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Quasichemical Equilibrium Approach to Superconductivity

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Abstract. A new approximation method for the partition function of a system of interacting Fermi particles is proposed. It consists in neglecting all dynamical correlations between more than pairs of particles, including however all statistical correlations. It is shown that this approximation is valid in the following two cases: (i) In a dilute gas of atoms capable of forming diatomic molecules one gets the thermodynamical theory of chemical equilibrium. (ii) For the electron gas in metals one gets an extension of the free-electron theory which takes into account the interactions to a first approximation. The validity of the approximation in this case is dependent on the quenching effect of the Pauli principle which forbids most scattering processes between electrons. The quenching of the dynamical correlation by the Pauli principle follows automatically from the theory. In both cases (i) and (ii) one finds that the thermodynamical properties of the system are given in the form of a chemical equilibrium between the fermions ("atoms") and diatomic "(pseudo-) molecules", the latter obeying Bose-statistics. They can, under certain conditions, undergo a Bose-Einstein condensation and, in case (ii), thereby produce a transition to a superconducting state. This depends on the properties of the correlation and is not followed in detail here. It is, however, shown qualitatively that the interaction of electrons through the phonon field should have the features required for such a transition.

1. Introduction.

It has been pointed out previously¹⁾ that an explanation of the phenomenon of superconductivity in metals might be found in terms of the Bose-gas model²⁾ by assuming a resonance in the scattering of electrons in the metal. As a provisional approach to the problem, it was then assumed that such a resonance could be treated like a bound state with negative binding energy, and chemical equilibrium between free electrons and these resonant states was then assumed. This provisional approach suffered from several defects, some of

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which will be discussed later in this section, and no quantitative agreement with experiment could be reached. Still, the trend of the results was encouraging enough to warrant a further investigation of the question. It is the purpose of this paper to develop a new systematic approximation procedure for the partition function of a system of interacting particles which is especially suited for our purpose.

The approach we propose is essentially a quantum mechanical' generalization of the Ursell method³). Its basis is to study the correlations between the particles in the system. Such correlations are produced partly by the interaction ("dynamical correlations"), partly by the statistics of the particles ("statistical correlations"). These two kinds of correlations have to be carefully sorted out. The statistical correlations will always be taken into account exactly, since we want to study systems at low temperatures. Approximations are made on the dynamical correlations. They can be classified in a standard fashion into pair-correlations, triplet-, quadruplet-, and higher, correlations. Our approximation method consists in taking these types of correlations successively into account.

The zero-order approximation in this procedure is given by *Assumption 0: All dynamical correlations are neglected*. For the case of the electron gas of metals, the zero-order approximation is the free-electron theory of metals, which is known to work very well.

The first-order approximation is given by *Assumption I: All triplet- (and higher) dynamical correlations can be neglected; pair-correlations are taken into account exactly*. In a similar way, higher order approximations can be set up by taking into account even higher correlations; we shall not do so in this paper, but restrict ourselves to the study of the first-order approximation which we shall call the "*quasichemical equilibrium approximation*". The reason for this name will soon be seen.

Obviously, assumption I contains assumption 0 as a special case, and one would, therefore, expect that for all systems for which assumption 0 gives a good approximation, assumption I will give a consistent extension of this approximation. We shall apply our procedure to two cases:

(i) True chemical equilibrium between atoms and diatomic molecules in perfect gases. In this case, the quasichemical approximation yields the thermodynamical theory of chemical equilibrium (hence the name). This case serves as a useful test case for the theory.

(ii) The electron gas in metals. In this case, the quasichemical approximation is a systematic extension of the free-electron theory

of metals which allows correlations between electrons to be taken into account in a systematic way. This seems to be the appropriate formulation of the provisional approach in ref. ¹); one sees that the concept of "resonance" no longer explicitly enters the theory. At the same time, the quasichemical equilibrium approximation fulfills the requirement stated by PEIERLS⁴) in his criticism of the Fröhlich-Bardeen theory⁵) of superconductivity. PEIERLS says: "To take such terms" (namely non-diagonal terms in the electron-electron interaction due to the lattice vibrations) "into account one would, however, have to start from a wave function which allows for correlations between the electrons". This is exactly what the quasichemical approximation achieves.

Of course, the remarks made above are not in themselves sufficient to justify the applicability of the quasichemical equilibrium approximation to either case (i) or (ii). A more detailed discussion is contained in section 5, where criteria for the validity of the approximation are set up. An important role in these considerations will be played, for the case of the electron gas, by the "quenching" of the correlation by the Pauli principle. When the electron gas is highly degenerate, one expects the Pauli principle to have a strong influence on the "pseudomolecules", i.e. on the correlated pairs. In terms of scattering, one would expect only those scattering events to be allowed whose final states are not already occupied by free electrons. In a self-consistent way one might try replacing the dynamical correlation function between two free-particle states k_1 and k_2 , $\beta(k_1, k_2)$, by a "quenched" correlation function $\tilde{\beta}(k_1, k_2)$ designed to take this effect into account:

$$\tilde{\beta}(k_1, k_2) = (1 - n(k_1)) \beta(k_1, k_2) (1 - n(k_2)) \quad (1.1)$$

where

$$n(k) = \frac{1}{e^{\alpha(\epsilon(k) - \mu)} + 1} \quad (1.2)$$

is the Fermi distribution of the free atoms. Our treatment which, as mentioned, takes statistical correlations into account exactly, includes an exact treatment of this effect, without any self-consistency arguments, and the result turns out to be exactly the guess (1.1).

The importance of this effect for the discussion of the validity of the quasichemical approximation can be understood qualitatively in terms of the provisional approach of ref. ¹). In order for such an approach, in which a resonance is treated like a bound state, to be even approximately valid, one would have to postulate that the

width of the resonance be very small. Furthermore, in order not to get any room-temperature superconductors, the resonance would have to be confined to a small neighbourhood of the Fermi surface. Both these conditions would be very hard to fulfill, were it not for the quenching. Since the scattering phases will be largely quenched within the Fermi sphere, they will rise abruptly from zero to their unquenched value over the Fermi surface region. Such an abrupt rise of the phases corresponds to a resonance in the quenched scattering, and the position of this resonance is confined to the Fermi surface region. This argument indicates that strong quenching will be favourable to the quasichemical equilibrium approximation: this is borne out by the later discussion. For the case of Bose particles, the quenching would have the opposite effect, and the quasichemical equilibrium approximation does not, therefore, appear to be useful there except in the relatively trivial case of true chemical equilibrium.

