the detailed balance properties (16) are preserved for these more general operators and follow from the properties of their one-site factors. The dynamical semigroup $(\gamma_\phi(t))_{t \geqslant 0}$ is then defined by

$$\gamma_\phi(t) = e^{tL_\phi} \qquad \forall t \geqslant 0. \tag{17}$$

Remark that the detailed balance properties (16) guarantee that ω_ϕ is stationary under this dynamical semigroup, while any other (τ_t, β)-KMS state with a different phase-factor is not invariant.

Suppose now that our system is prepared in a β-KMS state $\omega_{-\phi}$ at time $t = 0$. Based on ideas from classical models [1–4], we apply at $t \geqslant 0$ an evolution $(\gamma_\phi(t))$ (17) with phase ϕ, and the system is forced to evolve accordingly. This implies that the system will ultimately relax to the equilibrium state ω_ϕ. The intermediate states ω_t are introduced by

$$\omega_t(\cdot) = \omega_{-\phi}(e^{tL_\phi} \cdot) \tag{18}$$

where the intermediate states ω_t are constructed by applying the dynamical semigroup $(\gamma_\phi(t))_{t \geqslant 0}$ (17) with phase ϕ to the initial equilibrium state $\omega_{-\phi}$ with phase $-\phi$. These states ω_t are, by construction, again product states, and their density matrices can explicitly be calculated. They are understood to describe a metastable regime. For t small enough the state ω_t will still be close to the initial state $\omega_{-\phi}$, while if t becomes large enough the system will be relaxing to the equilibrium state ω_ϕ, where the words 'close' and 'almost' have to attain a precise meaning.

We proceed now with the explicit construction of the metastable states ω_t (18). The spectral decomposition of the generator L_ϕ (15) and the dissipative evolution $\gamma_\phi(t)$ is given in terms of the matrix units (E_{ij}^ϕ) of the corresponding asymptotic effective Hamiltonian, which can be written as $h_\phi = kE_{++}^\phi - kE_{--}^\phi$. We compute that

$$L_\phi(\mathbf{1}) = 0 \qquad L_\phi(D) = -dD \qquad L_\phi(E_{+-}^\phi) = -cE_{+-}^\phi \qquad L_\phi(E_{-+}^\phi) = -cE_{-+}^\phi \tag{19}$$

where $d = 4\cosh(\beta k)$, $c = 2 + 2\cosh(\beta k)$ and $D = e^{\beta k} E_{++}^\phi - e^{-\beta k} E_{--}^\phi$. Hence, the expectation values for the operators (19) in the state ω_t (18) are given by

$$\begin{aligned}
\omega_t(\mathbf{1}) &= 1 \\
\omega_t(D) &= e^{-td} \omega_{-\phi}(D) \\
\omega_t(E_{+-}^\phi) &= e^{-tc} \omega_{-\phi}(E_{+-}^\phi) \\
\omega_t(E_{-+}^\phi) &= e^{-tc} \omega_{-\phi}(E_{-+}^\phi).
\end{aligned} \tag{20}$$

From these equations (20) and linearity, all expectation values in ω_t, and hence the density matrix ρ_t at time t, can be calculated.

4.1. Exit times and normal coordinates

Remark that any observable $X \in M_2^{sa}$ can be developed in its normal coordinates for the asymptotic equilibrium state ω_ϕ (16), i.e.

$$X = \omega_\phi(X)\mathbf{1} + a_\phi^+(X) + a_\phi^-(X) + a_\phi^0(X). \tag{21}$$

The operators $a_\phi^+(X)$ and $a_\phi^-(X)$ are understood to be the creation (respectively annihilation) operators of the normal modes determined by X; they are given in terms of X and the

projection operators E_{++}^ϕ and E_{--}^ϕ on the eigenspaces of the asymptotic effective Hamiltonian h_ϕ, corresponding to positive (negative) energy:

$$a_\phi^+(X) = E_{++}^\phi X E_{--}^\phi \tag{22}$$

$$a_\phi^-(X) = E_{--}^\phi X E_{++}^\phi \tag{23}$$

while $a_\phi^0(X)$ is the canonical constant of motion determined by X:

$$a_\phi^0(X) = E_{++}^\phi X E_{++}^\phi + E_{--}^\phi X E_{--}^\phi - \omega_\phi(X)\mathbf{1}. \tag{24}$$

