

## **Canonical versus Grand-Canonical Free Energies and Phase Diagrams of a Bipolaronic Superconductor Model**

**T. Gerisch,<sup>1</sup> R. Münzner,<sup>1</sup> and A. Rieckers<sup>1</sup>**

*Received March 5, 1998*

---

We continue the discussion of a bipolaronic superconductor (resp. an anisotropic antiferromagnet in quasispin formulation) as formulated in a previous work, based on a quantum-statistical, microscopic mean-field model. The grand-canonical thermodynamic limit is compared with the canonical thermodynamic limit in terms of a net of perturbations, becoming singular in the infinite lattice limit. A generalized thermostistical framework is elaborated which covers model potentials with infinite parts. The function of the limiting free energy density in selecting the (stable) phases with broken symmetry is graphically illustrated. The phase diagrams for the two types of ensembles are shown to differ in the region where both the gauge symmetry and the invariance under sublattice exchange are broken. In particular, the type of the phase transitions, the order of the critical points, and the shape of some phase boundaries are found to depend on the ensemble, which clarifies certain controversial topics for these models. The uniqueness of the limiting Gibbs states with free boundary conditions in all thermodynamic phase regions is proved, and their decomposition into pure phase states in terms of a symmetric measure is evaluated. The field operators of the condensed particles are determined in the representations over the limiting Gibbs states.

---

**KEY WORDS:** Canonical vs. grand-canonical ensemble; free energy; minimum principle; suppression of fluctuations by singular potentials; phase transitions of first and second kind; limiting Gibbs state; symmetry breakdown; approximately symmetric nets; lower semisymmetric nets; bipolaronic model for high- $T_c$  superconductivity.

---

<sup>1</sup>Institut für Theoretische Physik, Universität Tübingen, D-72076 Tübingen, Germany; e-mail: thomas.gerisch@uni-tuebingen.de, roland.muenzner@uni-tuebingen.de, alfred.rieckers@uni-tuebingen.de.

## 1. INTRODUCTION

In refs. 2 and 3 a Hamiltonian for a bipolaronic superconductor of the form

$$H = v \sum_{\langle i,j \rangle} \hat{n}_i \hat{n}_j - 2t \sum_{\langle i,j \rangle} (b_i^* b_j + b_i b_j^*) \quad (1.1)$$

has been introduced. Here  $b_i^*$  is the creation operator of a bipolaron at site  $i$  of a lattice in configuration space,  $\hat{n}_i$  the bipolaron number operator, and  $\sum_{\langle i,j \rangle}$  the sum over nearest neighbours. In ref. 4 (cf. also ref. 5) this Hamiltonian has been used for the discussion of high- $T_c$  superconductors. Transforming the algebraic relations for the operators  $b_i^*$ ,  $\hat{n}_i$ , into the quasi-spin formulation, one finds the correspondence of  $H$  to the Hamiltonian of an anisotropic antiferromagnet. In this correspondence the antiferromagnetic phase is called “charge ordered phase” in the superconductor interpretation, and the broken gauge symmetry in the latter is denoted as “spin flopped phase” in the antiferromagnetic interpretation. The possibility of having both types of symmetry breaking simultaneously (in each interpretation) led to a controversy in the literature, whether this happens in a mixed or in a pure phase.

We refer to the results in ref. 1, where a mean-field version of  $H$  has been investigated. This model is obtained by homogenizing the interaction, that is, the summation over nearest neighbours is replaced by a (lattice dependent) “long range summation.” This corresponds to the usual mean-field approximation, which has been often applied to the mentioned model classes. In the latter context also the question arose, whether one traverses a coexistence or a pure phase region in going from the superconducting to the charge ordered phases. The two possibilities affect the structure of critical points and critical lines. In fact, that the type of a phase transition changes under certain external conditions has already been discussed in the context of bi- and tetracritical points,<sup>(6-10)</sup> where more or less phenomenological explanations were given.

Here we discuss the two situations in terms of a microscopic theory for two different ensembles, founded on generalized nets of local Hamiltonians, which enable the incorporation of singular subsidiary conditions. Decisive for a clarification of the thermodynamic phase structure is the unambiguous introduction and use of the thermodynamic concepts based on global quantum statistical equilibrium states.

Our basic conceptual frame for the model discussion, concerning the operator algebraic introduction of the mean-field interaction and of the equilibrium states, is shortly described in Section 2. In Section 3 we summarize and supplement the results, which we gained in ref. 1 for the grand-

canonical ensemble. In particular the phase diagram is reproduced, which shows a coexistence region for different types of symmetry break down and macroscopic density fluctuations. It originates from the stable free energy density surface, which is here also depicted. (Note, that the logarithm of the partition function times the negative temperature is called “free energy” in quantum statistics. Its thermodynamic meaning depends, however, on the underlying ensemble.)

We then formulate in Section 4.1 a notion for the canonical ensemble, where the particle density fluctuations are suppressed in the thermodynamic limit by a net of density fixing perturbations. These kinds of potentials can be treated in the frame of “lower semisymmetric nets,” developed in ref. 11. Referring to results in ref. 11 we show that in this generalized frame the mathematical properties of the limiting free energy densities and the resulting structure for the thermodynamic equilibrium states, defined as the minimal free energy states, are analogous to those for approximately symmetric nets, employed in ref. 1. (Thus it is sufficient in the present paper to communicate this structure for the more general set up, only.) Especially, one finds that the quantum statistical equilibrium states constitute a stable face and Bauer simplex, denoted by  $\mathfrak{S}(\beta, \mu)$ , where  $\beta$  is the natural temperature and  $\mu$  the chemical potential. The  $w^*$ -closed extremal boundary of this simplex are exactly those homogeneous product states, which minimize the free energy. The latter are to be interpreted as pure thermodynamic phases, and every equilibrium state has a unique decomposition into these macroscopically pure, that is factorial, states. They form the most easily accessible part of the set of equilibrium states. As is shown in Section 4.2 they satisfy a selfconsistency condition, which involves an effective, state dependent Hamiltonian with, in general, broken symmetry, which is exact in the thermodynamic limit.

Section 4.3 is devoted to a detailed analysis, how the minimal free energy values select the stable pure phase states from the set of all solutions of the selfconsistency equation. In the canonical case, the additional subsidiary condition of a prescribed, sharp particle density must be taken into account. The interplay of the selfconsistency condition with the minimal free energy requirement and with the fixing of a sharp particle density is illustrated graphically in terms of free energy surfaces. All aspects are derived from the model Hamiltonians and determine the sets of equilibrium states  $\mathfrak{S}(\beta, \mu)$  for all values of the temperature and the chemical potential in a unique manner.

The resulting phase diagram is described in Section 4.4. In principle, a phase diagram in the thermostistical framework—in contrast to the phenomenological level—consists of the family of sets  $\mathfrak{S}(\beta, \mu)$  resp.  $\mathfrak{S}(\beta, n)$  of quantum statistical equilibrium states indexed by the (natural) temperature

and resp. chemical potential or particle density. A thermodynamic phase region is then defined as such a region of the parameters  $(\beta, n)$ , where the sets of equilibrium states  $\mathfrak{S}(\beta, n)$  are not “qualitatively” different. One indicates graphically the boundaries of the thermodynamic phase regions, as we do in Figs. 1 and 7. For our model that means, that in each thermodynamic phase region the pure phase states have the same broken symmetry group, giving a concise notion of “qualitative likeness.” For each point of the phase diagram there are, however, also symmetric equilibrium states, especially the limiting states under free (that is symmetric) boundary conditions, which are a statistical mixture of the pure phases over a symmetric measure.

Such a statistical mixture over pure phases of the same type must be discriminated from a mixture of (not necessarily pure) qualitatively different phases. Only the latter signify “phase coexistence” in the usual thermodynamic meaning.

In the canonical phase diagrams of our model, cf. especially Fig. 7, there occur product states with both a broken gauge and lattice exchange symmetry, as well as their statistical mixtures. They constitute the so-called M-phase region, which replaces the coexistence region of the grand-canonical phase diagram.

In Section 5 we collect the arguments, which lead to unique limiting Gibbs states in each part of the phase diagram. Due to the free boundary conditions these kinds of limiting equilibrium states possess all internal symmetries of the original local model Hamiltonians. (Symmetry breaking boundary conditions would lead to other types of limiting Gibbs states.) The here investigated limiting states are in fact the only symmetric equilibrium states in each simplex  $\mathfrak{S}(\beta, n)$  (which is a singleton in the normal phase region). In the present case, both purely thermodynamic concepts of global equilibrium states—minimizer of the free energy and limiting Gibbs states—imply each other and there arises a consistent thermodynamic formalism.<sup>(12,13)</sup> We give a general formula for the central decomposition of the limiting Gibbs states, which in turn leads to a general formula for the condensed fields. We discuss the difference between coexistence and M-phase states in terms of these decomposition formulas and draw some physical conclusions.

## 2. THE CONCEPTUAL FRAME OF THE MODEL DISCUSSION

Working in the frame of operator algebraic quantum statistical mechanics, cf. refs. 14–16 and references therein, we first have to specify the  $C^*$ -algebra  $\mathfrak{A}$  of observables for our electronic system. As we want to treat the model on a bipartite lattice  $\mathcal{X}$  in configuration space, we start with a

site-algebra of the form  $\mathfrak{B} = \tilde{\mathfrak{B}} \otimes \tilde{\mathfrak{B}}$ , where  $\tilde{\mathfrak{B}} \cong \mathbb{M}_2(\mathbb{C})$ . Later we will see that  $\tilde{\mathfrak{B}}$  describes the observables for a pair of fermions, while  $\mathfrak{B}$  describes two such pairs in different sub-lattices. As usual, we then form for each finite, local region  $A \in \mathcal{Q} := \{A' \subset \mathcal{X} \mid |A'| < \infty\}$ , the double-bar denoting the cardinality of a set, the algebra  $\mathfrak{A}_A := \otimes_{i \in A} \mathfrak{B}_i$ , where  $\mathfrak{B}_i$  is an isomorphic copy of  $\mathfrak{B}$  at site  $i$ . The algebra  $\mathfrak{A}$  of the whole lattice is the composition of all local observables, mathematically obtained by the  $C^*$ -inductive limit over the net  $\mathfrak{A}_A$ ,  $A \in \mathcal{Q}$ , with the canonical embedding of  $\mathfrak{A}_A$  in  $\mathfrak{A}_{A'}$  for  $A \subset A'$ .<sup>(17)</sup> This is written as the tensor product

$$\mathfrak{A} := \otimes_{i \in \mathcal{X}} \mathfrak{B}_i$$

where the local algebras  $\mathfrak{A}_A$  can be considered as subalgebras of  $\mathfrak{A}$ , such that  $\mathfrak{A} = \overline{\bigcup_{A \in \mathcal{Q}} \mathfrak{A}_A}^{\|\cdot\|}$ .