These remarks may suffice at present to justify the quasichemical approximation method. In sections 2–4 we carry through our programme without worrying about the applicability of the method; section 2 contains the simple case of Boltzmann statistics, sections 3 and 4 are devoted to the general case of particles obeying Fermi statistics. In section 5 we discuss some relevant properties of the pair-correlation and set up criteria for the validity of the quasichemical approximation method. Section 6 contains the application to the case of true chemical equilibrium; the thermodynamical theory of chemical equilibrium is derived and justified directly from statistical mechanics. In section 7, finally, we shall consider the application to the case of electrons in metals. It is shown that the criteria set up in section 5 are fulfilled, so that the quasichemical equilibrium approximation indeed furnishes a consistent extension of the free electron-theory of metals. The thermodynamical properties of the electron gas are then given by an expression which can be interpreted as stemming from the formation of “pseudomolecules” consisting of two electrons, in chemical equilibrium with the gas of free electrons. If the pair-correlation between electrons has certain special properties, those pseudomolecules can undergo a Bose-Einstein condensation and, thereby, produce a transition to a superconducting state. The special properties needed for this behaviour are just those which one would expect if the pair-correlation is produced by the intermediary of the sound waves in the lattice⁵). The pair-correlation due to this effect (in combination with the screened Coulomb repulsion) is, at present, not known. It will, however, be

established that under some reasonable assumptions about this correlation many of the equilibrium features of superconductivity can be understood.

In Appendix I, for convenience, we briefly recall the thermodynamical theory of chemical equilibrium in perfect gases. Appendix II contains the justification for an approximation made in section 4. Appendix III gives a simple semi-classical treatment of the "two-particle U -matrix" which sheds some additional light on the results of section 5.

2. The Boltzmann Case.

In this section we are going to develop our programme for the case of particles, called "atoms", obeying Boltzmann statistics. We consider a system of N identical atoms of mass m enclosed in a volume V . The free energy $F_N(V, T)$ is given by the partition function

$$e^{-\alpha F_N} = \frac{1}{N!} \text{Trace} (e^{-\alpha H_N}) \quad (2.1)$$

where H_N is the Hamiltonian for N atoms, $\alpha = 1/kT$. We evaluate the trace in the representation in which the momenta of the atoms are diagonal. (For simplicity, we restrict ourselves in this section to spinless particles; inclusion of the spin leads to no new aspects.) The partition function now becomes

$$e^{-\alpha F_N} = \frac{1}{N!} \sum_{\vec{k}_1, \vec{k}_2, \dots, \vec{k}_N} \langle \vec{k}_1, \vec{k}_2, \dots, \vec{k}_N | e^{-\alpha H_N} | \vec{k}_1, \vec{k}_2, \dots, \vec{k}_N \rangle. \quad (2.2)$$

The sum extends over all momenta independently for each \vec{k}_i .

We now define U -functions³⁾ and correlation functions:

(i) The "one-particle U -function" is the Boltzmann factor for a free atom:

$$U_1(\vec{k}) = \langle \vec{k} | e^{-\alpha H_1} | \vec{k} \rangle = e^{-\alpha \varepsilon(\vec{k})} \quad (2.3)$$

where

$$\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}. \quad (2.4)$$

(ii) The "two-particle U -function" $U_2(k_1, k_2)$ is defined by

$$U_2(\vec{k}_1, \vec{k}_2) = \langle \vec{k}_1, \vec{k}_2 | e^{-\alpha H_2} | \vec{k}_1, \vec{k}_2 \rangle - U_1(\vec{k}_1) U_1(\vec{k}_2). \quad (2.3')$$

(iii) The higher U -functions are to be defined similarly in a recursive way. E.g., the three-particle U -function is

$$\begin{aligned} U_3(\vec{k}_1, \vec{k}_2, \vec{k}_3) &= \langle \vec{k}_1, \vec{k}_2, \vec{k}_3 | e^{-\alpha H_3} | \vec{k}_1, \vec{k}_2, \vec{k}_3 \rangle - \\ &- [U_1(\vec{k}_1) U_2(\vec{k}_2, \vec{k}_3) + U_1(\vec{k}_2) U_2(\vec{k}_3, \vec{k}_1) + U_1(\vec{k}_3) U_2(\vec{k}_1, \vec{k}_2)] - \\ &- U_1(\vec{k}_1) U_1(\vec{k}_2) U_1(\vec{k}_3). \end{aligned} \quad (2.3'')$$

The n -particle correlation function, $\beta_n(\vec{k}_1 \dots \vec{k}_n)$, is defined by

$$\beta_n(\vec{k}_1 \dots \vec{k}_n) = \frac{U_n(\vec{k}_1 \dots \vec{k}_n)}{\prod_{i=1}^n U_1(\vec{k}_i)}. \quad (2.5)$$

Vanishing of β_n is equivalent to vanishing of U_n . Our fundamental assumption is:

Assumption I: All correlation functions β_n with $n \geq 3$, i.e. all functions U_n with $n \geq 3$, will be replaced by zero.

Using this, the matrix element in (2.2) can be reduced to sums of products of $U_1(\vec{k})$ and $U_2(\vec{k}_1, \vec{k}_2)$, and by rearranging terms we get

$$e^{-\alpha F_N} = \frac{1}{N!} \sum_{N_2} \frac{N!}{2^{N_2} N_2! (N - 2N_2)!} \frac{2^{N_2} N_2!}{N_2!} \times \\ \times \sum_{\vec{k}_1 \dots \vec{k}_N} U_2(\vec{k}_1, \vec{k}_2) \dots U_2(\vec{k}_{2N_2-1}, \vec{k}_{2N_2}) U_1(\vec{k}_{2N_2+1}) \dots U_1(\vec{k}_N). \quad (2.6)$$

The combinatorial factors in (2.6) are determined as follows:

(a) There are $N!/2^{N_2} N_2! (N - 2N_2)!$ ways of choosing the $k - s$ which are to be attached to a $U_1(\vec{k})$;

(b) The $2N_2$ momenta \vec{k} which go into $U_2 - s$ can be paired in $2^{N_2} (2N_2 - 1)(2N_2 - 3) \dots 5 \cdot 3 \cdot 1 = 2^{N_2} N_2! / N_2!$ ways. (One has to bear in mind here that since we are dealing with Boltzmann atoms, $U(\vec{k}, \vec{k}')$ is not symmetrical in (\vec{k}, \vec{k}') . We shall return to this point later in this section.)