Indeed, $a_\phi^0(X)$ is a constant of motion in the state ω_ϕ, since it commutes with the effective Hamiltonian h_ϕ and

$$\frac{\mathrm{d}}{\mathrm{d}t}\omega_\phi(A\tau_t(a_\phi^0(X))B) = \mathrm{i}\omega_\phi(A[h_\phi, \tau_t(a_\phi^0(X))]B) = 0 \qquad \forall A, B, X \in M_2.$$

Note that these operators (22)–(24) all have expectation value zero in the asymptotic state ω_ϕ. They are an expression for the fluctuations of X around its asymptotic equilibrium value $\omega_\phi(X)$ (see also below). Using (20) and (21) we obtain an expression for the expectation value of X in ω_t:

$$\omega_t(X) = \omega_\phi(X) + \omega_{-\phi}(a_\phi^+(X) + a_\phi^-(X))\mathrm{e}^{-tc} + \omega_{-\phi}(a_\phi^0(X))\mathrm{e}^{-td}. \tag{25}$$

The time limits $t \to 0$ and $t \to \infty$ of expression (25) yield clearly the equilibrium expectation values $\omega_{-\phi}(X)$ $(\omega_\phi(X))$:

$$\lim_{t \to 0} \omega_t(X) = \omega_{-\phi}(X)$$

$$\lim_{t \to \infty} \omega_t(X) = \omega_\phi(X)$$

i.e. this time evolution describes the transition between the two states under consideration, the transition from $\omega_{-\phi}$ to ω_ϕ.

In general, the evolution of $\omega_t(X)$ (25) can express two types of behaviour as a function of the time t. This is easily derived from the analysis the functions

$$f_X(t) : \mathbb{R}^+ \to \mathbb{R} : t \mapsto \omega_t(X) \qquad \forall X \in M_2^{sa} \tag{26}$$

and their time derivatives.

Let us illustrate this with two pictures (figure 1).

Firstly, $\omega_t(X)$ can relax monotonically to its asymptotic value $\omega_\phi(X)$, and thus behaves qualitatively as shown in figure 1(a). This behaviour is met if the function $f_X(t)$ (26) has only an extremum at $t = 0$. Calculating the time derivative of $f_X(t)$ (26), we see that this happens whenever

$$-\frac{\omega_{-\phi}(a_\phi^0(X))}{\omega_{-\phi}(a_\phi^+(X)) + \omega_{-\phi}(a_\phi^-(X))} \leqslant \frac{c}{d} \tag{27}$$
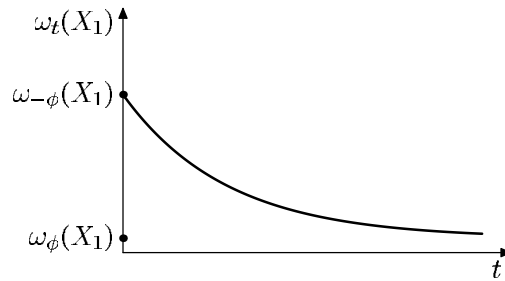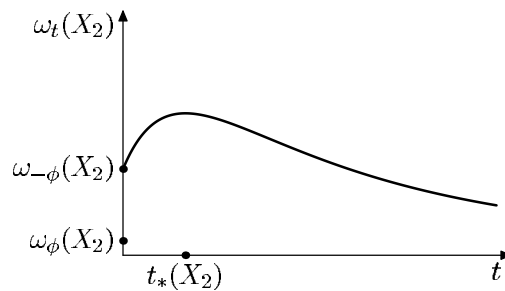
where

$$\frac{c}{d} = \frac{1 + \cosh(\beta k)}{2\cosh(\beta k)}.$$

This condition is satisfied if e.g. the second and the third term on the rhs of expression (25) have the same sign. The relaxation is exponentially fast and is determined by the constants $c = 2 + 2\cosh(\beta k)$ and $d = 4\cosh(\beta k)$ (19).