An infinite-lattice model is quite generally specified by the net of all local Hamiltonians  $H_A \in \mathfrak{A}_A \subset \mathfrak{A}$ , indexed with the finite lattice regions  $A \in \mathcal{Q}$ . The microscopic mean-field version on a bi-partite lattice of a Hubbard-like Hamiltonian with originally a local pair interaction, let be given by the special net of local Hamiltonians  $(H_A)_{A \in \mathcal{Q}}$ :<sup>(1)</sup>

$$H_A = \frac{1}{|A|} \left( v \sum_{i_1, i_2 \in A} \hat{n}_{i_1}^1 \hat{n}_{i_2}^2 - 2t \left( \sum_{i_1, i_2 \in A} b_{i_1}^{1*} b_{i_2}^2 + b_{i_1}^1 b_{i_2}^{2*} \right) \right) \in \mathfrak{A}_A \quad (2.1)$$

with  $x^1 = x \otimes \mathbb{1}$ ,  $x^2 = \mathbb{1} \otimes x \in \mathfrak{B}$  for  $x \in \tilde{\mathfrak{B}}$ .  $b_i^{r(*)}$ ,  $r = 1, 2$  is the annihilation (creation) operator of a local pair at the lattice site  $i$  in sub-lattice  $r$ , and  $\hat{n}_i^r := b_i^{r*} b_i^r$  is the occupation number operator. The particle algebra is characterized by the following commutation relations, which characterize so-called hard core Bosons:

$$\begin{aligned} [b_i^{r*}, b_j^r] &= b_i^{r*} b_j^r - b_j^r b_i^{r*} = \delta_{ij} (2\hat{n}_i^r - \mathbb{1}), \\ \{b_i^{r*}, b_i^r\} &= b_i^{r*} b_i^r + b_i^r b_i^{r*} = \mathbb{1}, \quad (b_i^r)^2 = 0 \end{aligned}$$

for  $r = 1, 2$  and  $i \in \mathcal{X}$ . All commutators between operators in different sub-lattices vanish. We assume  $v, t > 0$  and thus can set  $t \equiv 1$ . As shown in ref. 1,  $H_A$  may be obtained as the symmetrization of a Hamiltonian with nearest neighbour interaction,<sup>(2, 3)</sup> where the symmetrization respects the given sub-lattice structure. As a consequence of this symmetrization,  $H_A$  is invariant under the action of the permutation group  $\mathcal{P}(A)$  of  $A$ :

$$\Theta_\sigma(H_A) = H_A, \quad \text{for all } \sigma \in \mathcal{P}(A) \quad \text{and} \quad A \in \mathcal{Q}$$

where  $\Theta_\sigma: \mathfrak{A} \rightarrow \mathfrak{A}$  is defined on elementary tensors by  $\Theta_\sigma(\bigotimes_{i \in A'} x_i) := \bigotimes_{i \in A'} x_{\sigma(i)}$  for all  $A' \in \mathfrak{Q}$ , where we set  $\sigma(i) = i$  for  $i$  outside from  $A$ .

Besides the permutation symmetry (spatial homogeneity) of the Hamiltonian, there are additional symmetries, the so-called internal symmetries, which can be broken in temperature states. Here are of interest the gauge transformations and the exchange of the two sub-lattices.<sup>(1)</sup>

In order to determine the global thermodynamic equilibrium states (that are those of the infinite quantum lattice system), one has still to define the boundary and subsidiary conditions for the local equilibrium states and to specify the limiting behaviour of the parameters involved. This formalization of the averaged influence of the surroundings as well as of the interest of the macroscopic observer is a necessary prerequisite to obtain a well-defined notion of global thermodynamic equilibrium.

Assume the equilibrium states of each finite system at inverse temperature  $\beta = (1/k_B T) > 0$  be given in terms of the local Hamiltonian  $H_A$ ,  $A \in \mathfrak{Q}$ , which may be that of Eq. (2.1) or a modification thereof. The corresponding so-called local Gibbs states  $\omega^{\beta, H_A} \in \mathfrak{S}(\mathfrak{A}_A)$  have the form

$$\omega^{\beta, H_A}: \mathfrak{A}_A \rightarrow \mathbb{C}, A \mapsto \langle \omega^{\beta, H_A}; A \rangle := \frac{\text{tr}(\exp\{-\beta H_A\} A)}{\text{tr}(\exp\{-\beta H_A\})}$$

Without changing the notation we consider  $\omega^{\beta, H_A}$  as a state on  $\mathfrak{A}$  by continuation in terms of the trace state.

Given the net of local Gibbs states the global equilibrium states may be introduced purely thermodynamically, that is without using the dynamics and the KMS-condition in two ways, at least. The most direct one is to determine the limiting Gibbs states. A limiting Gibbs state  $\omega$  is by definition a  $w^*$ -accumulation point of the net of local Gibbs states. Since the state space  $\mathfrak{S}(\mathfrak{A})$  of  $\mathfrak{A}$  is compact in the weak\*-topology, at least one accumulation point exists.<sup>2</sup> It is evident, that a limiting state retains a symmetry, which is shared by all members of the converging sub-net. If the set of  $w^*$ -accumulation points is a singleton, the whole net converges, and we call the limit *the limiting Gibbs state*.

We study here two forms of limiting Gibbs states. In Section 3 we replace the  $H_A$  of Eq. (2.1) by the reduced local Hamiltonians, where the local chemical potentials are determined by a given, fixed mean particle density, and deal in this way with the grand canonical limiting states. In the subsequent part of our work, we supplement the local Hamiltonians  $H_A$  of Eq. (2.1) by perturbations, which fix the exact value of the particle density in the limit. This leads to the canonical limiting Gibbs states.

<sup>2</sup>  $w^*$ -convergence is defined by the convergence of all expectation values.

Having evaluated the limiting Gibbs states, a set of further global equilibrium states is obtained by their central decompositions. (For this basic notation cf., e.g., ref. 14.) Since the supports of the central measures consist of factor states with sharp classical properties, we interpret this as a decomposition into pure phase states.

The second way to find global equilibrium states is to calculate the minimizer of the limiting free energy density. This non-equilibrium free energy density is determined in first line again by the net of local Hamiltonians. But one has also to prescribe a selected set of states, as the domain of definition for this thermodynamic functional. Observe that the selection of the domain is again a version of incorporating subsidiary conditions.

For a consistent thermodynamic formalism, both ways to treat global equilibrium states should be compatible in the sense, that the limiting Gibbs states are special minimizers in the domain of the free energy density. Then their central supports are minimizers, too, under quite general conditions.

We investigate here the global equilibrium states under both aspects, starting computationally from the pure phase minimizers of the free energy density.

### 3. THE GRAND CANONICAL PHASES

We now discuss the model at a given mean particle density  $n \in ]0, 2[$ . To fix it in the local Gibbs state, we incorporate the local chemical potential  $\mu_A$  via

$$H_A(\mu_A) = H_A - \mu_A N_A, \quad N_A := \sum_{i \in A} (\hat{n}_i^1 + \hat{n}_i^2) \quad (3.1)$$

It holds  $[H_A, N_A] = 0$  and for each  $n \in ]0, 2[$  there is a unique  $\mu = \mu_A(n) \in \mathbb{R}$ , such that

$$\frac{1}{|A|} \langle \omega^{\beta, H_A(\mu)}; N_A \rangle = n$$

For each local region  $A$ , the unique  $\mu \in \mathbb{R}$  is denoted by  $\mu_A$ . For the ensemble with fixed mean particle density, we are interested in the limiting Gibbs state  $\omega^{\beta, n} := w^* \text{-}\lim_{A \in \mathfrak{A}} \omega^{\beta, H_A(\mu_A)}$  (the limit exists, see below!). Due to construction, the state  $\omega^{\beta, n}$  of the infinite system also has mean particle density  $n$ , given by

$$\lim_{A \in \mathfrak{A}} \frac{1}{|A|} \langle \omega^{\beta, n}; N_A \rangle = n$$

Since  $H_A(\mu_A)$  is invariant under permutations  $\sigma \in \mathcal{P}(A)$ , each limiting Gibbs state  $\omega^{\beta, n}$  has to be homogeneous, i.e., it is an element of  $\mathfrak{S}^P(\mathfrak{A}) = \{\omega \in \mathfrak{S}(\mathfrak{A}) \mid \omega \circ \theta_\sigma = \omega \text{ for all } \sigma \in \mathcal{P} = \bigcup_{A \in \mathfrak{Q}} \mathcal{P}(A)\}$ . The set of homogeneous states  $\mathfrak{S}^P(\mathfrak{A})$  has a well known structure: It is a Bauer-simplex with extremal boundary  $\partial_e \mathfrak{S}^P(\mathfrak{A}) = \{\otimes \varrho \mid \varrho \in \mathfrak{S}(\mathfrak{B})\}$ ,<sup>(18)</sup> where  $\otimes \varrho$  denotes the product state with  $\langle \otimes \varrho; \otimes_{i \in A} x_i \rangle = \prod_{i \in A} \text{tr}(\varrho x_i)$  for all  $A \in \mathfrak{Q}$  and  $\otimes_{i \in A} x_i \in \mathfrak{A}$ . The decomposition of  $\omega \in \mathfrak{S}^P(\mathfrak{A})$  into extremal homogeneous states corresponds to the central decomposition<sup>(14)</sup> of  $\omega$  into classical pure phases (factorial states):

$$\omega = \int_{\mathfrak{S}(\mathfrak{B})} \otimes \varrho \, d\mu_\omega(\varrho) \quad (3.2)$$

While the product states  $\otimes \varrho$  are elements of  $\partial_e \mathfrak{S}^P(\mathfrak{A})$ , they are not necessarily invariant under the internal symmetries. Since a limiting Gibbs state  $\omega^{\beta, n}$  has the full symmetry, the central measure  $\mu_{\beta, n}$  of  $\omega^{\beta, n}$  (we identify it with  $\mu_{\omega^{\beta, n}}$  of 3.2, which uses the parametrization  $\mathfrak{S}(\mathfrak{B})$  of  $\partial_e \mathfrak{S}^P(\mathfrak{A})$ ) has to be non-trivial. In the simplest case it corresponds to the Haar measure of the broken group of internal symmetries. Then the support of the central measure  $\mu_{\beta, n}$  reflects the kind of broken internal symmetry.<sup>(19, 20)</sup>

In ref. 1 the limiting Gibbs state  $\omega^{\beta, n}$  at fixed particle density is determined in the following way: For each  $n \in ]0, 2[$  there is a  $\mu_0$ , such that  $\lim_{A \in \mathfrak{Q}} \mu_A(n) = \mu_0$ . The limiting Gibbs state  $\omega^{\beta, n}$  as well as the pure phase states  $\otimes \varrho \in \partial_e \mathfrak{S}^P(\mathfrak{A})$  in the support of  $\mu_{\beta, n}$  minimize the free energy density  $f(\beta, \mu_0, \omega)$ ,  $\omega \in \mathfrak{S}^P(\mathfrak{A})$ , according to the general theory of mean-field systems defined by *approximately symmetric nets* of local, specific Hamiltonians. Recall that the free energy density of  $\omega \in \mathfrak{S}^P(\mathfrak{A})$  with local density matrices  $\varrho_A(\omega)$  for given  $(\beta, \mu_0)$  is defined by:

$$f(\beta, \mu_0, \omega) := \lim_{A \in \mathfrak{Q}} \frac{1}{|A|} \left[ \text{tr}_A \left\{ \varrho_A(\omega) H_A(\mu_0) + \frac{1}{\beta} \varrho_A(\omega) \ln \varrho_A(\omega) \right\} \right]$$

