Superconducting fullerenes in a nonconventional thermodynamical model

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A CRYSTALLINE SOLID of C_{60} (a fullerene) is expected to be an insulator or a semiconductor. However, one of the most striking properties of C_{60} – related materials is the observation of relatively high temperature superconductivity in alkali metal doped M_3C_{60} and in various alkaline earth doped compounds. So, the interstitial diffusion of impurities considerably influences the superconductivity phase. The value of the critical temperature below which the superconducting phase exists, strongly depends on many other external influences (electromagnetic, thermal, mechanical, etc.). The paper deals with construction of a phenomenological macroscopic model of interactions between physical fields in fullerenes, basing on the extended thermodynamics with internal variables and with the use of Liu's theorem in order to apply the entropy inequality.

1. Introduction

MATERIALS of specific properties, particularly smart materials very sensitive to external influences which vary due to mutual interactions between physical fields and such materials, are of great interest for researchers and engineers. One of the most spectacular examples of such materials are fullerenes, the allotropic variety of carbon. Fullerenes have large closed cage polyhedral molecules of carbon atoms, the most common fullerene being C_{60}. As the molecular crystal they form a *fcc* or *bcc* lattice. Since each carbon atom has its valence requirements fully satisfied (each carbon atom has four valence electrons), a crystalline solid of C_{60} is expected to be an insulator or a semiconductor. However, one of the most striking properties of C_{60}-related materials is the observation of relatively high temperature superconductivity in alkali metal doped M_3C_{60} and in various alkaline earth doped compounds. In the synthesis of C_{60}, larger fullerenes are also formed, e.g. C_{70}, C_{76}, C_{78}, C_{80}, C_{84}, C_{240}, C_{330}. In principle, the smallest possible fullerene is C_{20} though no C_{20} fullerenes have been reported experimentally. Thus, C_{60} is the only fullerene host for which superconductivity has been identified. For the physical properties of fullerenes see [1]. There are three ways to introduce foreign atoms into a C_{60}-based solid. One of them involves the addition of a rare earth, an alkaline earth or an alkali metal ion into the interior

of the fullerene molecule. However, no superconductivity has been observed in such doped fullerene and it may remain the insulator or the semiconductor.

The second method is the substitutional doping of an impurity atom in a different valence state for a carbon atom on the surface of a fullerene molecule. However, because of atom diameters and distances on the C_{60} surface, only boron and nitrogen might be dopants in that case. And again, no superconductivity has been observed in the above structure.

In the third method of doping fullerene solids, the dopant is introduced into the interstitial positions between adjacent molecules. In this doping, a charge transfer can take place between the impurities and the molecules. That transfer forms a situation when superelectrons (the Cooper pairs) self-consistently coexist with each other creating (being) the carriers of the supercurrent. It is known that within the region of one Cooper pair, there are many centers of the other pairs. Thus the Cooper pairs (superelectrons) cannot be treated independently since they form a very complicated interlaced structure, the stability of which is extremely important for the existence of the superconducting state. There are numerous examples of superconductivity in such doped C_{60}.

The last method is most important for us since the interstitial mass diffusion processes (the intermolecular diffusion in the fullerene molecular crystal) might considerably influence conductivity properties of fullerenes; those properties can vary during such a process. However, not only diffusion of impurities and their concentration influence the value of critical temperature below which the superconducting phase exists. That value and even the existence of superconducting phase strongly depend also on many other external influences, like the magnitude of applied magnetic or electric fields, the density of electric current existing in the fullerene, the thermal conditions and properties (heat flux, temperature, heat capacity or heat conductivity vs. temperature) which accompany the processes running in the C_{60} as superconductors [2].

In nonequilibrium (and even in equilibrium) states of superconductors, in temperatures different from zero, a part of the pairs is thermally dissociated and the density of superelectrons depends on the number of nondissociated pairs. Since the process of the Cooper pairs creation is selfconsistent, any change of their number produced by external fields, like temperature, electromagnetic field and diffusion of impurities, strongly influences characteristic properties of superelectrons. If the quantities characteristic for the above fields reach their critical values, the continuous transition from superconducting to normal state of the fullerene occurs.