The second possibility is that condition (27) is violated, i.e. if

$$-\frac{\omega_{-\phi}(a_\phi^0(X))}{\omega_{-\phi}(a_\phi^+(X)) + \omega_{-\phi}(a_\phi^-(X))} > \frac{1 + \cosh(\beta k)}{2\cosh(\beta k)}. \tag{28}$$

(a) $f_{X_1}(t) : t \mapsto \omega_t(X_1)$

(b) $f_{X_2}(t) : t \mapsto \omega_t(X_2)$

Figure 1. Typical pictures of monotonic (*a*) and metastable (*b*) relaxation.

In this case the function $f_X(t) : t \mapsto \omega_t(X)$ (26) has an extremum, reached at a time $t_*(X) > 0$, which may depend on the observable X. A typical picture of such a behaviour is shown in figure 1(*b*).

The interpretation of this extremum is the following. The time $t_*(X)$ is a timescale which indicates where the expectation value $\omega_t(X)$ leaves the metastable regime and the relaxation to the asymptotic equilibrium value $\omega_\phi(X)$ starts. For $t < t_*(X)$, $\omega_t(X)$ moves away from the original equilibrium value $\omega_{-\phi}(X)$; this behaviour with an increasing distance from equilibrium corresponds to the metastable regime. At time $t = t_*(X)$, this evolution comes to an end since $\omega_t(X)$ is now at its maximum distance from the equilibrium value $\omega_{-\phi}(X)$. For $t > t_*(X)$, we see another type of behaviour. The system is again approaching equilibrium, but $\omega_t(X)$ is not returning to the initial equilibrium value $\omega_{-\phi}(X)$, it now relaxes (monotonically) to its new equilibrium value $\omega_\phi(X)$.

Since the time $t_*(X)$ marks where $\omega_t(X)$ leaves metastability and the relaxation to the asymptotic value is started, we call $t_*(X)$ the exit time for the observable X. The exit time $t_*(X)$ can be found calculating the extrema of function (26), i.e. $t_*(X)$ is the time t for which $\frac{d}{dt} f_X(t)\big|_t = 0$; it is readily computed, being

$$t_*(X) = \frac{1}{d-c}\left(\log\frac{d}{c} + \log\left|\frac{\omega_{-\phi}(a_\phi^0(X))}{\omega_{-\phi}(a_\phi^+(X)) + \omega_{-\phi}(a_\phi^-(X))}\right|\right). \tag{29}$$

In this expression, it is clear that the exit time for the expectation value of an observable $t_*(X)$ is determined by the constants c, d (19) and the ratio between the initial-state expectation values of the normal coordinates of X (22)–(24).

In general we can formulate the following statement,

Metastable relaxation for the BCS model. A system prepared in a initial product state $\omega_{-\phi}$ on $\mathcal{B} = \bigotimes_{i=1}^{\infty} M_2$ will relax to a superconducting equilibrium state ω_ϕ (4) at subcritical temperature β (8) according to the evolution induced by a dynamical semigroup (17) with a dissipative generator L_ϕ (15), satisfying the quantum detailed balance conditions in state ω_ϕ. The behaviour of this relaxation depends on the chosen observables $X \in M_2^{sa}$:

- *Monotonic relaxation*
  The relaxation of the expectation value of an observable $X \in M_2^{sa}$ is monotonic if the following holds:

  $$-\frac{\omega_{-\phi}(a_\phi^0(X))}{\omega_{-\phi}(a_\phi^+(X)) + \omega_{-\phi}(a_\phi^-(X))} \leqslant \frac{1 + \cosh(\beta k)}{2\cosh(\beta k)}$$

  where $a_\phi^+(X)$, $a_\phi^-(X)$ and $a_\phi^0(X)$ are the normal coordinates of X in the equilibrium state ω_ϕ as defined by equation (21), and $k = \sqrt{\epsilon^2 + \lambda^2}$, the positive eigenvalue of the effective Hamiltonians at inverse temperature β (5).