Going over to the grand canonical ensemble by

$$e^{-\alpha \Omega} = \sum z^N e^{-\alpha F_N} \quad (2.7)$$

with

$$z = e^{\alpha \mu} \quad (2.8)$$

where μ is the chemical potential, z the "activity", we get

$$e^{-\alpha \Omega} = \sum_N \sum_{N_2} \frac{z^N}{N_2! (N - 2N_2)!} \sum_{\vec{k}_1 \dots \vec{k}_N} U_2(\vec{k}_1, \vec{k}_2) \dots U_2(\vec{k}_{2N_2-1}, \vec{k}_{2N_2}) \times \\ \times U_1(\vec{k}_{2N_2+1}) \dots U_1(\vec{k}_N) = \sum_{N_1} \sum_{N_2} \frac{z^{N_1+2N_2}}{N_1! N_2!} \times \\ \times \sum_{\vec{k}_1 \dots \vec{k}_{2N_2}} U_2(\vec{k}_1, \vec{k}_2) \dots U_2(\vec{k}_{2N_2-1}, \vec{k}_{2N_2}) \sum_{\widehat{k}_1 \dots \widehat{k}_{N_1}} U_1(\widehat{k}_1) \dots U_1(\widehat{k}_{N_1}) \quad (2.9)$$

with $N_1 = N - 2N_2$. The last expression splits into two factors, so that

$$\Omega = \Omega_1 + \Omega_2 \quad (2.10)$$

with

$$e^{-\alpha\Omega_1} = \sum_{N_1} \frac{z^{N_1}}{N_1!} \sum_{\vec{k}_1 \cdots \vec{k}_{N_1}} U_1(\vec{k}) \cdots U(\vec{k}_{N_1}) \quad (2.11)$$

and

$$e^{-\alpha\Omega_2} = \sum_{N_2} \frac{z^{2N_2}}{N_2!} \sum_{\vec{k}_1 \cdots \vec{k}_{2N_2}} U_2(\vec{k}_1, \vec{k}_2) \cdots U_2(\vec{k}_{2N_2-1}, \vec{k}_{2N_2}). \quad (2.12)$$

Equation (2.10) expresses the chemical equilibrium property (law of partial pressures). Equation (2.11) is the grand canonical partition function for a free gas of atoms. A standard evaluation leads to

$$\Omega_1(\mu) = -kT e^{\alpha\mu} \sum_{\vec{k}} U_1(\vec{k}) \quad (2.13)$$

or, using (2.3')

$$\Omega_1(\mu) = -kT e^{\alpha\mu} \frac{V}{\lambda^3} \quad (2.14)$$

where

$$\lambda = \left[4\pi \frac{\hbar^2}{2m kT} \right]^{\frac{1}{2}} \quad (2.15)$$

is the mean thermal wave length of a particle. Equation (2.12) can be expressed by the second virial coefficient per particle, b . One has⁶⁾

$$\sum_{\vec{k}_1 \vec{k}_2} U_2(\vec{k}_1, \vec{k}_2) = -\frac{V}{\lambda^6} b. \quad (2.16)$$

The virial coefficient b can be written⁶⁾

$$b = -(\sqrt{2}\lambda)^3 \left\{ \sum_s e^{-\alpha E_s} + \sum_l \frac{2l+1}{\pi} \int_0^\infty dE' e^{-\alpha E'} \frac{d\eta_l(E')}{dE'} \right\} \quad (2.17)$$

where E_s are the energies of the bound states, $\eta_l(E')$ the scattering phase to angular momentum l at energy E' . Inserting this, we get

$$\Omega_2(\mu) = \Omega'_2(\mu) + \Omega''_2(\mu) \quad (2.18)$$

with

$$\Omega'_2(\mu) = -kT e^{2\alpha\mu} \frac{V \cdot 2^{3/2}}{\lambda^3} \sum_s e^{-\alpha E_s} \quad (2.19)$$

$$\Omega''_2(\mu) = -kT e^{2\alpha\mu} \frac{V \cdot 2^{3/2}}{\lambda^3} \sum_l \frac{2l+1}{\pi} \int_0^\infty dE' \frac{d\eta_l}{dE'} e^{-\alpha E'}. \quad (2.20)$$

If there is no appreciable scattering, then $\Omega_2'' = 0$. If then we measure the energy levels E_s from the ground state energy E_0 of the molecule:

$$E'_s = E_s - E_0 \quad (2.21)$$

we can write (2.20) as follows:

$$\Omega_2'(\mu) = -kT e^{\alpha(2\mu - E_0)} \frac{V}{(\lambda/\sqrt{2})^3} \sum_s e^{-\alpha E'_s}. \quad (2.22)$$

This is identical with the grand canonical partition function of a system of Boltzmann particles with mass $2m$ ($\lambda/\sqrt{2}$ is the mean thermal wave length for mass $2m$) with an internal degree of freedom (s) giving rise to energy levels E'_s , and at a chemical potential $2\mu - E_0$. (2.18), therefore, becomes identical with the thermodynamic recipe. (Appendix I, Equation 7.)

Since we have consistently employed Boltzmann statistics, the sum over the internal states (s) of the molecule includes all dynamically possible such states, regardless of their symmetry properties. For actual gases, however, even in the high-temperature region where Boltzmann statistics holds for the translational motion, the symmetry properties are important for the internal wave function. They require that in (2.22) one should take into account only properly symmetrized states. This forbids one out of every two rotational levels. In the limit of temperatures high enough so that kT is large compared to the spacing of rotational levels, this amounts to reducing the sum over s in (2.22) by half. (2.22) should, therefore, be replaced by

$$\Omega_2'(\mu) = -kT e^{\alpha(2\mu - E_0)} \frac{V}{(\lambda/\sqrt{2})^3} \frac{1}{2} \sum_s e^{-\alpha E'_s}. \quad (2.22')$$

The insertion of this factor $\frac{1}{2}$ is a well-known recipe in Boltzmann statistics; it enables the latter to be applied in a region where it is strictly no longer valid. Our treatment could easily be refined so as to yield the factor $\frac{1}{2}$ automatically, by symmetrizing $U_2(\vec{k}_1, \vec{k}_2)$. Since, however, this will automatically be achieved by the general treatment in the later sections, we are not going into this question here.

In the general case when the scattering is not negligible, (2.18/20) furnish the required quasi-chemical equilibrium approximation for

an interacting Boltzmann gas. Defining the number of "molecules", N'_2 , and the number of "pseudomolecules", N''_2 , by

$$\begin{aligned} N'_2 &= -\frac{\partial \Omega_2'}{\partial \mu} \\ N''_2 &= -\frac{\partial \Omega_2''}{\partial \mu} \end{aligned} \quad (2.23)$$

and calling $N'_2 + N''_2 = N_2$, $N_2 = -\partial \Omega_2 / \partial \mu$, the equation of state becomes

$$pV = NkT \left(1 - \frac{N_2}{N}\right) \quad (2.24)$$

where

$$\frac{N_2}{(N - N_2)^2} = \frac{b}{V}. \quad (2.25)$$

This is *not* identical with the virial series up to the second term; it reduces to it for $N_2 \ll N$. For bound states only, (2.25) is, in fact, the law of mass action. For the general case, $N_2 \neq 0$, the discussion of the validity of assumption I in section 5 indicates that for a Boltzmann system, where there is no quenching, assumption I can only be valid as long as $N''_2 \ll N$, and, therefore, the quasi-chemical equilibrium theory (2.18/20) reduces to the virial expansion as far as scattering states are concerned. We are, therefore, not going to discuss the Boltzmann case any further.