The dependence of the constitutive superconductor parameters on pressure or mechanical stresses are also interesting. Great number of various properties of the fullerenes shown above, strong dependence of material coefficients in superconducting phase on many physical fields, phase transitions occurring during processes, and the like, indicate that any description of thermodynamical states and processes is rather very complicated. There exist several attempts to de-

scribe physical interactions in deformable superconductors in the framework of nonequilibrium thermodynamical phenomenological models. For the most characteristic ones see [3–9, 15–17].

The paper deals with construction of a model of interactions between physical fields in fullerenes within their superconducting phase. A specific definition of the state vector has been proposed. It consists of field controllable variables and additionally, of internal variables responsible for the electrical conductivity properties of the $M_x C_{60}$ material. An extended-like thermodynamical model [10] with the use of that state vector and consequences of its introduction are presented. The superscripts N and S concern the "normal" and "superconducting" states of the fullerene, respectively.

2. Conductivity phases of fullerenes

As we have mentioned before, a pure molecular crystal C_{60} is expected to be an insulator and/or semiconductor when doped. Dopants change its conductivity properties according to their positions in the lattice. Those positions depend on the impurity concentration. Doping, for instance, with an alkaline earth impurity, e.g. Ca, when two Ca atoms are placed at the tetrahedral sites of the *fcc* C_{60} lattice and the third Ca atom is placed either at an on-center or at an off-center position of the octahedral interstitial site, causes that $Ca_3 C_{60}$ becomes a semiconductor. In the case of the superconducting phase, three Ca atoms are at off-centered positions of the octahedral interstitial site [1]. So, two different properties of the fullerene depend on the concentration of impurities:

i) the conductivity property – whether it is a semiconductor or a superconductor,

ii) the conductivity property – the existence of the superconducting phase in the normal semiconducting phase where the former one results from the density of the Cooper pairs.

Thus, any description of state of the fullerene when the superconducting phase also exists, seems to be very complicated. For the thermoelastic and doped fullerene C_{60} in which relaxation of thermal field, diffusion and electric current is observed, the vector of state (the set of independent variables) concerning any conductivity phase can be generally presented in the form (extended irreversible thermodynamical (EIT) model)

$$(2.1) \qquad \mathcal{A} = \{\varepsilon, \mathcal{R}, T, \nabla T, c, \nabla c, \mathbf{q}, \mathbf{j}^c, \aleph, \mathbf{j}\},$$

where ε is the linear small strain tensor, because it is difficult to expect that within the superconducting phase existing in the relatively low temperature, large elastic deformations are possible, $\mathcal{R}$ is a vector of electromagnetic field variables (see comments below), T is the temperature and $\mathbf{q}$ is the heat flux, c is the concentration of impurities and $\mathbf{j}^c$ is the flux of impurity mass (cf. [12]),

$\aleph$ is an internal variable responsible for the generally understood electric charge carrier density, and $\mathbf{j}$ is the flux of the carrier field, i.e. the electric current. The vector $\mathcal{R}$ is defined as

$$(2.2) \qquad \mathcal{R} = \begin{cases} \{\mathcal{E}, \mathbf{B}\} \\ \text{or} \\ \{\varphi, \mathbf{A}, \nabla\varphi, \nabla\mathbf{A}\}, \end{cases}$$

where $\mathcal{E}$ – the electromotive intensity in the moving frame and $\mathbf{B}$ – the magnetic induction, φ – the scalar and $\mathbf{A}$ – the vector electromagnetic potentials, respectively. They can be equivalently chosen as independent electromagnetic variables [3–9, 15–17]. Situation with the internal variable $\aleph$ and its flux $\mathbf{j}$ is much more complicated. They can be defined as

$$(2.3) \quad \aleph = \begin{cases} \{n, p, \nabla n, \nabla p\} & \text{for the normal semiconducting phase [11]} \\ \text{and/or} \\ \{\psi, \psi^*, \nabla\psi, \nabla\psi^*\} & \text{for the superconducting phase [4–9],} \end{cases}$$

$$(2.4) \quad \mathbf{j} = \begin{cases} \{\mathbf{j}^n, \mathbf{j}^p\} & \text{for the normal semiconducting phase [11]} \\ \text{and/or} \\ \{\mathbf{j}^S\} & \text{for the normal superconducting phase [3],} \end{cases}$$