- *Metastable relaxation*
  The expectation value of an observable $X \in M_2^{sa}$ relaxes metastably if the following is true:

  $$-\frac{\omega_{-\phi}(a_\phi^0(X))}{\omega_{-\phi}(a_\phi^+(X)) + \omega_{-\phi}(a_\phi^-(X))} > \frac{1 + \cosh(\beta k)}{2\cosh(\beta k)}.$$

In this case we define the *exit time* for the observable X, $t_*(X)$, as the time when the expectation value of X has passed its extremal value and the relaxation to equilibrium starts. $t_*(X)$ is then given by the expression

$$t_*(X) = \frac{1}{2\cosh(\beta k) - 2} \left(\log \frac{2\cosh(\beta k)}{1 + \cosh(\beta k)} + \log \left| \frac{\omega_{-\phi}(a_\phi^0(X))}{\omega_{-\phi}(a_\phi^+(X)) + \omega_{-\phi}(a_\phi^-(X))} \right| \right).$$

An interesting point of these considerations is that the decomposition (21) and the construction of the exit times is in terms of operators which are closely related to quantum fluctuations. Quantum fluctuations $F_\omega(X)$ are the limits $n \to \infty$ of operators $F_n(X)$ defined by

$$F_n(X) = \frac{1}{\sqrt{n}} \sum_{i=1}^{n} X_i - \omega(X),$$

where X is a local observable and X_i is a copy of X, translated to site i. In [17, 18] one has proved the existence of the limit

$$\lim_{n \to \infty} \omega(F_n(X)^2) = \tilde{\omega}(F_\omega(X)^2)$$

defining a dynamical system on the level of the algebra of fluctuations $\{F_\omega | X\}$, and defining a state $\tilde{\omega}$ on the algebra of fluctuations. Also a dynamics $(\tilde{\tau}_t)$ of fluctuations induced by the original one (τ_t), is defined by the formula

$$\tilde{\tau}_t F_\omega(X) = F_\omega(\tau_t X). \tag{30}$$

In [17, 18] it is proved this dynamical system is always a bosonic system. This is worked out in great detail. We refer to [17, 18] for more details and more precise information on this

subject. The point is that the exit times (29) can formally be expressed in term of fluctuations, as follows:

$$t_*(X) = \frac{1}{d-c}\left(\log\frac{d}{c} + \log\left|\frac{\tilde{\omega}_{-\phi}(F_\phi(X_0))}{\tilde{\omega}_{-\phi}(F_\phi(Q_X))}\right|\right)$$

where

$$F_\phi(Q_X) = \lim_{n\to\infty}\frac{1}{\sqrt{n}}\sum_{i=1}^{n}(a_\phi^+(X) + a_\phi^-(X))_i$$

$$F_\phi(X_0) = \lim_{n\to\infty}\frac{1}{\sqrt{n}}\sum_{i=1}^{n}(a_\phi^0(X))_i$$

and $\tilde{\omega}_{-\phi}$ is the limiting state with phase $-\phi$ on the fluctuation algebra. The thermodynamic limit in numerator and denominator is taken jointly. Although the mathematical formulation of this computation is far from completely coherent with the general theory of quantum fluctuations [17, 18], we are tempted to conjecture that this construction might be the key to the understanding of metastability in a broader class of quantum systems.

4.2. Invariant observables under the gauge transformation group

Let us now continue the study of the metastable relaxation in the BCS model between two equilibrium states, in particular the evolution from $\omega_{-\phi}$ to ω_ϕ for gauge invariant observables. As explained, these superconducting states are not invariant under the gauge symmetry α_ψ, $\psi \in [0, 2\pi]$ (9) of the BCS Hamiltonians (1); in particular

$$\omega_\phi = \omega_{-\phi} \circ \alpha_{2\phi}.$$

Observables $X \in M_2$ which are invariant under this gauge transformation group $\mathcal{G}$ (9) i.e. satisfying

$$\alpha_\psi(X) = X \qquad \text{or} \qquad [\sigma^z, X] = 0 \tag{31}$$

have the same expectation value in all superconducting phase states, hence

$$\omega_{-\phi}(X) = \omega_\phi(X).$$

Developing the observable X in normal coordinates w.r.t. ω_ϕ (21) yields

$$\omega_{-\phi}(a_\phi^+(X)) + \omega_{-\phi}(a_\phi^-(X)) + \omega_{-\phi}(a_\phi^0(X)) = 0.$$

Hence we can rewrite equation (25), yielding

$$\omega_t(X) = \omega_\phi(X) - \omega_{-\phi}(a_\phi^0(X))(e^{-tc} - e^{-td}).$$