3. The Fermi Case: Quenching Factors.

We shall now carry through our programme for the general case of "atoms" obeying the exclusion principle. We attack the problem quite generally, allowing for internal degrees of freedom (spin) of the atoms, and even allowing external fields. The partition function for N interacting atoms then is

$$e^{-\alpha F_N} = \text{Trace} (e^{-\alpha H_N}) \quad (3.1)$$

where H_N is the Hamiltonian for the free-particle system, and the trace is to be extended over completely antisymmetrical states only. In terms of the eigenstates (k) of H_1 for a single particle (3.1) can be written

$$e^{-\alpha F_N} = \frac{1}{N!} \sum_P (-1)^P \sum_{k \dots k_N} \langle k_1, \dots, k_N | e^{-\alpha H_N} | k'_1, \dots, k'_N \rangle \quad (3.2)$$

where each k_1 runs independently over all single-particle states, and where \sum_P is a summation over all permutations

$$P = \begin{pmatrix} k_1, \dots, k_N \\ k'_1, \dots, k'_N \end{pmatrix}. \quad (3.3)$$

Instead of the U -functions and correlation functions of section 2 we now have to consider “ U -matrices” and “correlation matrices”:

(i) “One-particle U -matrix”:

$$\langle k_1 | U_1 | k'_1 \rangle \equiv \langle k_1 | e^{-\alpha H_1} | k'_1 \rangle = \delta_{k_1 k'_1} U_1(k_1) \quad (3.4)$$

where

$$U_1(k_1) = e^{-\alpha \varepsilon_{k_1}} \quad (3.5)$$

is the Boltzmann factor, and where

$$H_1 |k\rangle = \varepsilon_k |k\rangle. \quad (3.5')$$

(ii) “Two-particle U -matrix”:

$$\langle k_1 k_2 | U_2 | k'_1 k'_2 \rangle = \langle k_1 k_2 | e^{-\alpha H_2} | k'_1 k'_2 \rangle - \langle k_1 | U_1 | k'_1 \rangle \langle k_2 | U_1 | k'_2 \rangle \quad (3.4')$$

$\langle k_1 k_2 | U_2 | k'_1 k'_2 \rangle$ is not in general diagonal; its diagonal elements are the two-particle U -function of equation (2.3'). The “two-particle correlation matrix” is

$$\langle k_1 k_2 | \beta_2 | k'_1 k'_2 \rangle = \frac{\langle k_1 k_2 | U_2 | k'_1 k'_2 \rangle}{[U_1(k_1) U_1(k_2) U_1(k'_1) U_1(k'_2)]^{1/2}}. \quad (3.6)$$

(iii) The higher U -matrices and correlation matrices can be defined correspondingly; we are not going to do so explicitly, since our basic assumption again is:

Assumption I: All higher U -matrices, and, therefore, all higher correlation matrices can be neglected.

As in section 2, this enables us to express (3.1) in terms of U_1 and U_2 only:

$$\begin{aligned} e^{-FN} &= \sum_{k_1 \dots k_N} \sum_P \sum_{N_2} \frac{1}{N!} \frac{N!}{2^{N_2} (N-2N_2)!} \frac{2^{N_2} N_2!}{N_2!} (-1)^P \times \\ &\times \langle k_1 k_2 | U_2 | k'_1 k'_2 \rangle \dots \langle k_{2N_2-1} k_{2N_2} | U_2 | k'_{2N_2-1} k'_{2N_2} \rangle \times \\ &\times \langle k_{2N_2+1} | U_1 | k'_{2N_2+1} \rangle \dots \langle k_N | U_1 | k'_N \rangle. \end{aligned} \quad (3.7)$$

Let us consider herein a term with fixed number N_2 of U_2 -factors and fixed states k_i , and investigate the effect of the various permutations P . First, consider a permutation

$$P' = \begin{pmatrix} k_1, \dots, k_{2N_2}, k_{2N_2+1}, \dots, k_{i-1}, k_i, k_{i+1}, \dots, k_j, \dots, k_N \\ k'_1, \dots, k'_{2N_2}, k'_{2N_2+1}, \dots, k'_{i-1}, k_j, k'_{i+1}, \dots, k_i, \dots, k'_N \end{pmatrix} \quad (3.8)$$

in which, among other things, two states k_i and k_j belonging to U_1 -s, are interchanged. The contribution from P' can be combined with the one from the permutation P in which this interchange of k_i and k_j has been reversed, other things remaining equal:

$$P = (k_i k_j) \cdot P'$$

where $(k_i k_j)$ is the interchange of k_i and k_j . Since U_1 is diagonal, P' only gives a contribution when $k_i = k_j$; furthermore, $(-1)^P = -(-1)^{P'}$; therefore, the contribution from P' just cancels the contribution from P in case $k_i = k_j$ and is zero for $k_i \neq k_j$. We can, therefore, restrict ourselves in (3.7) to the subclass of permutations P which do not contain any interchange among states belonging to U_1 -factors, provided we restrict the summation over the states appearing in U_1 so that no two of them are equal, i.e. provided we fulfill the requirement of the Pauli principle.

Next, we consider permutations P' leading from a U_2 -factor to a U_1 -factor:

$$\begin{pmatrix} k_1, \dots, k_i, \dots, k_{2N_2}, k_{2N_2+1}, \dots, k_j, \dots, k_N \\ k'_1, \dots, k'_j, \dots, k_{2N_2}, k'_{2N_2+1}, \dots, k_i, \dots, k'_N \end{pmatrix} \quad (3.10)$$

Again, we can absorb the contribution of P' into the one of

$$P = (k_i k_j) \cdot P'. \quad (3.11)$$

As above, since U_1 is diagonal, P' gives zero contribution unless $k_i = k_j$; if $k_i = k_j$, the contribution of P' just cancels the contribution from P . Therefore, we may drop all the permutations linking U_2 -factors to U_1 -factors, provided we restrict the sum over states in (3.7) in such a way that no k_i ($i = 1, 2, \dots, 2N_2$) may equal any of the k_{2N_2+1}, \dots, k_N .