In particular, we have for the specific free energy in dependence on the pure phase product states

$$\begin{aligned} f(\beta, \mu_0, \otimes \varrho) &= v \langle \varrho; \hat{n}^1 \rangle \langle \varrho; \hat{n}^2 \rangle - 2(\langle \varrho; b^{1*} \rangle \langle \varrho; b^2 \rangle + \langle \varrho; b^1 \rangle \langle \varrho; b^{2*} \rangle) \\ &\quad - \mu_0 \langle \varrho; \hat{n}^1 + \hat{n}^2 \rangle + \frac{1}{\beta} \langle \varrho; \ln \varrho \rangle \end{aligned} \quad (3.3)$$



Each minimizer  $\otimes \varrho$  of  $f(\beta, \mu_0, \cdot)$  has to satisfy  $df(\beta, \mu_0, \cdot) = 0$  and is thus obtained by a solution of the selfconsistency condition:

$$\varrho = \frac{\exp(-\beta(h_{\text{eff}}(\varrho) - \mu_0 \hat{n}))}{\text{tr}\{\exp(-\beta(h_{\text{eff}}(\varrho) - \mu_0 \hat{n}))\}} \tag{3.4}$$

with  $\hat{n} = \hat{n}_1 + \hat{n}_2$ , and the effective one-particle Hamiltonian

$$h_{\text{eff}}(\varrho) = v(\text{tr}(\varrho \hat{n}^2) \hat{n}^1 + \text{tr}(\varrho \hat{n}^1) \hat{n}^2) - 2(\text{tr}(\varrho b^2) b^{1*} + \text{tr}(\varrho b^{2*}) b^1) - 2(\text{tr}(\varrho b^1) b^{2*} + \text{tr}(\varrho b^{1*}) b^2) \tag{3.5}$$

The minimal free energy  $f(\beta, \mu_0)$  is the grand canonical potential of phenomenological thermodynamics, that is the two-fold Legendre transformation  $u^{[1,2]}(\beta, \mu_0)$  of the internal energy density  $u = u(s, n)$ . In its natural variables  $(T, \mu_0)$  the potential  $f(T, \mu_0)$  is a concave function. From the convexity of  $n \rightarrow u^{[1]}(T, n)$  we derive the thermodynamic stability condition

$$\left(\frac{\partial \mu}{\partial n}\right)_T \geq 0 \tag{3.6}$$

As we are interested in the case which exhibits a complex structure of equilibrium phases, we assume in the following that  $v > 4$  and  $T < T_c$ , where  $T_c$  is a solution of  $k_B T = (\sqrt{1 - 4k_B T/v}) / (\text{artanh}(\sqrt{1 - 4k_B T/v}))$ . We find (comp. Fig. 1, resp. Fig. 2 and ref. 1): There are three particle densities  $n_1 < n_2 < n_3 < 1$ , such that for

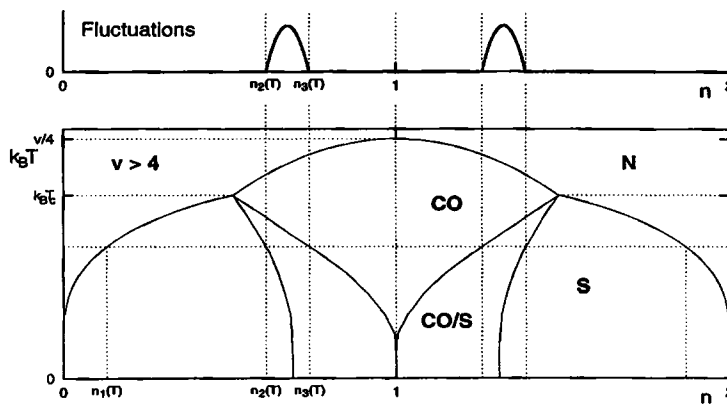


Fig. 1.  $(n, T)$ -phase diagram and fluctuations of the particle density  $n$  for the ensemble with fixed  $n \in ]0, 2[$ .

$n \leq n_1$  ( $n > 2 - n_1$ ):

$$\omega^{\beta, n} = \omega_N = \otimes \varrho_N, \quad \text{with } \varrho_N = \exp(-\xi - \beta h_{\text{eff}})$$

$$\text{and } h_{\text{eff}} = \left( v \frac{n}{2} - \mu \right) (\hat{n}^1 + \hat{n}^2)$$

$n_1 < n \leq n_2$  ( $2 - n_1 > n \geq 2 - n_2$ ):

$$\omega^{\beta, n} = \omega_S = \int_0^{2\pi} \otimes \varrho_{\vartheta} \frac{d\vartheta}{2\pi} \quad \text{with } \varrho_{\vartheta} = \exp(-\xi - \beta h_{\text{eff}}^{\vartheta}) \quad \text{and}$$

$$h_{\text{eff}}^{\vartheta} = \left( v \frac{n}{2} - \mu \right) \hat{n}^1 - \Delta (e^{-i\vartheta} b^{1*} + e^{i\vartheta} b^1) \\ + \left( v \frac{n}{2} - \mu \right) \hat{n}^2 - \Delta (e^{-i\vartheta} b^{2*} + e^{i\vartheta} b^2) \quad \text{for } \vartheta \in [0, 2\pi[$$

$n_2 < n < n_3$  ( $2 - n_2 > n > 2 - n_3$ ):  $\omega^{\beta, n} = \lambda \omega_S + (1 - \lambda) \omega_{\text{CO}}$ ,  $\lambda \in ]0, 1[$

$n_3 \leq n \leq 1$  ( $2 - n_3 \geq n \geq 1$ ):

$$\omega^{\beta, n} = \omega_{\text{CO}} = \frac{1}{2} \otimes \varrho_{12} + \frac{1}{2} \otimes \varrho_{21} \quad \text{with } \varrho_{ik} = \exp(-\xi - \beta h_{\text{eff}}^{ik})$$

$$\text{and } h_{\text{eff}}^{ik} = (vn^i - \mu) \hat{n}^1 + (vn^k - \mu) \hat{n}^2 \quad \text{for } i \neq k = 1, 2 \quad (3.7)$$

$\omega_N = \otimes \varrho_N$  is the normal phase with no broken symmetry,  $\omega_{\text{CO}}$  is a charge ordered state with broken invariance of the sub-lattice exchange, and  $\omega_S$  is a superconducting state with broken gauge symmetry.

All states with  $n_2 \leq n \leq n_3$  ( $2 - n_2 \geq n \geq 2 - n_3$  resp.) exist only as mixed-type phase states with the same chemical potential  $\mu_0$ . Each  $\lambda \in [0, 1]$  fixes in the state  $\omega^{\beta, n} = \lambda \omega_S + (1 - \lambda) \omega_{\text{CO}}$  the ratio of the superconducting and charge ordered phase type. The components of this kind of phase mixing in the coexistence region of a first order phase transition at  $\mu_0$  are in general also mixed phases. The value of  $\lambda$  is uniquely determined by  $n = \lambda n_2 + (1 - \lambda) n_3$ , because we have  $\lim_{A \in \mathfrak{L}} (1/|A|) \langle \omega_S; N_A \rangle = n_S \equiv n_2 < n_3 \equiv n_{\text{CO}} = \lim_{A \in \mathfrak{L}} (1/|A|) \langle \omega_{\text{CO}}; N_A \rangle$ .

For  $n_2 < n < n_3$  we find non-vanishing fluctuations of the particle density in the state  $\omega^{\beta, n}$ , given by

$$\lim_{A \in \mathfrak{L}} \frac{1}{|A|^2} \langle \omega^{\beta, n}; N_A^2 \rangle - \lim_{A \in \mathfrak{L}} \left[ \frac{1}{|A|} \langle \omega^{\beta, n}; N_A \rangle \right]^2 = (n - n_2)(n_3 - n) > 0$$

The minimizing free energy density of the grand-canonical ensemble, which corresponds thermodynamically to the grand-canonical potential, is

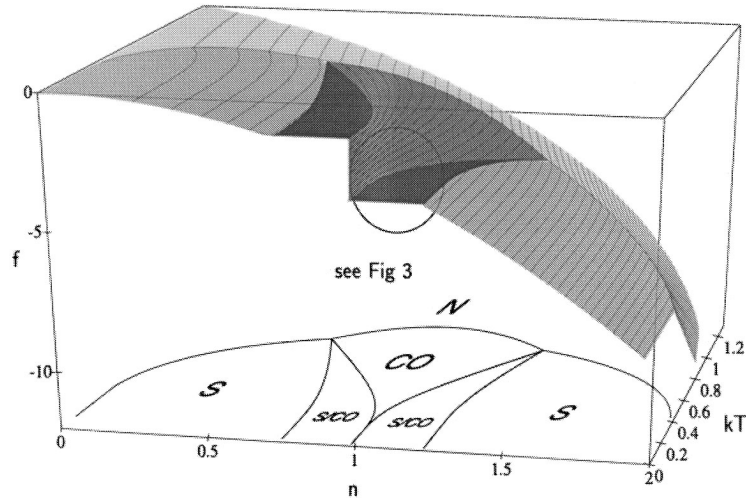


Fig. 2. Grand-canonical potential as function of the particle density and the temperature: S-phase, CO-phase and coexistence region.

drawn in Fig. 2. As the free energy density is considered as a function of the particle density, which can be done due to the relation  $\mu(n)$ , and not as a function of its “natural” variable  $\mu$ , not all points in the  $(kT, n)$ -plane can be identified with factor states  $\otimes \varrho$  in  $\partial_e \mathfrak{S}(kT, n)$ . For the coexistence region of the first order phase transition—represented by the two flat parts of the free energy density—the corresponding states are given by  $\lambda \otimes \varrho_S + (1 - \lambda) \otimes \varrho_{CO}$ .

The free energy density becomes discontinuous for  $n = 1$  and  $T \rightarrow 0$ , according to the fact, that the function  $\mu(n)$  is not bijective for  $n = 1$  and  $T = 0$ . Therefore we find different free energy densities over the two coexistence regions with  $n < 1$  and  $n > 1$ , respectively. From general reasoning<sup>(13)</sup> one knows that  $(T, n) \rightarrow f(T, n)$  is upper semi-continuous, which implies the upper value for  $f(T = 0, n = 1)$ .

Furthermore we observe the concavity of the grand-canonical potential in the chosen variables. For the distinction of the phase transitions by the differentiability of the free energy density we refer to Fig. 4.

Finally, let us recall from ref. 1 that a limiting Gibbs state  $\omega^{\beta, n}$  is determined here uniquely by the minimum condition for the free energy density (not all solutions of Eq. (3.4) minimize (3.3)), the internal symmetries, and the given particle density  $n$ . Thus we have for each given temperature and particle density a unique limiting Gibbs state.

As is illustrated in the upper part of Fig. 1, there are particle density fluctuations only in the coexistence regions. In the charge ordered and

superconducting regions the set  $\mathfrak{S}(\beta, \mu)$  has mixed phase states but, all of them with a sharp particle density. In the coexistence region one obtains also a unique limiting Gibbs state, which is, however, dependent on the properties of the net  $\mu_A(n)$  for itself, and not only on its limiting value  $\mu_0$ .