This implies that the relaxation for observables invariant under the gauge transformation group $\mathcal{G}$ (9) is of the metastable type. The transition between the metastable regime and the relaxation regime happens at the same moment, i.e. the invariant observables $\alpha_\psi(X) = X$ share the same exit time (29):

$$t_* = \frac{\log d - \log c}{d-c} = \frac{\sqrt{1-4k^2}}{2\sqrt{1-4k^2}-2}\log\left(\frac{1}{2} + \sqrt{1-4k^2}/2\right). \tag{32}$$

The time t_* gives a timescale for the transition between the metastable regime $t < t_*$, during which the system evolves away from equilibrium, and the relaxation regime $t > t_*$, where the system evolves towards the new equilibrium state.

4.3. Explicit computations

Let us now illustrate the metastability in the BCS model with a few special observables. Using (20) or (25) we calculate the expectation values in the intermediate states (18) of some typical observables:

$$\omega_t(\sigma^+ e^{-i\phi} + \sigma^- e^{i\phi}) = 2\lambda\left(1 - 2\sin^2(\phi)\left(\lambda^2 e^{-td} + \epsilon^2 e^{-tc}\right)/k^2\right) \tag{33}$$

$$\omega_t(i\sigma^+ e^{-i\phi} - i\sigma^- e^{i\phi}) = 2\lambda\sin(2\phi)e^{-tc}. \tag{34}$$

In equations (33) and (34), the monotonic exponential relaxation towards the state ω_ϕ is clear. The limits $t \to 0(\infty)$ of the expectation values give again the equilibrium values in the states $\omega_{-\phi}(\omega_\phi)$; in particular one computes also

$$\lim_{t\to 0}\omega_t(\sigma^+) = \lambda e^{-i\phi} = \omega_{-\phi}(\sigma^+)$$

$$\lim_{t\to\infty}\omega_t(\sigma^+) = \lambda e^{i\phi} = \omega_\phi(\sigma^+).$$

Note that we have the following bound on the time evolution of the 'condensate': $\lambda(t) = |\omega_t(\sigma^+)| \leqslant \lambda$, indicating that the 'condensation' is suppressed in the intermediate states.

The situation is different for the evolution of the expectation value of σ^z, the generator of the gauge group (9):

$$\omega_t(\sigma^z) = -2\epsilon - 4\sin^2(\phi)\frac{\epsilon\lambda^2}{k^2}\left(e^{-tc} - e^{-td}\right). \tag{35}$$

Clearly, this is an example of an observable invariant under the gauge transformation group $\mathcal{G}$ (31), and its relaxation is metastable. In the time limits $t \to 0(\infty)$, $\omega_t(\sigma^z)$ (35) tends to the equilibrium value -2ϵ, but $|\omega_t(\sigma^z) - \omega_{\pm\phi}(\sigma^z)|$ goes through a maximum, attained at t_* (32), the exit time for invariant observables.

4.4. Temperature dependence

To conclude this section about the relaxation behaviour, we make some remarks on the dependence on the temperature. At the critical point (8), i.e. if $(T \uparrow T_c)$ or $(\beta \downarrow \beta_c)$, the order parameter λ vanishes. This also implies the following equalities for $T = T_c$:

$$\omega_{-\phi}(X) = \omega_t(X) = \omega_\phi(X) \qquad t \geqslant 0 \qquad \forall X \in \mathcal{B}$$

and the metastability effects disappear completely. The constants (c, d), governing the speed of relaxation, decrease to the values $c_c = 2 + 2\cosh(\beta\epsilon)$ (respectively $d_c = 4\cosh(\beta\epsilon)$). Since the expression for the exit times $t_*(X)$ (29) depends on the ratio of the expectation values $\omega_{-\phi}(a_\phi^0(X))$ and $\omega_{-\phi}(a_\phi^+(X)) + \omega_{-\phi}(a_\phi^-(X))$, the behaviour in the limit ($\lambda \to 0$) of $t_*(X)$ can be different for different observables $X \in M_2^{sa}$. Both $\omega_{-\phi}(a_\phi^0(X))$ and $\omega_{-\phi}(a_\phi^+(X)) + \omega_{-\phi}(a_\phi^-(X))$ tend to zero at the critical point ($\lambda \to 0$), but the speed at which they decay to zero can be different. This depends on the observable X under consideration.