Using these simplifications, we are now in a position to rewrite (3.7) in a way which allows the system to be separated into atoms and (pseudo-) molecules:

$$\begin{aligned} e^{-\alpha F_N} &= \sum_{N_2} \frac{1}{N_2!(N-2N_2)!} \sum_{P_2} (-1)^{P_2} \times \\ &\times \sum_{k_1 \dots k_{2N_2}} \langle k_1 k_2 | U_2 | k'_1 k'_2 \rangle \dots \langle k_{2N_2-1} k_{2N_2} | U_2 | k'_{2N_2-1} k'_{2N_2} \rangle \times \\ &\times \sum_{k_{2N_2+1} \dots k_N} U_1(k_{2N_2+1}) \dots U_1(k_N). \end{aligned} \quad (3.12)$$

P_2 here runs over all the permutations of the $2N_2$ states k_1, \dots, k_{2N_2} . The dash on the summation over the states k_{2N_2+1}, \dots, k_N indicates that the sum is subject to the limitations: (i) no two k_i ($i = 2N_2 + 1, \dots, N$) are to be equal; (ii) no k_i ($i = 2N_2 + 1, \dots, N$) may assume any of the values k_1, \dots, k_{2N_2} . Going over to the grand canonical ensemble

$$e^{-\alpha\Omega} = \sum_N e^{-\alpha F_N} z^N \quad (3.13)$$

we get, with $N_1 = N - 2N_2$:

$$e^{-\alpha\Omega} = \sum_{N_2} \frac{z^{2N_2}}{N_2!} \sum_{P_2} (-1)^{P_2} \sum_{k_1 \dots k_{2N_2}} \langle k_1 k_2 | U_2 | k'_1 k'_2 \rangle \dots \\ \dots \langle k_{2N_2-1} k_{2N_2} | U_2 | k'_{2N_2-1} k'_{2N_2} \rangle \sum_{N_1} \frac{z^{N_1}}{N_1!} \sum_{\hat{k}_1 \dots \hat{k}_{N_1}} U_1(\hat{k}_1) \dots U_1(\hat{k}_{N_1}) \quad (3.14)$$

where the \hat{k}_i run over all single-particle states with the exception of the set k_1, \dots, k_{2N_2} , and such that no two \hat{k}_i are identical. The sum

$$e^{-\alpha\Omega_1} \equiv \sum_{N_1} \frac{z^{N_1}}{N_1!} \sum'_{\hat{k}_1 \dots \hat{k}_{N_1}} U_1(\hat{k}_1) \dots U_1(\hat{k}_{N_1}) \quad (3.15)$$

under the above limitations can now easily be performed. It is equal to

$$e^{-\alpha\Omega_1} = \prod'_k [1 + z U_1(k)] \quad (3.16)$$

where k runs over all states with the exception of the set k_1, \dots, k_{2N_2} . We rewrite (3.16) as

$$e^{-\alpha\Omega_1} = \prod_k [1 + z U_1(k)] \cdot \prod_{i=1}^{2N_2} \frac{1}{1 + z U_1(k_i)} \quad (3.17)$$

where k now runs over all single-particle states. The first product in (3.17) is exactly the grand canonical partition function of a free Fermi gas:

$$e^{-\alpha\Omega_F} = \prod_k [1 + z U_1(k)] \quad (3.18)$$

and, therefore (3.14) becomes

$$e^{-\alpha\Omega(\mu)} = e^{-\alpha\Omega_F(\mu)} e^{-\alpha\Omega_M(\mu)} \quad (3.19)$$

with

$$e^{-\alpha\Omega_M(\mu)} = \sum_{N_2} \frac{z^{2N_2}}{N_2!} \sum_{P_2} (-1)^{P_2} \sum_{k_1 \dots k_{2N_2}} \times \\ \times \langle k_1 k_2 | U_2 | k'_1 k'_2 \rangle \dots \langle k_{2N_2-1} k_{2N_2} | U_2 | k'_{2N_2-1} k'_{2N_2} \rangle \cdot \prod_{i=1}^{2N_2} q(k_i) \quad (3.20)$$

where we have put

$$q(k) = 1 - n(k) = \frac{1}{1 + z U_1(k)}. \quad (3.21)$$

$n(k)$ is the Fermi occupation number of state k , and $q(k)$ is, therefore, the quenching factor (1.2). The quenching factors in (3.20) can now be absorbed into the U_2 -matrices. Since the set (k'_1, \dots, k'_{2N_2}) is merely a permutation of the set (k_1, \dots, k_{2N_2}) , we may replace

$$\prod_{i=1}^{2N_2} q(k_i) \quad \text{by} \quad \prod_{i=1}^{2N_2} [q(k_i) q(k'_i)]^{\frac{1}{2}}.$$

Now we define the "quenched" U_2 -matrix \tilde{U}_2 by

$$\langle k_1 k_2 | \tilde{U}_2 | k'_1 k'_2 \rangle \equiv [q(k_1) q(k_2)]^{\frac{1}{2}} \langle k_1 k_2 | U_2 | k'_1 k'_2 \rangle [q(k'_1) q(k'_2)]^{\frac{1}{2}} \quad (3.22)$$

so that U_2 is a hermitian matrix. Equation (3.20) then becomes (dropping the now superfluous subscripts 2):

$$e^{-\alpha \Omega_M(\mu)} = \sum_N \frac{z^{2N}}{N!} \sum_P (-1)^P \sum_{k_1 \dots k_{2N}} \times \\ \times \langle k_1 k_2 | \tilde{U}_2 | k'_2 k'_2 \rangle \cdots \langle k_{2N-1} k_{2N} | \tilde{U}_2 | k'_{2N-1} k'_{2N} \rangle \quad (3.23)$$

The chemical equilibrium property now follows from (3.18, 19, 23):

$$\Omega(\mu) = \Omega_F(\mu) + \Omega_M(\mu) \quad (3.24)$$

The grand canonical partition function is the sum of the partition functions of two independent⁷⁾ systems: a free Fermi gas and a system described by Ω_M . The task of evaluating the latter is taken up in section 4.

4. Evaluation of $\Omega_M(\mu)$.

So far, we have shown that, as long as assumption I holds, the gas of interacting Fermi atoms behaves like a free Fermi gas in chemical equilibrium with another independent system which is determined by the "quenched" \tilde{U}_2 -matrix only. We now proceed to evaluate the partition function of the latter system as given by (3.23). We follow as closely as possible the "cycle integral" treatment of the perfect Bose gas⁸⁾ which in the k -representation runs as follows:

For a perfect Bose gas, the grand canonical partition function is

$$e^{-\alpha\Omega_B} = \sum_N \frac{z^N}{N!} \sum_P \sum_{k_1 \dots k_N} \langle k_1 | U_1 | k'_1 \rangle \dots \langle k_N | U_1 | k'_N \rangle \quad (4.1)$$

where $P = \binom{k'}{k}$ runs over all permutations. Decomposing P into cycles, the product of N factors U_1 splits in the same way into "cycle-products" of the type

$$\langle k_{i_1} | U_1 | k_{i_2} \rangle \langle k_{i_2} | U_1 | k_{i_3} \rangle \dots \langle k_{i_{l-1}} | U_1 | k_{i_l} \rangle \langle k_{i_l} | U_1 | k_{i_1} \rangle \quad (4.2)$$