In the following Section, we compare this phase scenario with the one, where the thermodynamic limit is evaluated under the subsidiary conditions “fixed mean particle density” and “strictly suppressed fluctuations.”

#### 4. CANONICAL PHASE DIAGRAMS

##### 4.1. The Canonical Ensemble in Terms of Lower Semisymmetric Nets

We consider in this Section the thermodynamic with a fluctuation free particle density  $n \in ]0, 2[$  (canonical ensemble). To illustrate the problem we start with the local equilibrium states given by

$$\omega_{Q_A}^{\beta H_A} := \frac{\langle \omega^{\beta H_A}; Q_A \cdot Q_A \rangle}{\langle \omega^{\beta H_A}; Q_A \rangle}$$

Here  $Q_A$  denotes the projection onto the eigenspace of  $N_A$  with particle number  $[n|A|]$  ( $[x]$  is the smallest integer greater than  $x \in \mathbb{R}_+$ ). We can express this state in a preliminary fashion as the equilibrium state, where the Hamiltonian  $H_A$  is perturbed by  $\infty Q_A^\perp$ ,  $Q_A^\perp := \mathbb{1} - Q_A$ . With the convention  $0 \cdot \infty = 0$ ,  $\infty Q_A^\perp$  is interpretable as a  $w^*$ -lower semicontinuous functional on  $\mathfrak{S}(\mathfrak{A}_A)$ :

$$\mathfrak{S}(\mathfrak{A}_A) \ni \omega \rightarrow \langle \omega; \infty Q_A^\perp \rangle := \infty \langle \omega; Q_A^\perp \rangle \quad (4.1)$$

Such functionals are generalizations of lower bounded selfadjoint operators in  $\mathfrak{A}_A$ . Moreover, they can be considered as Hamiltonians of an extended model class, which has been theoretically mastered rather recently.<sup>(11, 21)</sup> Especially, a well-defined perturbation theory has been developed in terms of a variational principle for the relative free energy density.<sup>(21)</sup> Equation (4.1) is an example of an *extended valued, lower bounded operator affiliated with  $\mathfrak{A}_A$* . We are going to demonstrate, that the infinite system with non-fluctuating particle density is characterized in equilibrium by the  $w^*$ -accumulation points of a variant of the net  $\mathfrak{Q} \ni A \rightarrow \omega_{Q_A}^{\beta H_A}$ .

To avoid some technical problems, we use a “smoothed” version of the projection  $Q_A$ , starting from the (extended valued) identity

$$\infty Q_A^\perp = \infty |A| \left( \frac{N_A}{|A|} - \frac{[n|A|]}{|A|} \right)^2$$

and replacing the r.h.s. by the expression  $P_A := g_A |A| (N_A/|A| - n)^2$ , with the assumption that  $g_A$  is large but finite. While in the definition of  $Q_A$  the use of  $[n|A|]$  is essential (otherwise  $Q_A \equiv 0$ ), we can replace  $[n|A|]$  by  $n|A|$  in the selfadjoint operator  $P_A$ . Finally, we have to specify the asymptotic behaviour of  $g_A$ : Choose a net  $A \rightarrow g_A$  such that

$$g_A \rightarrow \infty, \quad \text{for increasing } A \quad \text{and} \quad \lim_{A \in \Omega} \frac{g_A}{|A|} = 0$$

Thus the whole perturbation

$$P_A := g_A |A| \left( \frac{N_A}{|A|} - n \right)^2 \tag{4.2}$$

scales super-extensively in dependence on the size of the local regions. The physical meaning of  $P_A$  is obvious: inserted into the exponent of the local distributions it has the tendency to suppress fluctuations of the particle number density around the expectation value  $n$ , while going into the thermodynamic limit in an arbitrary manner.<sup>3</sup> In this sense it is a smoothed out version of  $\infty Q_A^\perp$ , and  $\omega^{\beta H_A + P_A}$  is an approximation of  $\omega^{\beta H_A}$ .

Using the properties of extended valued, lower bounded operators, a variational principle for the  $w^*$ -accumulation points of the net  $(\omega^{\beta H_A + P_A})_{A \in \Omega}$  has been derived in ref. 11. It generalizes the results of refs. 22 and 23 and constitutes a kind of noncommutative large deviation principle.<sup>(24)</sup> With the asymptotic behaviour of  $A \rightarrow g_A$  as prescribed above, the conditions for a *lower semisymmetric* net [ref. 11, Definition 10]<sup>4</sup> are satisfied. We find, that the density of the internal energy, given by

$$u(\omega) := \lim_{A \in \Omega} \frac{1}{|A|} \langle \omega; H_A + P_A \rangle$$

<sup>3</sup>The choice of  $P_A$  is rather arbitrary. Other examples can be constructed with the help of a positive function of the particle density operator with an absolute minimum at the given  $n \in ]0, 2[$ .

<sup>4</sup>In ref. 11 everything is formulated for sequences. If we use sequences  $(A_n)_{n \in \mathbb{N}}$  with  $A_n \subset A_{n+1}$  for all  $n \in \mathbb{N}$  that satisfy the following condition; for each  $A \in \Omega$ , there exists a  $n \in \mathbb{N}$ , such that  $A \subset A_n$ , and the limits are independent of the chosen sequence, then the net limit exists [ref. 25, Appendix]. For our model, this is always the case. In this sense we replace the results and definitions for sequences by those for nets.

exists for all  $\omega \in \mathfrak{S}^P(\mathfrak{A})$ , but only in the sense that  $\omega \rightarrow u(\omega)$  is an extended-valued,  $w^*$ -lower semicontinuous function. Together with the entropy density

$$\mathfrak{S}^P(\mathfrak{A}) \ni \omega \rightarrow s(\omega) := - \lim_{A \in \mathfrak{A}} \frac{1}{|A|} \text{tr}(\varrho_A(\omega) \ln \varrho_A(\omega))$$

(where  $\varrho_A(\omega)$  is the density matrix which represents  $\omega|_{\mathfrak{A}_A}$ ), we find that the free energy density exists in a generalized, but well-defined sense, and constitutes again the basis for a concise theory of thermo-statistical equilibrium states.

**Theorem 4.1.** Let the model be defined by the lower semisymmetric net  $(1/|A|)(H_A + P_A)$ , as introduced above, and let the thermodynamic limit be performed along the directed set  $\mathfrak{A}$ .

(i) The limiting free energy density  $\tilde{f}(\beta, n, \omega)$  exists as an extended-valued,  $w^*$ -lower semicontinuous, affine function of  $\omega$  and is given by  $\mathfrak{S}^P(\mathfrak{A}) \ni \omega \rightarrow \tilde{f}(\beta, n, \omega) := u(\omega) - (1/\beta) s(\omega)$ , where the right hand side is described in the preceding paragraph.

(ii) The set of equilibrium states  $\mathfrak{S}(\beta, n)$ , defined as the minimizers of  $\tilde{f}(\beta, n, \omega)$ , is a  $w^*$ -compact Bauer-simplex and a stable face of  $\mathfrak{S}(\mathfrak{A})$  (where *stability* is meant in the sense of ref. 14: Each barycentric, orthogonal decomposition of a state in  $\mathfrak{S}(\beta, n)$  is supported in  $\mathfrak{S}(\beta, n)$ ).

(iii) Any  $w^*$ -accumulation point  $\tilde{\omega}^{\beta, n}$  of the net  $(\omega^{\beta H_A + P_A})_{A \in \mathfrak{A}}$  minimizes the free energy density  $\mathfrak{S}^P(\mathfrak{A}) \ni \omega \rightarrow \tilde{f}(\beta, n, \omega)$ .

(iv) The unique extremal decomposition in  $\mathfrak{S}(\beta, n)$  (which defines physically the decomposition into pure phases) coincides with the central decomposition and with the unique decomposition into product states  $\otimes_{\varrho \in \partial_e(\mathfrak{S}^P(\mathfrak{A}))}$ . Thus the minimum of  $\mathfrak{S}^P(\mathfrak{A}) \ni \omega \rightarrow \tilde{f}(\beta, n, \omega)$  attained in a limiting Gibbs state  $\tilde{\omega}^{\beta, n}$  is attained also in the set of product states  $\otimes_{\varrho \in \partial_e \mathfrak{S}^P(\mathfrak{A})}$ :

$$\begin{aligned} \tilde{f}(\beta, n, \tilde{\omega}^{\beta, n}) &= \inf \{ \tilde{f}(\beta, n, \omega) \mid \omega \in \mathfrak{S}^P(\mathfrak{A}) \} \\ &= \inf \{ \tilde{f}(\beta, n, \omega) \mid \omega \in \partial_e \mathfrak{S}^P(\mathfrak{A}) \} \\ &= \inf \{ \tilde{f}(\beta, n, \otimes_{\varrho} \varrho) \mid \varrho \in \mathfrak{S}(\mathfrak{B}) \} =: \tilde{f}(\beta, n) \end{aligned} \quad (4.3)$$

(v) The minimal free energy  $\tilde{f}$  has the natural variables  $(T, n)$  and has the meaning of a free energy in phenomenological thermodynamics, that is the first Legendre transform of  $u(s, n)$ . It is concave in  $T$  and convex in  $n$ .

*Proof.* Since our net of local Hamiltonians  $H_A$  with perturbations  $P_A$  fulfils the assumptions for a lower semisymmetric net, we can apply ref. 11 to our situation to get (i). We then observe that the Bauer maximum principle in the form of ref. 14 (read as a minimum principle for a concave, lower semicontinuous function on a compact, convex set) implies the set of minimal states  $\mathfrak{S}(\beta, n)$  to form a stable,  $w^*$ -compact face of  $\mathfrak{S}^P(\mathfrak{A})$ . Then by the face property the extremal boundary of  $\mathfrak{S}(\beta, n)$  is the compact intersection of  $\mathfrak{S}(\beta, n)$  with  $\partial_e \mathfrak{S}^P(\mathfrak{A})$  and thus the extremal decomposition in  $\mathfrak{S}(\beta, n)$  coincides with the extremal decomposition in  $\mathfrak{S}^P(\mathfrak{A})$ . By means of the theory of large automorphism groups,<sup>(26)</sup> applied to the permutation automorphisms, one shows the latter to equal the central decomposition. By the preceding arguments the extremal decomposition in  $\mathfrak{S}(\beta, n)$  is unique and  $\mathfrak{S}(\beta, n)$  is a simplex with compact extremal boundary, i.e., a Bauer simplex, which gives (ii). Property (iii) we take again from ref. 11. In (iv) the foregoing results are combined and supplemented by the fact, that each state in  $\partial_e \mathfrak{S}^P(\mathfrak{A})$  is a product state. Thus the pure phase states are indexed by density operators in  $\mathfrak{S}(\mathfrak{B})$ , and the minimalization of the free energy density may be reduced to run over  $\mathfrak{S}(\mathfrak{B})$ . (v) follows directly from (i) and from  $(s, n) \rightarrow u(s, n)$  being convex in both variables. ■

#### 4.2. The Canonical Pure Phases

According to the results of the preceding subsection we have for our singular, particle density fixing Hamiltonians the same structure of equilibrium states as for usual mean-field theories in terms of approximately symmetric nets, and thus we have the analogous scheme for calculating the pure phase states.