If we consider the metastable evolution between two ground states ($T = 0$, $\beta = \infty$), we find that there are no intermediate states, since the constants c, d (19) governing the relaxation speed blow up to infinity as β tends to infinity, hence

$$\omega_t = \begin{cases} \omega_{-\phi} & \text{for} \quad t = 0 \\ \omega_\phi & \text{for} \quad t > 0. \end{cases}$$

This results from the fact that the dynamical semigroup which we consider (17) becomes trivial for ground states. The detailed analysis of the dynamics when $T \to 0$ indicates the existence of a non-trivial evolution only on a different timescale.

Hence, if one would like to compare the dynamics at different temperatures, one has to rescale the time with an appropriate, temperature-dependent, scaling factor. This scaling and the resulting dynamics require an independent analysis and are out of the scope of our considerations here.

5. Stability–instability properties of the intermediate states

Here we consider the stability properties of the intermediate states $\omega_t(\cdot)$ (18) on the basis of the correlation inequalities (13); i.e., we consider the equilibrium or stability conditions

$$\beta\omega_t(X^*[h_t, X]) \geqslant \omega_t(X^*X) \log\left(\frac{\omega_t(X^*X)}{\omega_t(XX^*)}\right) \tag{36}$$

where h_t stands for the effective Hamiltonian in the state ω_t:

$$h_t = \epsilon\sigma^z - \omega_t(\sigma^+)\sigma^- - \omega_t(\sigma^-)\sigma^+. \tag{37}$$

From section 3 we know that ω_t is a β-KMS state if and only if equation (36) is satisfied for all operators $X \in \mathcal{B}$. In this section we analyse to what extent the intermediate states (18) are still stable, i.e. we check for which operators $X \in M_2$ these states ω_t satisfy the inequalities (36). The meaningful operators in this context are the matrix units in the base of the spectral decomposition of h_t (37), denoted by $\{E(t)_{++}, E(t)_{+-}, E(t)_{-+}, E(t)_{--}\}$. Compute first the expectation values

$$\begin{aligned}
\omega_t(E(t)_{--}) &= \tfrac{1}{2} + k_t + \epsilon f_t/(2k_t)\\
\omega_t(E(t)_{-+}) &= -\lambda_t f_t/k_t
\end{aligned} \tag{38}$$

with $\lambda_t = |\omega_t(\sigma^+)|$, $k_t = \sqrt{\epsilon^2 + \lambda_t^2}$, the positive eigenvalue of h_t (37) and $f_t = 4\sin^2(\phi)\epsilon\lambda^2\left(e^{-tc} - e^{-td}\right)/k^2$. The expectation values of the other matrix units can be determined from the expressions (38), since $\omega_t(E(t)_{++}) = 1 - \omega_t(E(t)_{--})$ and $\omega_t(E(t)_{+-}) = \overline{\omega_t(E(t)_{-+})}$.

5.1. ω_t is not an invariant state

A first observation is that the states ω_t, $t > 0$ are not invariant under the Hamiltonian evolution: this is easily derived from the expressions (38), calculating

$$\omega_t([h_t, E(t)_{+-}]) = 2k_t\omega_t(E(t)_{+-}) \neq 0. \tag{39}$$

5.2. Stability

The position Q_X and momentum P_X observables of a normal mode are constructed in the usual way, by means of the creation and annihilation operators,

$$a_t^+(X) = E(t)_{++}XE(t)_{--} \tag{40}$$
$$a_t^-(X) = E(t)_{--}XE(t)_{++} \tag{41}$$

yielding the following expression for Q_X and P_X:

$$Q_X = \frac{1}{\sqrt{2}}(a_t^+(X) + a_t^-(X)) \tag{42}$$

$$P_X = \frac{i}{\sqrt{2}}(a_t^+(X) - a_t^-(X)). \tag{43}$$

These observables (Q_x, P_X) satisfy the canonical dynamical equations:

$$i[h_t, Q_X] = 2k_t P_X$$
$$i[h_t, P_X] = -2k_t Q_X$$

justifying the name *normal coordinates*. For the sake of completeness we also give $a_t^0(X)$, the canonical constant of motion of X:

$$a_t^0(X) = E(t)_{++} X E(t)_{++} + E(t)_{--} X E(t)_{--} - \omega_t(X)\mathbf{1}. \tag{44}$$