The important property here is that such a cycle product contains with every k_i also the permuted one $k'_i = k_j$, so that there are no "links" between cycles. Now we define the "cycle coefficient" Φ_l by

$$\Phi_l = \frac{1}{l!} \sum_{P'} \sum_{k_1, \dots, k_l} \langle k_1 | U_1 | k'_1 \rangle \dots \langle k_l | U_1 | k'_l \rangle \quad (4.3)$$

where P' runs over all $(l-1)!$ cyclic permutations of k_1, \dots, k_l . Using this, (4.1) can be written

$$e^{-\alpha\Omega_B} = \sum_N \frac{z^N}{N!} \sum_{\substack{(m_1, \dots, m_N) \\ (\sum m_l l = N)}} A^N(m_1, m_2, \dots, m_N) (1! \Phi_1)^{m_1} (2! \Phi_2)^{m_2} (l! \Phi_l)^{m_l} \quad (4.4)$$

where $A^N(m_1, m_2, \dots, m_N)$ is the number of permutations of N elements which split into m_1 cycles of length 1, m_2 cycles of length 2, \dots , m_N cycles of length N ; or, in other words, the number of partitions of N elements into $m_1 \cdot 1 + m_2 \cdot 2 + \dots + m_N \cdot N$. This number is

$$A^N(m_1, m_2, \dots, m_N) = \frac{N!}{\prod_{l=1}^N m_l! l^{m_l}}. \quad (4.5)$$

Inserting this into (4.4) we get

$$e^{-\alpha\Omega_B} = \sum_N z^N \sum_{\substack{(m_1, \dots, m_N) \\ (\sum m_l l = N)}} \prod_{l=1}^N \frac{(l! \Phi_l)^{m_l}}{l! m_l! m_l!} = \sum_{(m_l)} \prod_{l=1}^{\infty} \frac{z^{l m_l} \Phi_l^{m_l}}{m_l!} = \prod_{l=1}^{\infty} e^{z^l \Phi_l} \quad (4.6)$$

or, finally,

$$-\alpha\Omega_B = \sum_{l=1}^{\infty} z^l \Phi_l \quad (4.7)$$

Φ_l , (4.3), can be easily evaluated in this case, using (3.4):

$$\Phi_l = \frac{(l-1)!}{l!} \sum_k [U_1(k)]^l. \quad (4.8)$$

Inserted into (4.7) this yields the well-known result for the perfect Bose gas

$$-\alpha \Omega_B = + \sum_k \sum_l \frac{[z U_1(k)]^l}{l} = - \sum_k \log (1 - z U_1(k)). \quad (4.9)$$

In order to pattern the evaluation of (3.23) along the above treatment, we have to define a "reducibility" of permutations which serves the same purpose as the cycle decomposition in (4.1). Matters are complicated in this case by the fact that the matrices \tilde{U}_2 in (3.23) always contain pairs of states, so that a cycle within P does not, in general, lead to a chain of U_2 -matrices which has no "links" to others. We therefore define "reducibility" of a permutation P by just the required property: A permutation P is called reducible if there exists a subset of l ($< N$) matrices U_2 whose rear indices (k') form a permutation of the front indices of the same matrices. E.g. for $N = 3$,

$$\langle k_1 k_2 | \tilde{U}_2 | k_3 k_4 \rangle \langle k_3 k_4 | \tilde{U}_2 | k_1 k_2 \rangle \langle k_5 k_6 | \tilde{U}_2 | k_6 k_5 \rangle$$

belongs to a reducible permutation. It is made up of the irreducible permutation.

and

$$\langle k_1 k_2 | \tilde{U}_2 | k_3 k_4 \rangle \langle k_3 k_4 | \tilde{U}_2 | k_1 k_2 \rangle$$

$$\langle k_5 k_6 | \tilde{U}_2 | k_6 k_5 \rangle$$

On the other hand,

$$\langle k_1 k_2 | \tilde{U}_2 | k_3 k_5 \rangle \langle k_3 k_4 | \tilde{U}_2 | k_1 k_6 \rangle \langle k_5 k_6 | \tilde{U}_2 | k_4 k_2 \rangle$$

belongs to an irreducible permutation.

Now we define

$$\Phi_l = \frac{1}{l!} \sum_P' (-1)^P \sum_{k_1 \dots k_{2l}} \langle k_1 k_2 | \tilde{U}_2 | k'_1 k'_2 \rangle \dots \langle k_{2l-1} k_{2l} | \tilde{U}_2 | k'_{2l-1} k'_{2l} \rangle \quad (4.10)$$

where the sum Σ' is restricted to irreducible permutations. (3.23) can then be written, in analogy to (4.4)

$$e^{-\alpha \Omega_M} = \sum_N \frac{z^{2N}}{N!} \sum_{\substack{(m_1, \dots, m_N) \\ (\Sigma l m_l = N)}} B^N(m_1, \dots, m_N) (1! \Phi_1)^{m_1} \dots (N! \Phi_N)^{m_N}. \quad (4.11)$$

The number $B^N(m_1, m_2, \dots, m_N)$ of permutations of N pairs of states which are reducible into $m_1 \cdot 1$ pair, $m_2 \cdot 2$ pairs etc. is equal to the number of partitions of N pairs into $m_1 \cdot 1 + m_2 \cdot 2 + \dots + m_N \cdot N$

pairs, and is, therefore, equal to $A^N(m)$ (4.5). Inserting this into (4.11) we get, in complete analogy to (4.7)

$$-\alpha \Omega_M = \sum_{l=1}^{\infty} \Phi_l z^{2l} = \sum_{l=1}^{\infty} \Phi_l e^{2\alpha \mu l} \quad (4.12)$$

with Φ_l given by (4.10).

In order to proceed with the evaluation of the "cycle coefficients" Φ_l we bring the matrix \tilde{U}_2 into diagonal form:

$$\langle \sigma | \tilde{U}_2 = u_\sigma \langle \sigma | \quad (4.13)$$

or

$$\langle k_1 k_2 | \tilde{U}_2 | k'_1 k'_2 \rangle = \sum_{\sigma} \langle k_1 k_2 | \sigma \rangle u_\sigma \langle \sigma | k'_1 k'_2 \rangle \quad (4.14)$$

where

$$\sum_{k_1 k_2} \langle \sigma_1 | k_1 k_2 \rangle \langle k_1 k_2 | \sigma_2 \rangle = \delta_{\sigma_1 \sigma_2} \quad (4.15)$$

The nature of the spectrum u_σ will be discussed in the next section.