where n and p are the mass densities of electrons and holes in a semiconductor, respectively, ψ denotes the complex wave function describing the entire ensemble of superelectrons such that [2]

$$(2.5) \qquad n^S = \psi\psi^* = |\psi|^2$$

is the probability density or local density of superelectrons (ψ^* is the complex conjugate to ψ) [2], then $\mathbf{j}^n$ and $\mathbf{j}^p$ are the fluxes of electrons and holes in the semiconducting phase and $\mathbf{j}^S$ is the flux of superelectrons (the Cooper pairs) or simply supercurrent. Remark that in $\mathcal{R}$ (2.2), either electromagnetic variables or electromagnetic potentials are responsible for electromagnetic field, contrary to $\aleph$ (2.3) and $\mathbf{j}$ (2.4). $\aleph$ and $\mathbf{j}$ can be taken in their full not alternative forms creating the set of independent variables (the vector of state) for the semiconducting normal phase and the superconducting one.

Another comment is necessary to be mentioned here. It deals with the time evolution of $\aleph$ and $\mathbf{j}$. In a case of the semiconducting phase we have the laws of conservation of electron and hole as the evolution equations for $\mathbf{j}^n$ and $\mathbf{j}^p$ as related to relaxation semiconductors [11]. For the superconducting phase, the evolution equation of the wave function ψ is the generalized Schrödinger equation, then the generalized first London equation describes the evolution of the supercurrent $\mathbf{j}^S$ [2].

3. Extended-like thermodynamical model

From now on we confine our considerations only to the semiconducting phase of a fullerene. The semiconducting normal phase of that material can be described within one of the existing thermodynamical models of deformable semiconductors (see [11], for instance). To obtain a description of both the semiconducting and superconducting coexisting phases of the fullerene, one has to superpose the model presented below with that proposed, among others, in [11]. We aim at investigating a thermoelastic (for the reason mentioned before) superconducting fullerene in which the impurity (mass) diffusion occurs and the relaxation features of supercurrent, thermal and diffusion fields are taken into account. The latter one is included in the model only for formal reasons. Finally, it will be dropped out by the use of a proper gauging (the relaxation time of the mass diffusion field is too long as compared to the remaining two relaxation times concerning the supercurrent and the thermal fields). Electromagnetic properties resulting from possible electrical polarization or magnetization are excluded from our considerations. For such a fullerene body, its superconducting state is described by the following set of independent variables (the vector of state) selected from $(2.1)-(2.4)$:

$$(3.1) \qquad \mathcal{C} = \left\{ \varepsilon_{ij}, \varphi, A_i, T, T_{,i}, c, c_{,i}, \psi, \psi^*, \psi_{,i}, \psi^*_{,i}, q_i, j_i^c, j_i^S \right\}$$

and all of them are evaluated at the same point and time. Also all the fields in (3.1) as well as the fullerene are assumed to be continuous. The physical processes occurring in the above-defined situation are governed by three groups of fundamental laws. The first group concerns the balances of mass, momentum, moment of momentum and internal energy.

The balance of diffusing (impurity) mass resulting from the continuity equations for the constituents (impurities and a fullerene) reads [12]

$$(3.2) \qquad \varrho\dot{c} + j^c_{k,k} = 0.$$

The superimposed dot denotes the material time derivative.

The momentum balance for nonpolarized and nonmagnetized body with other electromagnetic interactions takes the form (cf.[13, 15–17])

$$(3.3) \qquad \varrho\dot{v}_k - \sigma_{jk,j} - \epsilon_{kij}j_iB_j - f_k = 0,$$

where v_k is the velocity of the body point, σ_{ik} denotes the stress tensor and f_k is a body force density.

The moment of momentum balance is assumed in its classical form that indicates the symmetry of the stress tensor for any spin, and skew-symmetric features can be omitted in the fullerene crystal entity [1, 13, 14]:

$$(3.4) \qquad \epsilon_{ijk}\sigma_{jk} = 0.$$

However, we must remember about the domain structure of superconductors, because the conductivity and superconductivity phases coexist. Hence skew-symmetric features of the fullerene may occur during deformation processes. Moreover, the vortex properties of the magnetic flux in the superconductors also give a contribution to the moment of momentum [2]. So, the balance (3.4) is understood as the first approximation in the description of interactions between the mechanical and other physical fields in fullerenes.