The limiting free energy density for pure phases  $\otimes_{\varrho} \in \partial_e \mathfrak{S}^P(\mathfrak{A})$  is calculated directly as

$$\begin{aligned} \tilde{f}(\beta, n, \otimes_{\varrho}) &= u(\otimes_{\varrho}) - \frac{1}{\beta} s(\otimes_{\varrho}) \\ &= \begin{cases} v\langle \varrho; \hat{n}^1 \rangle \langle \varrho; \hat{n}^2 \rangle - 2(\langle \varrho; b^{1*} \rangle \langle \varrho; b^2 \rangle + \langle \varrho; b^1 \rangle \langle \varrho; b^{2*} \rangle) \\ \quad + \frac{1}{\beta} \langle \varrho; \ln \varrho \rangle & \text{for } \langle \varrho; \hat{n}^1 + \hat{n}^2 \rangle = n \\ + \infty & \text{for } \langle \varrho; \hat{n}^1 + \hat{n}^2 \rangle \neq n \end{cases} \quad (4.4) \end{aligned}$$

This means, that the minimum of the free energy density is attained only for states  $\otimes_{\varrho}$  with particle density  $n$ , since for other states the free energy

is infinitely large. This implies that each limiting state  $\tilde{\omega}^{\beta, n}$ , which minimizes the free energy, has a fluctuation-free particle density. Because of this the equilibrium states of the new ensemble *must* differ—at least in the coexistence region of the phase transition—from the grand-canonical equilibrium states, which exhibit density fluctuations. In the following, we use the free energy (Eq. (4.4)) and Theorem 4.1 to determine the pure phases  $\otimes \varrho$ .

Each  $\varrho \in \mathfrak{S}(\mathfrak{B})$  with  $\tilde{f}(\beta, n, \otimes \varrho) = \tilde{f}(\beta, n)$  is a product state  $\varrho_1 \otimes \varrho_2$  with  $\varrho_{1,2} \in \mathfrak{S}(\mathfrak{B})$ : Take an arbitrary  $\varrho \in \mathfrak{S}(\mathfrak{B})$  and set  $\varrho_1 := \varrho|_{\mathfrak{B} \otimes 1}$ ,  $\varrho_2 := \varrho|_{1 \otimes \mathfrak{B}}$ . Then we find

$$\begin{aligned} & \tilde{f}(\beta, n, \otimes \varrho) - \tilde{f}(\beta, n, \otimes (\varrho_1 \otimes \varrho_2)) \\ &= \frac{1}{\beta} (\text{tr}(\varrho \ln \varrho) - \text{tr}((\varrho_1 \otimes \varrho_2) \ln(\varrho_1 \otimes \varrho_2))) \\ &= \frac{1}{\beta} (\text{tr}(\varrho \ln \varrho) - \text{tr}(\varrho \ln(\varrho_1 \otimes \varrho_2))) \\ &= -\frac{1}{\beta} S(\varrho | \varrho_1 \otimes \varrho_2) \geq 0 \end{aligned}$$

$S(\cdot | \cdot)$  is the relative entropy on  $\mathfrak{S}(\mathfrak{B})$  with sign and notation as in ref. 15. Equality holds if and only if  $\varrho = \varrho_1 \otimes \varrho_2$ . Thus we find for  $\tilde{f}(\beta, n, \otimes \varrho) = \tilde{f}(\beta, n)$ , that  $\varrho = \varrho_1 \otimes \varrho_2 \in \mathfrak{S}(\mathfrak{B})$ .

The minimum principle for the free energy  $\mathfrak{S}(\mathfrak{B}) \ni \varrho \rightarrow \tilde{f}(\beta, n, \otimes \varrho)$ , Eqs. (4.3), (4.4), may be expressed in terms of a function  $f: M \rightarrow \mathbb{R}$ ,  $M := \{h = h_1 \otimes h_2 \in \mathfrak{B} \mid \text{spectrum}(h_{1,2}) \subset [0, 1]\}$ ,

$$\begin{aligned} M \ni h \rightarrow f(h) := & v \text{tr}(h_1 \hat{n}^1) \text{tr}(h_2 \hat{n}^2) - 2(\text{tr}(h_1 b^{1*}) \text{tr}(h_2 b^2) \\ & + \text{tr}(h_1 b^1) \text{tr}(h_2 b^{2*})) + \frac{1}{\beta} \text{tr}(h \ln h) \end{aligned}$$

which has to be minimized under the subsidiary conditions

$$\begin{aligned} \text{tr}(h) = \text{tr}(h_1) = \text{tr}(h_2) = 1, \quad \text{and} \\ \text{tr}(h(\hat{n}^1 + \hat{n}^2)) = \text{tr}(h_1 \hat{n}^1) + \text{tr}(h_2 \hat{n}^2) = n \end{aligned} \tag{4.6}$$

The first condition in Eq. (4.6) guarantees that the minimizer  $h$  of  $f$  is a product state on  $\mathfrak{B}$ , and the second one fixes the particle density according to Eq. (4.4). Note that the minimizers of Eqs. (4.5), (4.6) are in the interior



of  $M$ , i.e., if  $\varrho = \varrho_1 \otimes \varrho_2$  with  $\tilde{f}(\beta, n, \otimes \varrho) = \tilde{f}(\beta, n)$ , neither  $\varrho_1$  nor  $\varrho_2$  is a pure state in  $\mathfrak{S}(\mathbb{M}_2(\mathbb{C}))$ . This is shown directly by the variation of  $f$  near the boundary of  $M$  with states  $\varrho$ , where  $\text{tr}(\varrho(\hat{n}^1 + \hat{n}^2))$  is fixed (comp. ref. 23).

Thus  $f$  in Eq. (4.5) is minimized in the interior of  $M$ , i.e., in  $\{h = h_1 \otimes h_2 \in \mathfrak{B} \mid \text{spectrum}(h_{1,2}) \subset ]0, 1[ \}$  which is an open set in  $\mathfrak{B}$ . We determine the extrema of  $f$  with the subsidiary condition Eq. (4.6) in a standard manner by introducing Lagrange parameters [ref. 23, Section 5] and find the following necessary condition for the minimizers  $\varrho$  of  $f(\beta, n, \otimes \varrho)$ , expressing extremality of the free energy under a subsidiary condition:

**Proposition 4.2.** Each  $\varrho \in \mathfrak{S}(\mathfrak{B})$  with  $\tilde{f}(\beta, n, \otimes \varrho) = \tilde{f}(\beta, n)$  is a solution of

$$\varrho = \frac{\exp(-\beta(h_{\text{eff}}(\varrho) - \mu\hat{n}))}{\text{tr}\{\exp(-\beta(h_{\text{eff}}(\varrho) - \mu\hat{n}))\}} \quad \text{and} \quad n = \frac{\text{tr}\{\exp(-\beta(h_{\text{eff}}(\varrho) - \mu\hat{n})) \hat{n}\}}{\text{tr}\{\exp(-\beta(h_{\text{eff}}(\varrho) - \mu\hat{n}))\}} \quad (4.7)$$

The Lagrange parameter  $\mu$  is determined by the second equation as a function of  $n$ , and  $h_{\text{eff}}(\varrho)$  is the state-dependent effective Hamiltonian, given in Eq. (3.5).

Observe that Eq. (4.7) is rather similar to Eq. (3.5), but in fact more involved, since here the value of the chemical potential has also to be calculated selfconsistently. After having solved Eq. (4.7) the physical (stable) solutions are selected by the minimality of the free energy.

### 4.3. Comparison of Free Energies

Let us compare the pure phases  $\otimes \varrho$  for the grand-canonical and canonical subsidiary conditions and by this identify the latter equilibrium states. As described in the preceding subsection in both cases they minimize a functional of the free energy (Eq. (3.3) and (4.4), respectively). While in the first case the variation is extended at a fixed chemical potential  $\mu_0(n)$  over all states  $\otimes \varrho$ ,  $\varrho \in \mathfrak{S}(\mathfrak{B})$ , we vary in the second case over all states  $\otimes \varrho$  with  $\langle \varrho; \hat{n} \rangle = n$  and have  $\mu_0 = 0$  in the free energy. A necessary condition for the minima is expressed in terms of the selfconsistency conditions, Eq. (3.4) and (4.7), which formally have the same form. Because of the subsidiary condition  $\langle \varrho; \hat{n} \rangle = n$  for the second ensemble, the Lagrange multiplier  $\mu$  is varied to find solutions of (4.7), while the chemical potential  $\mu_0$  in Eq. (3.4) is fixed. Consequently, the lowest value of the free energy

density  $f(\beta, \mu_0(n), \otimes \varrho)$ , Eq. (3.3), may differ from the minimum value of  $\tilde{f}(\beta, n, \otimes \varrho)$ , Eq. (4.4). While the chemical potential  $\mu_0$  in Eq. (3.3) arises as a consequence of a constraint at each step toward the thermodynamic limit, the condition for the particle density in the second case appears only after the thermodynamic limit having been performed, and only then  $\mu$  attains via  $n$  a well determined value.

Let us analyze the phase selection in the grand-canonical case more closely. In the coexistence region in between of the S-CO boundaries, there are N- and M-phase solutions of Eq. (3.4) that do not minimize the free energy. In Fig. 3 this fact is illustrated, showing the free energy density for the M-phase of the grand-canonical ensemble forming an arch over the coexistence region.

Other aspects are exhibited in the  $(T, \mu)$ -diagram, where the coexistence regions of the S-type and CO-type phases shrink to lines. They are determined by the intersection of the two corresponding grand-canonical free energy densities as is shown in the first part of Fig. 4. This visualizes that the free energy densities for the S- and the CO-phases respectively, where they are not minimal, do correspond to non-equilibrium states.

By means of the second part of Fig. 4 the different types of phase transitions can be observed in a straightforward manner:  $f(kT, n)$  varies smoothly on the S-N and on the N-CO boundary, whereas it has different left-hand and right-hand derivatives on the S-CO boundary. For the latter fact look again to the first part of Fig. 4.

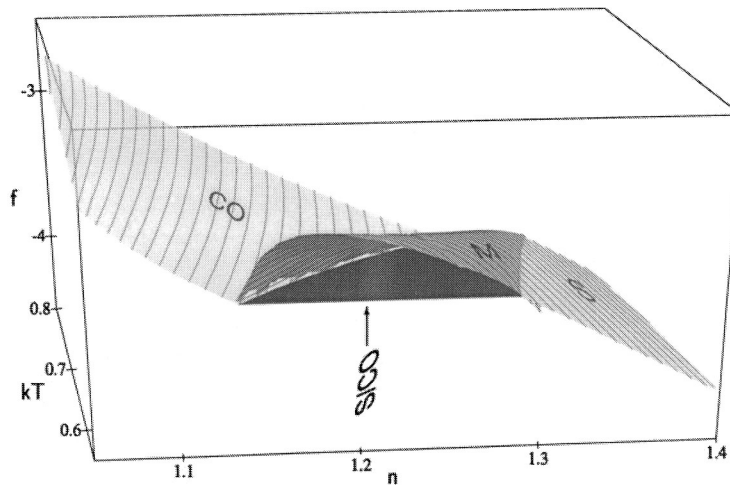


Fig. 3. Grand canonical potential as function of the particle density and temperature: S-phase, CO-phase, coexistence region and M-phase.