It is useful also at this stage to introduce symmetrized and anti-symmetrized wave functions by

$$\langle \sigma | k_1 k_2 \rangle = \frac{1}{\sqrt{2}} \langle \sigma | [k_1 k_2] \rangle + \frac{1}{\sqrt{2}} \langle \sigma | \{k_1 k_2\} \rangle \quad (4.16)$$

$$\langle \sigma | [k_1 k_2] \rangle = - \langle \sigma | [k_2 k_1] \rangle; \quad \langle \sigma | \{k_1 k_2\} \rangle = + \langle \sigma | \{k_2 k_1\} \rangle \quad (4.17)$$

$$\sum_{k_1 k_2} \langle \sigma_1 | [k_1 k_2] \rangle \langle [k_1 k_2] | \sigma_2 \rangle = \delta_{\sigma_1 \sigma_2} \quad (4.18)$$

We now insert (4.13/18) into (4.10); obviously, due to the factor $(-1)^P$, the symmetrical wave functions always cancel, and we get

$$\begin{aligned} \Phi_l = & \frac{1}{2^l l!} \sum_P (-1)^P \sum_{\sigma_1 \dots \sigma_l} u_{\sigma_1} \dots u_{\sigma_l} \sum_{k_1 \dots k_{2l}} \times \\ & \times \langle [k_1 k_2] | \sigma_1 \rangle \langle \sigma_1 | [k'_1 k'_2] \rangle \dots \langle [k_{2l-1} k_{2l}] | \sigma_l \rangle \langle \sigma_l | [k'_{2l-1} k'_{2l}] \rangle \end{aligned} \quad (4.19)$$

The permutation P here runs over all irreducible permutations of the $2l$ states k_1, \dots, k_{2l} . We now interpret the states $\langle \sigma | [k_1 k_2] \rangle$ as states of a (pseudo-) molecule composed of the two atoms 1 and 2. Most permutations P in fact interchange atoms between molecules; only the subclass of permutations which leaves each "natural pair" (k_{2i-1}, k_{2i}) intact actually interchanges molecules. We show here that by restricting ourselves to this subclass of permutations

in (4.19) we get Bose statistics for the molecules. In Appendix I, (4.19) is evaluated generally, and it is shown there that the permutations which exchange atoms between different molecules give negligible contribution, although their number by far outweighs the number of permutations interchanging molecules as a whole.

The irreducible permutations which interchange molecules as a whole are easily characterized: Each such permutation consists of an irreducible, i.e. cyclic permutation of the l "natural pairs" (k_{2i-1}, k_{2i}) ($i = 1, \dots, l$), multiplied by an arbitrary number of transpositions $(k_{2i-1}, k_{2i}) \rightarrow (k_{2i}, k_{2i-1})$ of natural pairs. There are, therefore, $(l-1)! 2^l$ such permutations. Each of them gives the same contribution, since the minus sign occurring in the wave function of a molecule upon transposition of its arguments is taken care of by the factor $(-1)^P$ in front. The contribution of these permutations to (4.19) can, therefore, be written

$$\begin{aligned} \Phi_l^1 = & \frac{2^l(l-1)!}{2^l l!} \sum_{\sigma_1 \dots \sigma_l} u_{\sigma_1} u_{\sigma_2} \dots u_{\sigma_l} \times \\ & \times \sum_{k_1 \dots k_{2l}} \langle [k_1 k_2] | \sigma_1 \rangle \langle \sigma_1 | [k_3 k_4] \rangle \langle [k_3 k_4] | \sigma_2 \rangle \langle \sigma_2 | [k_5 k_6] \rangle \dots \\ & \dots \langle [k_{2l-1} k_{2l}] | \sigma_l \rangle \langle \sigma_l | [k_1 k_2] \rangle. \end{aligned} \quad (4.20)$$

The summation over the states k can now easily be performed, using (4.18), and we get

$$\Phi_l^1 = \frac{1}{l} \sum_{\sigma} (u_{\sigma})^l. \quad (4.20')$$

Inserting this into (4.12) we get for the contribution of the terms considered to the potential Ω_M :

$$-\alpha \Omega'_M = \sum_{l=1}^{\infty} \sum_{\sigma} \frac{(z^2 u_{\sigma})^l}{l} = - \sum_{\sigma} \log(1 - z^2 u_{\sigma}) \quad (4.21)$$

which has indeed the form of Bose statistics (4.9). In sections 5 and 6 we shall discuss this result in detail.

5. The Correlation Matrix for Free Particles.

This section is devoted to a study of the spectrum u_{σ} of the matrix \tilde{U}_2 . Whereas, however, up to now we have not specified the states k of the free atoms, thereby including in our treatment particles in external fields, we now restrict ourselves to free particles

*

in a volume V with periodical boundary conditions. The states k of the free atoms are then given by a wave vector \vec{k} and an "internal" variable s which takes only discrete values, like e.g. the spin: $(k) \rightarrow (\vec{k}, s)$. Furthermore, we are only going to consider translationally invariant interactions, so that \tilde{U}_2 conserves total momentum. Introducing, therefore, for a pair of atoms $(\vec{k}_1, s_1; \vec{k}_2, s_2)$ the center of gravity momentum $\vec{K}_{12} = \vec{k}_1 + \vec{k}_2$ and the relative momentum $\vec{\kappa}_{12} = \frac{1}{2}(\vec{k}_1 - \vec{k}_2)$, we can write

$$\begin{aligned} \langle \vec{k}_1 s_1, \vec{k}_2 s_2 | \tilde{U}_2 | \vec{k}'_1 s'_1, \vec{k}'_2 s'_2 \rangle = \\ = \langle \vec{\kappa}_{12}, s_1 s_2 | \tilde{U}_2(\vec{K}_{12}) | \vec{\kappa}'_{12} s'_1 s'_2 \rangle \delta(\vec{K}_{12} - \vec{K}'_{12}). \end{aligned} \quad (5.1)$$

It follows at once that the eigenvectors $\langle \sigma | [\vec{k}_1 s_1; \vec{k}_2 s_2] \rangle$ of \tilde{U}_2 must have the form

$$\langle \vec{K} S | [\vec{k}_1 s_1, \vec{k}_2 s_2] \rangle = \delta(\vec{k}_1 + \vec{k}_2 - \vec{K}) \langle \vec{K} S | \vec{\kappa}_{12} s_1 s_2 \rangle$$

where

$$\langle \vec{K} S | \vec{\kappa}_{12} s_1 s_2 \rangle = - \langle \vec{K} S | \vec{\kappa}_{21} s_2 s_1 \rangle. \quad (5.2)$$

Here, S is some "internal quantum number" of the molecule. The eigenvalue of \tilde{U}_2 in the state $\langle \vec{K} S |$, (5.2), shall be written $u_S(\vec{K})$; the equation determining $u_S(\vec{K})$ is

$$\begin{aligned} \sum_{\vec{\kappa}'_{12} s'_1 s'_2} \langle \vec{K} S | \vec{\kappa}'_{12} s'_1 s'_2 \rangle \langle \vec{\kappa}'_{12} s'_1 s'_2 | \tilde{U}_2(\vec{K}) | \vec{\kappa}_{12} s_1 s_2 \rangle = \\ = u_S(\vec{K}) \langle \vec{K} S | \vec{\kappa}_{12} s_1 s_2 \rangle. \end{aligned} \quad (5.3)$$