The internal energy balance is taken in the following form [3–9, 12, 15–17]:

$$(3.5) \qquad \varrho \dot{U} - \sigma_{ji} v_{i,j} + q_{k,k} - j_i \mathcal{E}_i - \varrho r = 0,$$

where U denotes the internal energy density per unit mass and r is the heat source distribution density.

The second group of laws deals with the electromagnetic field. *The Maxwell equations* are taken in their classical form disregarding the displacement current and the free charge density [2]:

$$(3.6) \qquad \epsilon_{ijk} E_{k,j} + \frac{\partial B_i}{\partial t} = 0,$$

$$(3.7) \qquad \epsilon_{ijk} H_{k,j} - j_i = 0,$$

$$(3.8) \qquad B_{k,k} = 0,$$

$$(3.9) \qquad D_{k,k} = 0.$$

The above laws must be complemented by the relations

$$(3.10) \qquad \mathcal{E}_i = E_i + \epsilon_{ijk} v_j B_k,$$

$$(3.11) \qquad j_i = j_i^n + j_i^p + j_i^S = j_i^N + j_i^S,$$

$$(3.12) \qquad E_k = -\varphi_{,k} - \frac{\partial A_k}{\partial t},$$

$$(3.13) \qquad B_k = \epsilon_{kij} A_{j,i},$$

$$(3.14) \qquad D_k = \epsilon E_k,$$

$$(3.15) \qquad B_k = \mu_0 H_k.$$

j_i^N denotes the *normal* current which satisfies Ohm's law in conductors and additionally in semiconductors, the diffusion law of the charge carriers, ϵ is the permittivity of the fullerene and μ_0 is the permeability of vacuum.

The third group of fundamental laws concerns the time evolution of internal variables and fluxes. So, we postulate the following equations:

• *the evolution equation for the heat flux*

$$(3.16) \qquad \overset{*}{q}_k - Q_k(\mathcal{C}) = 0,$$

- *the evolution equation for the wave function*

$$(3.17) \qquad \dot{\psi} - \Psi(\mathcal{C}) = 0,$$

and *its complex conjugate*

$$(3.18) \qquad \dot{\psi}^* - \Psi^*(\mathcal{C}) = 0,$$

- *the evolution equation for the mass flux*

$$(3.19) \qquad \overset{*}{j^c_k} - J^c_k(\mathcal{C}) = 0,$$

and *the evolution equation for the supercurrent*

$$(3.20) \qquad \overset{*}{j^S_k} - J^S_k(\mathcal{C}) = 0.$$

The superimposed asterisk denotes the Zaremba – Jaumann time derivative. We must comment on the relation of Eqs. (3.17) and (3.18) with the supercurrent density j^S_k, the density of the superelectrons n^S and eventually Eq. (3.20). On using the relation (2.5) and the evolution equations (3.17) and (3.18), we obtain [2]

$$(3.21) \qquad \frac{\partial n^S}{\partial t} + j^S_{k,k} = N^S(\mathcal{C})$$

which may be treated as the balance of superelectrons, where

$$(3.22) \qquad j^S_{k,k} - N^S(\mathcal{C}) = \left(\psi^* \psi_{,k} + \psi \psi^*_{,k} \right) - [\psi^* \Psi(\mathcal{C}) + \psi \Psi^*(\mathcal{C})].$$