These definitions are analogous to those in equations (22)–(24) in section 4 with an important difference. In section 4, we need the normal modes for the asymptotic equilibrium state ω_ϕ (16), whereas the expressions (40), (41) and (44) define the normal modes w.r.t. the intermediate state ω_t. We can now formulate the following stability statements:

- *The correlation inequalities (36) are satisfied for all linear combinations $aQ_X + bP_X$, with $a, b \in \mathbb{C}$ and Q_X and P_X as in (42) (respectively (43)).*
  For such an operator the correlation inequalities yield

  $$\omega_t(E(t)_{--}) \geqslant \omega_t(E(t)_{++}).$$

  Since $k_t + \epsilon f_t/(2k_t) > 0$ (38), this condition is satisfied for every intermediate state ω_t.
- *The constants of motion, e.g. $a_t^0(X)$ (44), satisfy the correlation inequalities.*
  An operator $C \in M_2$ is a constant of motion in ω_t if it satisfies $[h_t, C] = 0$; such operators can be written as $C = aE(t)_{++} + bE(t)_{--}$ with $a, b \in \mathbb{C}$. It is easy to check that the correlation inequalities (36) are trivially satisfied. Moreover, this stability property holds for any operator $C \in M_2$ satisfying $[h_\rho, C] = 0$ in a general symmetric product state with density matrix ρ and effective Hamiltonian h_ρ (see e.g. (13)).

5.3. Instability

The instability of the intermediate states is reflected in the following statements: *the correlation inequalities are satisfied for the creation operators $a_t^+(X)$ (40), $\forall X \in M_2$, but not for the annihilation operators $a_t^-(X)$ (41).*

Substituting the operators $a_t^+(X)$ (40) (respectively $a_t^-(X)$ (41)) for X in the energy–entropy balance inequalities (36) yields

$$\text{if} \quad X = a_t^+(X) \qquad \text{then} \quad \frac{\omega_t(E(t)_{--})}{\omega_t(E(t)_{++})} \leqslant e^{\beta 2k_t} \tag{45}$$

$$\text{if} \quad X = a_t^-(X) \qquad \text{then} \quad \frac{\omega_t(E(t)_{--})}{\omega_t(E(t)_{++})} \geqslant e^{\beta 2k_t} \tag{46}$$

i.e. ω_t could only be stable under both $a_t^+(X)$ and $a_t^-(X)$, $\forall X \in M_2$, if the equality holds. It follows from the gap equation (7) that these equalities holds only for equilibrium states. The intermediate states are stable under the creation operators (45), but not under the annihilation operators (46). This can be seen as follows: using (38), it is readily computed that for all $t > 0$ the strict inequality (45) holds in the limit $\epsilon \to 0$. Suppose now that there exists a point in parameter space (t', ϵ'), with $t' > 0$, $\epsilon' > 0$, such that at that point the inequality (46) holds. By continuity of the state in parameter space, we have continuity of the function $f : (t, \epsilon) \mapsto \omega_t(E(t)_{--}) - e^{\beta 2k_t}\omega_t(E(t)_{++})$. Since $f(t', 0) < 0$ and $f(t', \epsilon') > 0$, there must exist a point where this function is zero; this would imply that the intermediate state at that point is an equilibrium state, which cannot be true (see e.g. (39)). This proves that condition (45) is always satisfied in the intermediate states, while (46) yields that the stability is violated for the annihilation operators $a_t^-(X)$.

6. Outlook

All results in this paper concern the BCS model, and rely very much on the mean-field character [14] of this model: all the states under consideration are chosen within the set of symmetric product states; the extension of these results to other mean-field models [12] is straightforward. However, this work should be considered as a prototype model of a scheme which can be generalized to *bona fide* interacting systems. The main argument for this is that metastability is formulated in terms of fluctuation operators and their dynamics. Relying on the general theory of quantum fluctuations [17, 18] these fluctuation systems are quasi-free or generalized free systems, and therefore we are confident that our results have a much wider validity far beyond the model considerations of above. We reserve this generalization to interacting systems for a future contribution.

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