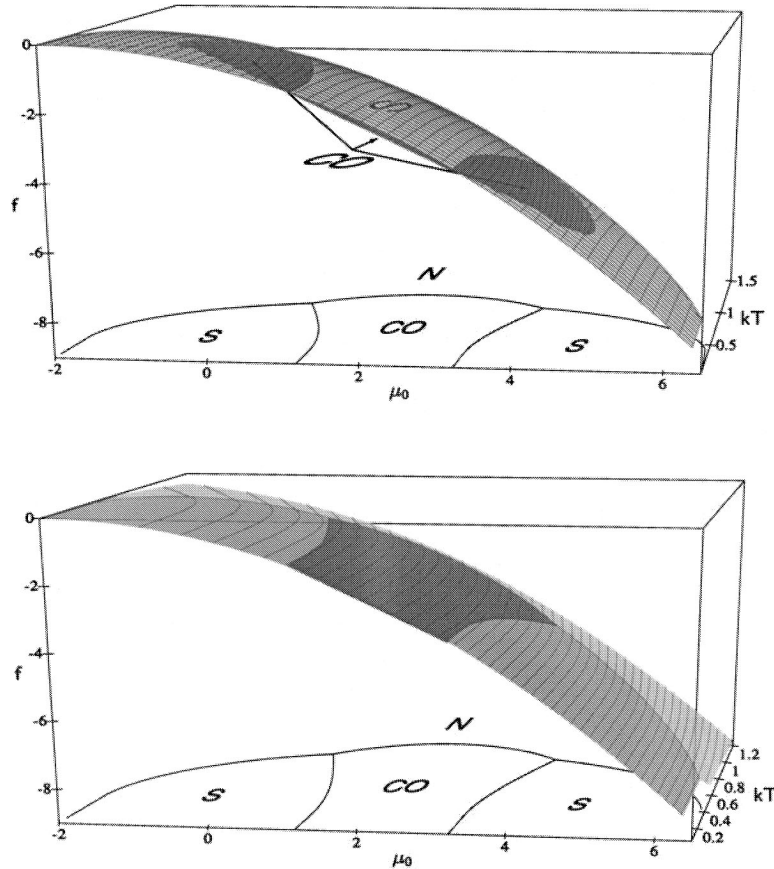


Fig. 4. Grand-canonical potential as function of the chemical potential and temperature: The first picture shows the complete surfaces of the grand-canonical potentials for the S-phase and the CO-phase, which means equilibrium and non-equilibrium values. The second picture shows only the minimizing (equilibrium) values for the grand-canonical potentials of the N-, S- and CO-phase.

An overview on the different phase regions is also provided by the  $(\mu, n)$ -diagram of Fig. 5. The solid line  $\mu = \mu(n)$  refers to the stable phases of the grand-canonical ensemble. The horizontal part of this line with  $\mu(n) = \mu_c$  describes the coexistence region with the extremal densities  $n_2$  and  $n_3$ . This coexistence region replaces by its lower values of the free energy three parts of the pure phase regions: the superconducting phase  $n \in [n_2, n'_2]$ , the mixed phase  $n \in [n'_2, n'_3]$ , and the charge ordered phase  $n \in [n'_3, n_3]$ . The function  $\mu = \mu(n)$  along the pure phase states in  $n \in [n_2, n_3]$  is depicted by a dashed line. This dashed line violates the stability

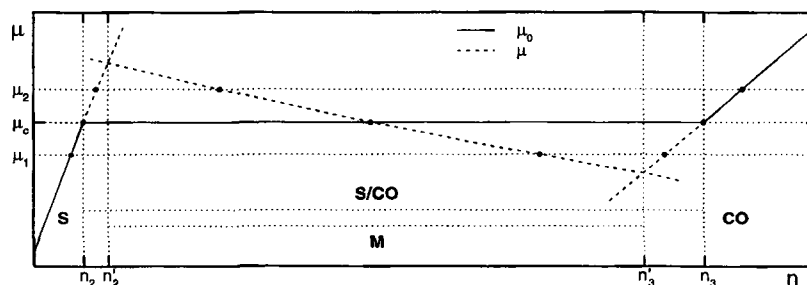


Fig. 5. The chemical potentials  $\mu_0$  and the particle density  $n$  for S-, CO- and M-type solutions of Eqs. (3.4), (4.7). The solid line should be read as  $n(\mu_0)$  for the minimizers of  $f(\beta, \mu_0, \cdot)$ , Eq. (3.3), while the dashed line  $\mu(n)$  results from the chemical potential  $\mu$ , Eq. (4.7), for minimizers of  $\tilde{f}(\beta, n, \cdot)$ , Eq. (4.4).

condition (3.6) for  $n \in [n'_2, n'_3]$ . Observe that the coexistence condition  $\mu(n_2) = \mu(n) = \mu(n_3)$ ,  $\forall n \in [n_2, n_3]$ , which leads for fluid systems to the Maxwell rule, is accompanied here by  $f(T, \mu_c, n_2) = f(T, \mu_c, n) = f(T, \mu_c, n_3)$ ,  $\forall n \in [n_2, n_3]$ . This is a direct consequence of the intersection of the free energy surfaces, cf. Fig. 4, and has no counterpart with fluid systems.

In contrast to the above, for the canonical ensemble we have to use the variational principle for  $\tilde{f}(\beta, n, \cdot)$ , Eq. (4.4), which depends on the particle density  $n$  via the subsidiary condition for the one-cell states  $\varrho$ . Observing this one finds that for  $n \leq n'_2$  ( $n \geq n'_3$ ) the S-solutions (CO-solutions) minimize the functional  $\tilde{f}(\beta, n, \cdot)$  and for  $n'_2 < n < n'_3$  the M-phase states are now the physical (stable) solutions.

Figure 6 shows the canonical free energy density for the S-, CO- and the M-phase. The free energy density for the M-phase, being the minimum of the three surfaces, corresponds to the stable thermodynamic equilibrium state, whereas the corresponding free energy densities for the S- and the CO-phase on this region of  $\partial_e \mathfrak{E}(kT, n)$  are non-equilibrium free energy densities. This leads to a drastic change in the phase diagram.

#### 4.4. Canonical Phase Diagram

In the preceding Subsection the canonical,  $n$ -dependent free energy has chosen the physical states among the solutions of the selfconsistency equations. Let us analyze the resulting phase diagram, which is depicted in Fig. 7 and again in Fig. 8 with the stable thermodynamic free energy surface.

The N-CO and N-S boundaries have not changed in comparison to the phase diagram in Fig. 1. But we have already noted that the first order transition between the S- and the CO-phase cannot take place due to a too

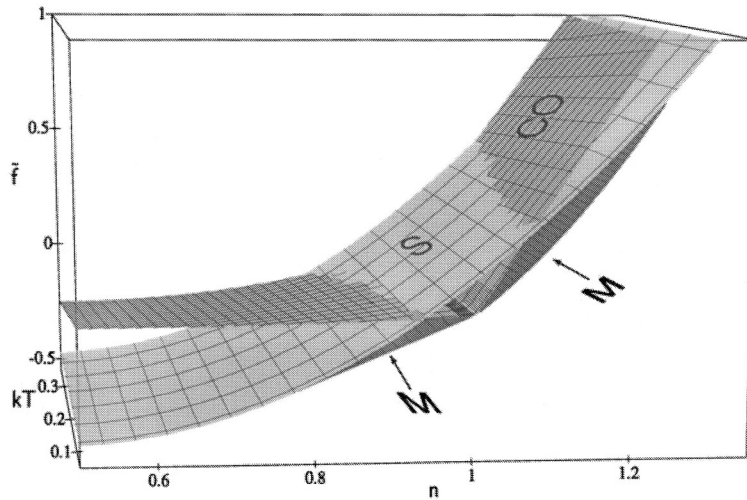


Fig. 6. Canonical Free Energy: S-Phase, CO-Phase and M-Phase.

high free energy, Eq. (4.4). At least in the S-CO coexistence region there have to be differences in the phase-diagrams: For particle densities  $n'_2 < n < n'_3$  (or  $2 - n'_3 < n < 2 - n'_2$ ) and  $T < T_c$  there is a new kind of a phase, the so-called M-phase, with broken gauge symmetry *and* broken invariance under sub-lattice exchange. The arising S-M and the CO-M transitions are continuous with a qualitative change of the equilibrium states. This is made manifest not only in the different broken symmetries of the pure phase states, but also in the different topological structures of the sets  $\mathfrak{S}(\beta, n)$ . From the latter one sees the combination of qualitative changes with smoothness, which is described in general mathematical

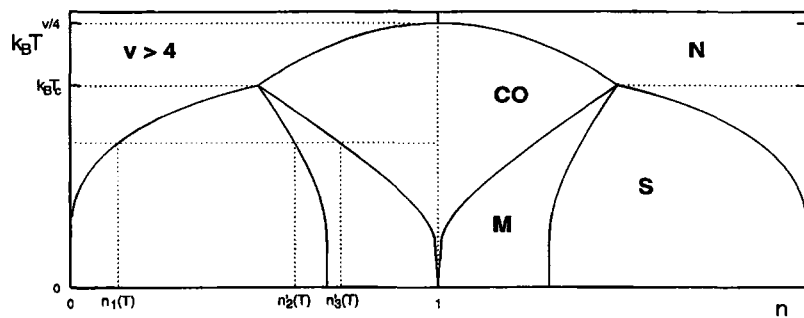


Fig. 7.  $(n, T)$ -phase diagram of the model (thermodynamic limit at particle density  $n \in ]0, 2[$  with suppressed fluctuations).

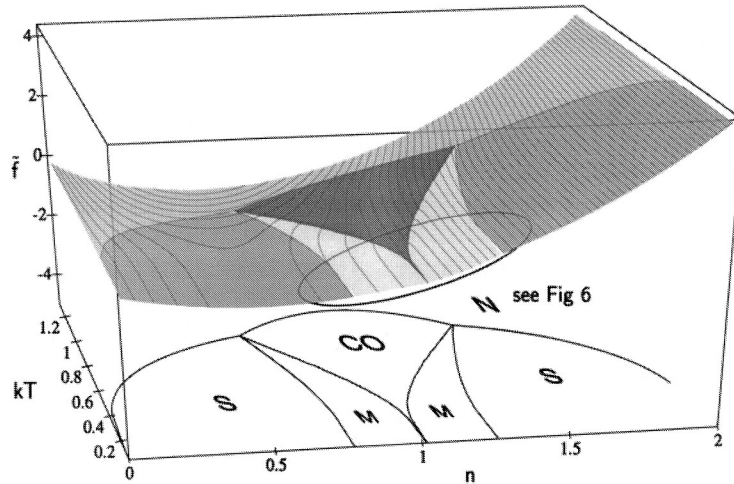


Fig. 8. Canonical free energy as function of the particle density and the temperature: N-phase, S-phase, CO-phase and M-phase.

terms in ref. 13. Thus the S-M and M-CO transitions are phase transitions of the second kind and the transition points, which make up the boundary lines of the M-phase region, are critical points. The boundaries can be determined by a Landau expansion of the free energy density in Eq. (4.4) together with the selfconsistency condition, Eq. (4.7).