Equation (3.21) is a generalization of the conservation law for the Cooper pairs [2] to external influences of various physical fields. The source-like term in (3.21) $N^S(\mathcal{C})$ is assumed to vanish if there are no influences of the elastic, thermal and mass diffusion fields on the state of the fullerene. It means that in such situation the superelectron charge is conserved. If we want to describe the processes considered above in a proper way, we must demand that they should be admissible from the thermodynamical point of view, i.e. they should not contradict the second law of thermodynamics. The latter written in local form, takes the form of the entropy inequality

$$(3.23) \qquad \varrho \dot{S} + \Phi_{k,k} - \frac{\varrho r}{T} \geq 0,$$

where S denotes the entropy density and Φ_k is the entropy flux associated with the fields of the set $\mathcal{C}$. As a matter of fact, if we define the set

$$(3.24) \qquad \mathcal{Z} \left\{ \sigma_{ij}, \mu^c, U, Q_k, \Psi, \Psi^* J^c_k, J^S_k, S, \Phi_k \right\},$$

then we must look for general constitutive equations in the form

$$(3.25) \qquad\qquad \mathcal{Z} = \mathcal{Z}(\mathcal{C}),$$

where both $\mathcal{C}$ and $\mathcal{Z}$ are evaluated at the same point and time (we ignore hereditary and nonlocal effects).

To determine the explicit forms of (3.25), Liu's theorem [18] seems to be the most convenient tool to use for the analysis of the inequality (3.23). For the sake of simplicity the body forces and heat sources will be omitted in our discussion. μ^c will be defined in the sequel.

According to Liu's theorem, where all the balance and evolution equations are considered as mathematical constraints for the general validity of (3.23), we must introduce the so-called Lagrange–Liu's multipliers to account for equations (3.2), (3.3), (3.5)–(3.9), (3.16)–(3.20). The set of multipliers reads

$$(3.26) \qquad \Lambda = \left\{ \Lambda^c, \Lambda^v_r, \Lambda^u, \Lambda^E_i, \Lambda^E_4, \Lambda^B_i, \Lambda^B_4, \Lambda^Q_k, \Lambda^\psi, \Lambda^{\psi*}, \Lambda^{JC}_k, \Lambda^S_k \right\}.$$

Calling $\mathcal{F}^c, \mathcal{F}^v_r, \mathcal{F}^u, \mathcal{F}^E_i, \mathcal{F}^E_4, \mathcal{F}^B_i, \mathcal{F}^B_4, \mathcal{F}^Q_k, \mathcal{F}^\psi, \mathcal{F}^{\psi*}, \mathcal{F}^{JC}_k, \mathcal{F}^S_k$, the left-hand sides of equations (3.2), (3.3), (3.5)–(3.9), (3.16)–(3.20), respectively, according to the second requirement of Liu's theorem, we rewrite the inequality (3.23) in the form

$$(3.27) \qquad \varrho \frac{\partial S}{\partial t} + \varrho v_k S_{,k} + \Phi_{k,k} - \left\{ \Lambda^c \mathcal{F}^c + \Lambda^v_r \mathcal{F}^v_r + \Lambda^u \mathcal{F}^u + \Lambda^E_i \mathcal{F}^E_i + \Lambda^E_4 \mathcal{F}^E_4 \right.$$
$$\left. + \Lambda^B_i \mathcal{F}^B_i + \Lambda^B_4 \mathcal{F}^B_4 + \Lambda^Q_k \mathcal{F}^Q_k + \Lambda^\psi \mathcal{F}^\psi + \Lambda^{\psi*} \mathcal{F}^{\psi*} + \Lambda^{JC}_k \mathcal{F}^{JC}_k + \Lambda^S_k \mathcal{F}^S_k \right\} = 0.$$

We introduce now the scalar (free energy density) potential F and the vector thermodynamical potential K_i [10] as follows:

$$(3.28) \qquad\qquad F = U - TS,$$
$$(3.29) \qquad\qquad K_k = \varrho v_k F - T\Phi_k.$$

The considerations of processes based on the above theorem for which those potentials hold true, strongly suggest that

$$(3.30) \qquad\qquad \Lambda^u = \frac{1}{T}.$$

Thus the third requirement of Liu's theorem with the use of the relations

$$(3.31) \qquad\qquad \varepsilon_{ij} = \frac{1}{2}\left(u_{i,j} + u_{j,i} \right),$$

$$(3.32) \qquad\qquad v_{j,i} = \frac{\partial \varepsilon_{ij}}{\partial t} + w_{ij},$$

where u_i denotes the elastic displacement and w_{ij} is the antisymmetric part of the velocity gradient, leads us to the following groups of results:

- *the multipliers*

$$(3.33) \qquad \Lambda_r^v = 0, \qquad \Lambda_i^E = 0, \qquad \Lambda_4^E = 0, \qquad \Lambda_i^B = 0, \qquad \Lambda_4^B = 0,$$

$$(3.34) \qquad \begin{aligned} \Lambda^c &= -\frac{1}{T}\mu^c, \qquad \Lambda_i^Q = -\frac{1}{T}\Pi_i^Q, \qquad \Lambda_i^{JC} = -\frac{1}{T}\Pi_i^C, \\ \Lambda^\psi &= -\frac{1}{T}\Pi^\psi, \qquad \Lambda^{\psi*} = -\frac{1}{T}\Pi^{\psi*}, \qquad \Lambda_k^S = -\frac{1}{T}\Pi_k^S\,; \end{aligned}$$

- *the laws of state*

$$(3.35) \qquad \begin{aligned} \sigma_{ij} &= \varrho\frac{\partial F}{\partial\varepsilon_{ij}}, \qquad \frac{\partial F}{\partial\varphi} = 0, \qquad \frac{\partial F}{\partial\varphi_{,k}} = 0, \qquad j_k^S = -\varrho\frac{\partial F}{\partial A_k}, \\ S &= -\frac{\partial F}{\partial T}, \qquad \frac{\partial F}{\partial T_{,i}} = 0, \qquad \mu^c = \frac{\partial F}{\partial c}\,; \end{aligned}$$

- *the affinities*

$$(3.36) \qquad \begin{aligned} \Pi_i^Q &= \varrho\frac{\partial F}{\partial q_i}, \qquad \Pi_i^C = \varrho\frac{\partial F}{\partial j_i^c}, \qquad \Pi_i^S = \varrho\frac{\partial F}{\partial j_k^S}, \\ \Pi^\psi &= \varrho\frac{\partial F}{\partial\psi} - \left(\varrho\frac{\partial F}{\partial\psi_{,k}}\right)_{,k}, \qquad \Pi^{\psi*} = \varrho\frac{\partial F}{\partial\psi^*} - \left(\varrho\frac{\partial F}{\partial\psi_{,k}^*}\right)_{,k}\,; \end{aligned}$$

- *the laws of processes*

$$(3.37) \qquad \begin{aligned} \frac{\partial K_k}{\partial\varepsilon_{ij}} &= 0, \qquad \frac{\partial K_k}{\partial\varphi_{,i}} = 0, \qquad \frac{\partial K_k}{\partial A_{i,j}} = 0, \qquad \frac{\partial K_k}{\partial T_{,i}} = 0, \\ \frac{\partial K_k}{\partial q_i} &= -\delta_{ik} + \Pi_i^Q v_k, \qquad \frac{\partial K_k}{\partial\psi_{,i}} = 0, \qquad \frac{\partial K_k}{\partial\psi_{,i}^*} = 0, \\ \frac{\partial K_k}{\partial j_i^S} &= \Pi_i^S v_k, \qquad \frac{\partial K_k}{\partial j_i^c} = \mu^c\delta_{ik} + v_k\Pi_i^C\,; \end{aligned}$$

and

- *the residual inequality*

$$(3.38) \qquad \begin{aligned} -\frac{\partial K_k}{\partial\varphi}\varphi_{,k} + j_{k,k}^S\varphi + T\frac{\partial\Phi_k}{\partial A_i}A_{i,k} + T\frac{\partial\Phi_k}{\partial T}T_{,k} \\ + T\frac{\partial\Phi_k}{\partial c}c_{,k} - \frac{\partial K_k}{\partial\psi}\psi_{,k} - \frac{\partial K_k}{\partial\psi^*}\psi_{,k}^* + j_i^N\mathcal{E}_i \\ - \Pi_i^Q Q_i - \Pi_i^C J_i^C - \Pi_i^S J_i^S - \Pi^\psi\frac{\partial\psi}{\partial t} - \Pi^{\psi*}\frac{\partial\psi^*}{\partial t} \geq 0. \end{aligned}$$

The particular analysis of the above results shows that:
- the free energy density takes the form (cf. [6, 17])

$$(3.39) \qquad F = F^N + F^S,$$

$$(3.40) \qquad F^N = F^N\left(\varepsilon_{ij}, T, c, q_i, j_i^c, j_i^S\right),$$

$$(3.41) \qquad F^S = F^S\left(\varepsilon_{ij}, T, c, A_i, \psi, \psi^*, \psi_{,k}, \psi_{,k}^*\right),$$

- the entropy flux after integration of relations (3.37) with the aid of (3.29) and the detailed investigations of the inequality (3.27), is as follows (cf.[6, 17]):

$$(3.42) \qquad \Phi_k = \Phi_k^N + \Phi_k^S,$$

$$(3.43) \qquad \Phi_k^N = \frac{1}{T}\left(q_k - \mu^c j_k^c\right),$$

$$(3.44) \qquad \Phi_k^S = -\frac{1}{T}\left(j_k^S + \varrho\frac{\partial F}{\partial \psi_{,k}}\dot\psi + \varrho\frac{\partial F}{\partial \psi_{,k}^*}\dot\psi^*\right).$$

Remark that F^N and F^S as well as Φ_k^N and Φ_k^S are independent of each other.

We see that the dissipation (cf. (3.38)) due to the supercurrent comes from the following reasons:
- the changes in time and interactions of the Cooper pairs density with the fields from the set C (see (3.21),
- the relaxation properties of the supercurrent (cf. (3.20)),
- the quantum side of the superconductivity phenomenon.

To this end, the general extended thermodynamical model of superconducting, elastic and doped fullerenes has been completed. We see that the model extends the relations obtained in [3–9, 15–17] on the influence of impurities on conductivity properties and includes, consistently with the theory, the relaxation of the supercurrent.

If we, however, decide that the gauge can be chosen such that the scalar electrical potential vanishes (see (3.22)) [9], then we follow the experimental observations that the supercurrent exists reasonably long in time and we assume the local density of Cooper pairs to be constant (this approach is true in many practical situations where the local fluctuations in density of superelectrons in steady state are of such length and time scales that are too small to be of engineering interest [2]), the residual inequality (3.38) can be approximated by

$$(3.45) \qquad T\frac{\partial \Phi_k}{\partial A_i}A_{i,k} + T\frac{\partial \Phi_k}{\partial T}T_{,k} + T\frac{\partial \Phi_k}{\partial c}c_{,k} + j_i^N \mathcal{E}_i - \Pi_i^Q Q_i - \Pi_i^C J_i^C \geq 0.$$

That situation leads to the following relations (cf. [2, 6]):

$$(3.46) \qquad \varrho\frac{\partial F}{\partial \psi} - \left(\varrho\frac{\partial F}{\partial \psi_{,k}}\right)_{,k} = 0,$$

$$(3.47) \qquad \varrho\frac{\partial F}{\partial \psi^*} - \left(\varrho\frac{\partial F}{\partial \psi^*_{i_k}}\right)_{,k} = 0,$$

$$(3.48) \qquad j^S_{k,k} = 0,$$

$$(3.49) \qquad \frac{\partial K_k}{\partial \psi} = 0, \qquad \frac{\partial K_k}{\partial \psi^*} = 0$$

and

$$(3.50) \qquad \frac{\partial F}{\partial j^S_i} = 0.$$

The latter result indicates that when the relaxation of the supercurrent fluid is not taken into account, the classical nonequilibrium thermodynamical model is sufficient to describe a superconductor. However, the extended – like thermodynamical model is, in general, much more complete. It includes all the basic equations dealing with the physical interactions in superconducting fullerenes described in the paper, i.e. when the proper constitutive theory in particular situations is developed, we obtain

- from (3.3) – a generalized form of the equation of motion,
- from (3.5) – a generalized form of the heat conduction equation,
- from (3.2) and (3.19) – a generalized form of the mass diffusion equation,
- from (3.6) – (3.9) – a generalized form of the equation of electromagnetic field distribution,
- from (3.17) – a generalized form of the Ginzburg–Landau equation,
- from (3.20) – a generalized form of the first London equation,
- from (3.20) and (3.6) – a generalized form of the second London equation

(cf. [2]) that is consistent with the Meissner effect.

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