The free energy density  $\tilde{f}(kT, n)$  in Fig. 8 varies smoothly on all phase boundaries, showing all phase transitions to be of second kind. We also obtain the confirmation, that the free energy density for the canonical ensemble is a convex function of  $n$  in contrast to the grand-canonical potential being concave. This indicates the two different types of thermodynamic ensembles, resp. potentials.

Apart from the choice of  $v$ ,  $t$ , and the parameterization of  $\mathfrak{S}(\mathfrak{B})$ , we have found the same boundaries as given in ref. 2. In particular, we find  $n_2 < n'_2$  and  $n'_3 < n_3$ , that is, the boundaries for the region of the pure phases with mixed properties are shifted with respect to the boundaries of the coexistence region in the grand-canonical case. Since all these features of our phase portrait coincide with those of the somewhat formal mean-field approximations for a short-range, bipolaronic superconductor model in ref. 2, we have succeeded in transforming the manipulations of ref. 2 into a microscopic model, which is uniquely given by a net of local Hamiltonians (including the density fixing perturbations).

Since the (unchanged) N-CO and N-S boundaries are also critical points, we have in the meeting points of all four phase regions examples of

tetra-critical points. The flat minimum of the free energy at this point is due to an extremality with respect to four order parameters.

## 5. LIMITING GIBBS STATES AND CONDENSED FIELDS

The calculation of the pure phase states reveals that for each type of symmetry break down, characterizing the different thermodynamic phase regions, one has just one orbit of lower symmetric pure phases with respect to the original internal symmetry group, or to the broken symmetry group. Since the local perturbations in the net of model Hamiltonians are invariant under gauge and lattice exchange transformations, this invariance takes over to the singular, density fixing perturbation in the thermodynamic limit and to the corresponding free energy. The associated net of local Gibbs states has, therefore, symmetric limit points, which are minimizers of the free energy, cf. Theorem 4.1. By the same reasoning as in ref. 1 we conclude, that in each thermodynamic phase region there is a unique canonical limiting Gibbs state. More specifically, the limiting Gibbs state in the N-, S-, and CO-phase regions are the same as  $\omega_N$ ,  $\omega_S$ , and  $\omega_{CO}$  for the model in the grand canonical equilibrium (comp. Eq. (3.7)). In the M-phase region the solutions  $\varrho$  of Eq. (4.7) with minimal free energy density  $\tilde{f}(\beta, n, \otimes \varrho) = \tilde{f}(\beta, n)$  constitute one orbit for the gauge transformations combined with the sub-lattice exchange. This allows in each phase region to express the central measure  $\tilde{\mu}_{\beta, n}$  of the unique limiting Gibbs state  $\tilde{\omega}^{\beta, n}$  in terms of the corresponding Haar measure of the broken symmetry group.<sup>(20, 19, 1)</sup> Since the Haar measure is unique up to normalization, we have in each  $\mathfrak{S}(\beta, \mu)$  just one state, which is invariant under the internal symmetries. Its central support comprises, therefore, all of the extreme boundary of  $\mathfrak{S}(\beta, \mu)$ . Given the limiting Gibbs state, one finds all of the pure phase states by the central decomposition, and thus all of  $\mathfrak{S}(\beta, \mu)$  by pure phase mixtures, where inversely  $\mathfrak{S}(\beta, \mu)$  gives the unique symmetric state, coinciding with the limiting Gibbs state.

Altogether we arrive at the following situation:

**Theorem 5.1.** Let the model in the canonical ensemble be defined by the lower semisymmetric net  $(1/|A|)(H_A + P_A)$ , as introduced previously.

(i) In each thermodynamic phase region there exists a unique limiting Gibbs state for this net. The central support of the limiting Gibbs state comprises all of the pure phase states, which constitute one orbit of the broken symmetry group defining the thermodynamic phase region. The whole Bauer simplex of the equilibrium states is thus uniquely determined by the limiting Gibbs state, and vice versa.

(ii) The limiting Gibbs state in each thermodynamic phase region is a special case of the following general integral representation, constituting the central decomposition:

$$\tilde{\omega}^{\beta, n} = \int_0^{2\pi} \left( \frac{1}{2} (\otimes \varrho_{12}^{\vartheta}) + \frac{1}{2} (\otimes \varrho_{21}^{\vartheta}) \right) \frac{d\vartheta}{2\pi}$$

with  $\varrho_{ik}^{\vartheta} = \exp(-\xi - \beta h_{ik}^{\vartheta}), \quad i \neq k \in \{1, 2\}$  (5.1)

where

$$h_{ik}^{\vartheta} = (vn_i - \mu) \hat{n}^1 - \Delta_i (e^{-i\vartheta} b^{1*} + e^{i\vartheta} b^1) + (vn_k - \mu) \hat{n}^2 - \Delta_k (e^{-i\vartheta} b^{2*} + e^{i\vartheta} b^2)$$

(5.2)

for  $\vartheta \in [0, 2\pi[$ . The quantities  $n_1 = \text{tr}(\varrho \hat{n}^1)$ ,  $n_2 = \text{tr}(\varrho \hat{n}^2)$ , and  $(\Delta_1/2) e^{-i\vartheta} = \text{tr}(\varrho b^1)$ ,  $(\Delta_2/2) e^{-i\vartheta} = \text{tr}(\varrho b^2)$  are determined by those solutions  $\varrho = \varrho_{ik}^{\vartheta}$  of Eq. (4.7) which minimize the free energy (4.4) for prescribed  $(\beta, n)$ .

*Proof.* The arguments for (i) have been given in the text preceding the present Theorem, and (ii) uses the solutions of the selfconsistency equations. It is clear that in the different thermodynamic phase regions different mean-field values in the effective one-cell Hamiltonian (5.2) arise. Especially in the M-phase region all mean-fields  $n_i$  and  $\Delta_i$  have non-vanishing values, which differ from each other in the sublattices. Thus, these values may be distributed among the two sublattices in two different manners, which gives the additive decomposition in the integrand of Eq. (5.1). One has now only to verify, that all pure phase states, as given in Eq. (3.7), are special cases of the integrand in Eq. (5.1). ■

The determined limiting Gibbs states describe the thermodynamic equilibrium in fully symmetric surroundings resp. state preparations, which have no bias with respect to the internal symmetries. The possible values of the order parameters, resulting from the spontaneous symmetry breaking, should be defined quite generally as the parameters for the central decomposition of the limiting Gibbs states. This is an essentially unique definition, which does not depend on a special calculation method as, e.g., the largest eigenvalues of a transfer matrix. For our special model class we obtain the mean-field values as order parameters. Thus the limiting Gibbs states play a basic role, although they may be evaluated directly as a limit only in the most simple forms of a superconductor model.<sup>(27)</sup> They determine also the Hilbert spaces of the reconstructed quantum theory via their GNS-representations, where the decomposition into the superselection sectors is given by the central decomposition Eq. (5.1) (cf. the spatial decomposition theory in ref. 14).



It is mostly in this representation, where the effective dynamics is formulated, with its spectrum depending on the thermodynamic state variables, that is here depending on  $(\beta, n)$ . As will be elaborated for the present model in detail elsewhere, one can also formulate a C\*-dynamical system (cf. also ref. 28). There not only the dynamics but also the C\*-algebra may be  $\beta$ -dependent. The set of its  $\beta$ -KMS-states will be shown to be much larger and less specific than the limiting Gibbs states together with their central decomposition states.

Using the central decomposition of the representation von Neumann algebra, gained by the weak closure of the represented quasilocal algebra (and comprising the just mentioned  $\beta$ -dependent C\*-algebra), we can determine the condensed field operators of the system, which are elements in the center of this von Neumann (resp. C\*-) algebra. Let us have a look on the annihilation operator for condensed pairs and on the macroscopic observable “particle density” (in a sub-lattice), constructively defined by the following mean ergodic averaging limits associated with the translation group:

$$b_{\beta, n}^r := \text{s-lim}_{\mathcal{A} \in \mathfrak{L}} \Pi^{\beta, n} \left( \frac{1}{|\mathcal{A}|} \sum_{i \in \mathcal{A}} b_i^r \right), \quad \text{and} \quad (5.3)$$

$$\hat{n}_{\beta, n}^r := \text{s-lim}_{\mathcal{A} \in \mathfrak{L}} \Pi^{\beta, n} \left( \frac{1}{|\mathcal{A}|} \sum_{i \in \mathcal{A}} \hat{n}_i^r \right)$$

with the sub lattice index  $r = 1, 2$ . These averages over the whole lattice exist in the strong operator topology of the GNS-representation  $\Pi^{\beta, n}$  of  $\tilde{\omega}^{\beta, n}$  and constitute a mapping (conditional expectation) into the center of the representation von Neumann algebra. (This mapping is characteristic for all so-called large automorphism groups.<sup>(26)</sup>) Using the central decomposition of  $\tilde{\omega}^{\beta, n}$ , Eq. (5.1), the charge ordering and superconductive collective properties are reflected in the structure of the diagonal field operators as follows:

$$b_{\beta, n}^1 = \frac{A_1}{2} \int_{[0, 2\pi[}^{\oplus} e^{-i\vartheta} \mathbb{1}_g \left( \frac{d\vartheta}{2\pi} \right) \oplus \frac{A_2}{2} \int_{[0, 2\pi[}^{\oplus} e^{-i\vartheta} \mathbb{1}_g \left( \frac{d\vartheta}{2\pi} \right) \quad (5.4)$$

$$b_{\beta, n}^2 = \frac{A_2}{2} \int_{[0, 2\pi[}^{\oplus} e^{-i\vartheta} \mathbb{1}_g \left( \frac{d\vartheta}{2\pi} \right) \oplus \frac{A_1}{2} \int_{[0, 2\pi[}^{\oplus} e^{-i\vartheta} \mathbb{1}_g \left( \frac{d\vartheta}{2\pi} \right) \quad (5.5)$$

and

$$\hat{n}_{\beta, n}^1 = n_1 \mathbb{1} \oplus n_2 \mathbb{1}, \quad \hat{n}_{\beta, n}^2 = n_2 \mathbb{1} \oplus n_1 \mathbb{1} \quad (5.6)$$

Again  $(\Delta_{1,2}/2) e^{-i\theta}$  and  $n_{1,2}$  are the sublattice expectation values of  $b^r$  and  $\hat{n}^r$  as introduced above. We see, that the condensed pair operators do not vanish in the superconducting phases, where by definition  $\Delta_{1,2} > 0$ , and the charge-ordering is expressed by  $n_1 \neq n_2$ . Consequently, we have  $b_{\beta,n}^1 \neq b_{\beta,n}^2$  and  $\hat{n}_{\beta,n}^1 \neq \hat{n}_{\beta,n}^2$  in the M-phase region. Both types of symmetry break down may be recognized in this way from the condensed pair operators. Since the central decomposition expresses an additive superposition of statistical possibilities, Eq. (5.4) indicates an equal likelihood for the phase angle values and the two amplitude values (gap parameters) of the averaged field on sublattice 1. Equation (5.5) gives the same for the condensed field on sublattice 2. Term-wise comparison of both integral expressions reveals a strict phase correlation and a strict anti-correlation for the amplitudes between the sublattices in the M-phase region. Note that the averaged field is often called “macroscopic wavefunction” (for an interesting comment on this notion cf. ref. 29 and for “off-diagonal long range order” in superconductors cf. ref. 30).

The order parameters  $\Delta/2 = \frac{1}{4}(\Delta_1 + \Delta_2)$  and  $\Delta_1/2$  for the S- and the M-phase are shown in Fig. 9. It is observed that  $\Delta_1/2$  approaches zero on the M-CO boundary and reaches the S-phase order parameter on the S-M boundary, attaining even larger values in between.

In the coexistence region of the grand canonical situation one has either superconductivity or charge ordering for a pure thermodynamic phase. That is, the amplitudes of the condensed field in the superconducting phase on the sublattices always are equal. The coexistence with the charge ordered phase multiplies the amplitude with a probability factor. Since both ordering phenomena are compatible and have apparently the

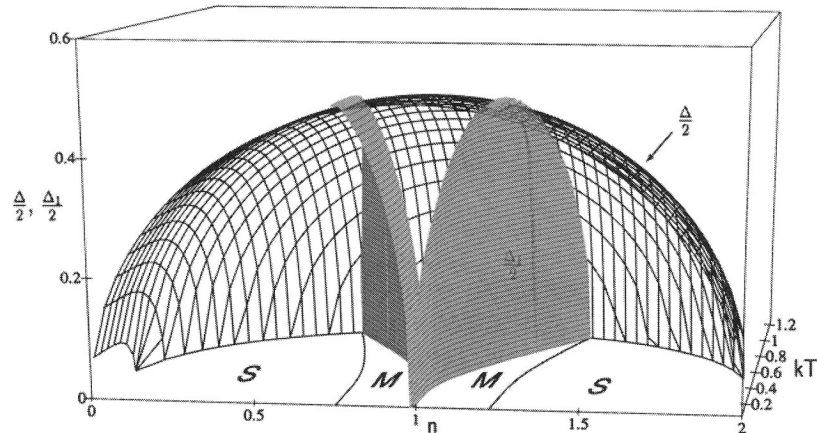


Fig. 9. Order Parameters  $\Delta$  and  $\Delta_1$ : S-Phase and M-Phase.

same specific weight the thermodynamic theory would predict preparation methods, where the coexisting charge ordered and superconducting phases are not spatially separated on a mesoscopic scale. The point is, that they can be separated, in principle. In the antiferromagnetic interpretation of our model a coexistence region for spin flopped and antiferromagnetic ordering has in fact been established.<sup>(31-33)</sup>

In sharp contrast to the coexistence phase the M-phase exhibits both ordering phenomena in each mesoscopic space region for any preparation method. Since the interpretation of the present model as a high- $T_c$  superconductor is rather involved,<sup>(5)</sup> it is not so clear, how to confirm experimentally the predicted M-phase. A related M-phase exists, however for superconductors with paramagnetic impurities.<sup>(34-36)</sup>

Instead of trying a spatial separation of two phases the traditional thermodynamic methods of studying the specific heat across the boundaries of the coexistence resp. M-phase region should reveal, whether one has a phase transition of the first (discontinuous) or second (continuous) kind. For most high- $T_c$  superconductors one has a singularity, indicating the second kind and M-phase.

As a final remark we want to relate the present model to another class of models discussed in the context of high- $T_c$  superconductors (see ref. 37 for a general overview), namely the Hubbard model in a generalized mean field approximation by the composite operator method.<sup>(38, 39)</sup>

Despite the big differences in both types of approaches to the Hubbard model here the bipolaronic and there the fermionic composite operator approach they both stress the importance of doping near half filling. For both kinds of models the combination (be it a pure phase or a coexistence region) of a charge ordered (antiferromagnetic) phase and a phase with broken gauge symmetry occurs around half filling. For a large class of materials the maximal  $T_c$  is reached by doping near half filling, what coincides with the present model, if the M-phase region is "small."

## ACKNOWLEDGMENTS

One of the authors (T.G.) would like to thank S. Zanzinger for stimulating discussions and critical remarks. The work is part of the project *Quantenstochastische Kopplungs- und Störungstheorie makroskopischer Vielteilchensysteme*, supported by the Deutsche Forschungsgemeinschaft (DFG).

## REFERENCES

1. T. Gerisch and A. Rieckers, Limiting gibbs states and phase transitions of a bipartite mean-field hubbard-model, *J. Stat. Phys.* **91**:759 (1998).

2. S. Robaszkiewicz, R. Micnas, and K. A. Chao, Thermodynamic properties of the extended Hubbard model with strong intra-atomic attraction and an arbitrary electron density, *Phys. Rev. B* **23**:1447–1458 (1981).
3. A. Alexandrov and J. Ranninger, Theory of bipolarons and bipolaronic bands, *Phys. Rev. B* **23**:1796–1801 (1981).
4. R. Micnas, J. Ranninger, and S. Robaszkiewicz, Superconductivity in narrow-band systems with local nonretarded attractive interactions, *Rev. Mod. Phys.* **62**:113–171 (1990).
5. A. S. Alexandrov and N. Mott, *Polarons and Bipolarons* (World Scientific, Singapore, 1995).
6. A. D. Bruce and A. Aharony, Coupled order parameters, symmetry-breaking irrelevant scaling fields, and tetracritical points, *Phys. Rev. B* **11**:478–499 (1975).
7. M. E. Fisher and D. R. Nelson, Spin flop, supersolids, and bicritical and tetracritical points, *Phys. Rev. Lett.* **32**:1350–1353 (1974).
8. Y. Imry, D. J. Scalapino, and L. Gunther, Phase transitions in systems with coupled order parameters, *Phys. Rev. B* **10**:2900–2902 (1974).
9. J. M. Kosterlitz, D. R. Nelson, and M. E. Fisher, Bicritical and tetracritical points in anisotropic antiferromagnetic systems, *Phys. Rev. B* **13**:412–432 (1976).
10. K.-S. Liu and M. E. Fisher, Quantum lattice gas and the existence of a supersolid, *J. Low Temp. Phys.* **10**:655–683 (1973).
11. R. F. Werner, Large deviations and mean-field quantum systems, In *Quantum Probability and Related Topics VII*, pp. 349–381 (World Scientific, Singapore, 1992).
12. R. B. Israel, *Convexity in the Theory of Lattice Gases* (Princeton University Press, 1979).
13. T. Gerisch, A. Rieckers, and H.-J. Volkert, Thermodynamic Formalism and Phase Transitions of Generalized Mean-Field Quantum Lattice Models, *Z. Naturforsch.* **53a**:179–207 (1998).
14. O. Bratteli and D. W. Robinson, *Operator Algebras and Quantum Statistical Mechanics*, Vol. I (Springer-Verlag, 1987).
15. O. Bratteli and D. W. Robinson, *Operator Algebras and Quantum Statistical Mechanics*, Vol. II (Springer-Verlag, 1981).
16. G. L. Sewell, *Quantum Theory of Collective Phenomena* (Clarendon Press, Oxford, 1986).
17. S. Sakai, *C\*-Algebras and W\*-Algebras* (Springer-Verlag, Berlin, 1971).
18. E. Størmer, Symmetric states of infinite tensor products of C\*-algebras, *J. Funct. Anal.* **3**:48–68 (1969).
19. T. Gerisch, Internal symmetries and limiting Gibbs states in quantum lattice mean field theories, *Physica A* **197**:284–300 (1993).
20. W. Fleig, Operatoralgebraische Quantenstatistik von zusammengesetzten langreichweitigen Gittersystemen, Ph.D. thesis (Dissertation), Universität Tübingen, 1985, unpublished.
21. M. J. Donald, Relative Hamiltonians which are not bounded from above, *J. Funct. Anal.* **91**:143–173, (1990).
22. G. A. Raggio and R. F. Werner, Quantum statistical mechanics of general mean field systems, *Helv. Phys. Acta* **62**:980–1003 (1989).
23. T. Gerisch and A. Rieckers, The quantum statistical free energy minimum principle for multi-lattice mean field theories, *Z. Naturforsch.* **45a**:931–945 (1990).
24. R. S. Ellis, *Entropy, Large Deviations, and Statistical Mechanics* (Springer, 1985).
25. T. Gerisch and A. Rieckers, Comparison of weakly inhomogeneous BCS- and Hubbard-models, *Physica A* **242**:439–466 (1997).
26. E. Størmer, Large groups of automorphisms of C\*-algebras, *Commun. Math. Phys.* **5**:1–22 (1967).
27. W. Fleig, On the symmetry breaking mechanism of the strong-coupling BCS-model, *Acta Phys. Austr.* **55**:135–153 (1983).

28. T. Gerisch and A. Rieckers, Limiting dynamics, KMS-states, and macroscopic phase angle for weakly inhomogeneous BCS-models, *Helv. Phys. Acta* **70**:727–750 (1997).
29. P. W. Anderson, Coherent matter field phenomena in superfluid, *Lectures of Belfer Graduate School of Sciences* **2**:21–40 (1967).
30. G. L. Sewell, Macroscopic quantum theoretic approach to superconductive electrodynamics, In *Superconductivity and Strongly Correlated Electronic Systems* (World Scientific, Singapore, 1994).
31. C. J. Gorter and T. van Peski-Tinbergen, Transitions and phase diagrams in an orthorhombic antiferromagnetic crystal, *Physica* **22**:273–287 (1956).
32. G. J. Butterworth and V. S. Zidell, Magnetothermal studies of the phase transitions in  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , *J. Appl. Phys. Suppl.* **40**:1033–1034 (1969).
33. K. W. Blazey, H. Rohrer, and R. Webster, Magnetocaloric effects and the angular variation of the magnetic phase diagram of antiferromagnetic  $\text{GdAlO}_3$ , *Phys. Rev. B* **4**:2287–2302 (1971).
34. E. Müller-Hartmann and J. Zittartz, Theory of magnetic impurities in superconductors—depression of the transition temperature, *Z. Physik* **234**:58 (1970).
35. E. Müller-Hartmann and J. Zittartz, Kondo effect in superconductors, *Phys Rev. Lett.* **26**:428 (1971).
36. S. V. Vonsowsky, Yu. A. Izyumov, and E. Z. Kurmaev, *Superconductivity of Transition Metals, Their Alloys and Compounds* (Springer, 1982).
37. N. Plakida, *High-Temperature Superconductivity* (Springer, Berlin, 1995).
38. F. Mancini, S. Marra, A. M. Allega, and H. Matsumoto, Mean field analysis of the Hubbard model, *Physica C* **240**:2253–2254 (1994).
39. F. Mancini, S. Marra, and H. Matsumoto, The two-dimensional t-t'-U Hubbard model as a minimal model for cuprate materials, preprint, cond-mat/9707088, 1997.