Equation (4.21) now reads

$$- \alpha \Omega'_M = - \sum_S \sum_{\vec{K}} \log(1 - z^2 u_S(\vec{K})). \quad (5.4)$$

In the limit of large volume V this becomes

$$- \alpha \Omega'_M = - \frac{V}{(2\pi)^3} \sum_S \int d^3 K \log(1 - z^2 u_S(\vec{K})). \quad (5.5)$$

We are now going to investigate the spectrum $u_S(\vec{K})$, i.e. the solutions of the "integral" equation (5.3). Going over to infinite volume, (5.3) goes over into

$$\begin{aligned} \sum_{s'_1 s'_2} \int d^3 \kappa' \varphi_{S\vec{K}}(\vec{\kappa}' s'_1 s'_2) \langle \vec{\kappa}' s'_1 s'_2 | \tilde{U}_2(\vec{K}) | \vec{\kappa} s_1 s_2 \rangle \\ = u_S(\vec{K}) \varphi_{S\vec{K}}(\vec{\kappa} s_1 s_2) \end{aligned} \quad (5.6)$$

where the eigenfunctions

$$\varphi_{S\vec{K}}(\vec{\kappa} s_1 s_2) \equiv \left(\frac{V}{(2\pi)^3} \right)^{\frac{1}{2}} \langle \vec{K} S | \vec{\kappa} s_1 s_2 \rangle \quad (5.7)$$

are now normalized by

$$\int d^3\kappa \sum_{s_1 s_2} \varphi_{S\vec{K}}^*(\vec{\kappa} s_1 s_2) \varphi_{S'\vec{K}}(\vec{\kappa} s_1 s_2) = \delta_{SS'} \quad (5.8)$$

(5.6) is an integral equation in $\varphi_{S,\vec{K}}$ with the symmetrical kernel

$$\begin{aligned} & \langle \vec{\kappa}' s_1' s_2' | \tilde{U}_2 | \vec{\kappa} s_1 s_2 \rangle = \\ & = \left[q\left(\frac{\vec{K}}{2} + \vec{\kappa}', s_1'\right) q\left(\frac{\vec{K}}{2} - \vec{\kappa}', s_2'\right) \right]^{\frac{1}{2}} \langle \vec{\kappa}' s_1' s_2' | U_2(\vec{K}) | \vec{\kappa} s_1 s_2 \rangle \times \\ & \times \left[q\left(\frac{\vec{K}}{2} + \vec{\kappa}, s_1\right) q\left(\frac{\vec{K}}{2} - \vec{\kappa}, s_2\right) \right]^{\frac{1}{2}} = \left[q\left(\frac{\vec{K}}{2} + \vec{\kappa}', s_1\right) q\left(\frac{\vec{K}}{2} - \vec{\kappa}', s_2\right) \right]^{\frac{1}{2}} \times \\ & \times \langle \vec{\kappa}' s_1' s_2' | e^{-\alpha H} - e^{-\alpha H_0} | \vec{\kappa} s_1 s_2 \rangle \left[q\left(\frac{\vec{K}}{2} + \vec{\kappa}, s_1\right) q\left(\frac{\vec{K}}{2} - \vec{\kappa}, s_2\right) \right]^{\frac{1}{2}} \quad (5.9) \end{aligned}$$

where H and H_0 are the total and the free-particle Hamiltonian of the two-particle system, respectively. Using

$$n(\vec{k}, s) = z U_1(\vec{k}, s) q(\vec{k}, s) \quad (5.10)$$

(5.9) can also be written as

$$\begin{aligned} & z^2 \langle \vec{\kappa}' s_1' s_2' | \tilde{U}_2(\vec{K}) | \vec{\kappa} s_1 s_2 \rangle = \left[n\left(\frac{\vec{K}}{2} + \vec{\kappa}', s_1'\right) n\left(\frac{\vec{K}}{2} - \vec{\kappa}', s_2'\right) \right]^{\frac{1}{2}} \times \\ & \times \langle \vec{\kappa}' s_1' s_2' | e^{\alpha/2 H_0} e^{-\alpha H} e^{\alpha/2 H_0} - 1 | \vec{\kappa} s_1 s_2 \rangle \left[n\left(\frac{\vec{K}}{2} + \vec{\kappa}, s_1\right) n\left(\frac{\vec{K}}{2} - \vec{\kappa}, s_2\right) \right]^{\frac{1}{2}} \quad (5.11) \end{aligned}$$

a form which is more useful for discussion.

The integral equation (5.6) will be a regular integral equation and have only discrete eigenvalues, provided

(i) The kernel $\langle \vec{\kappa}' s_1' s_2' | \tilde{U}_2(\vec{K}) | \vec{\kappa} s_1 s_2 \rangle$ decreases rapidly enough for large $|\vec{\kappa}|$, $|\vec{\kappa}'|$. This is clearly an assumption on the interaction $H - H_0$. We assume that $H - H_0$ is square integrable at large $|\vec{\kappa}|$, $|\vec{\kappa}'|$.

(ii) The kernel $\langle \vec{\kappa}' s_1' s_2' | \tilde{U}_2(\vec{K}) | \vec{\kappa} s_1 s_2 \rangle$ has no δ -function singularity at $\vec{\kappa} = \vec{\kappa}'$. This is the important requirement; its failure is responsible e.g. for the fact that the spectrum of $\langle \vec{\kappa}' s_1' s_2' | e^{-\alpha H_0} | \vec{\kappa} s_1 s_2 \rangle$ is not discrete; indeed,

$$\langle \vec{\kappa}' s_1' s_2' | e^{-\alpha H_0} | \vec{\kappa} s_1 s_2 \rangle = \delta_{s_1' s_1} \delta_{s_2' s_2} \delta(\vec{\kappa} - \vec{\kappa}') e^{-\alpha(\hbar^2 \kappa^2/m)}. \quad (5.12)$$

In $\langle \vec{\kappa}' s'_1 s'_2 | e^{-\alpha H} - e^{-\alpha H_0} | \vec{\kappa} s_1 s_2 \rangle$, however, the two terms have the same δ -singularities which in general cancel against each other. The requirement is best stated in x -space. Calling \vec{x} the relative coordinate of the two atoms, the Fourier transform of $\langle \vec{\kappa}' s'_1 s'_2 | \tilde{U}_2 | \vec{\kappa} s_1 s_2 \rangle$ is the x -space \tilde{U}_2 -matrix

$$\begin{aligned} \frac{1}{(2\pi)^3} \int d^3 \vec{\kappa} \int d^3 \vec{\kappa}' e^{i\vec{\kappa}' \cdot \vec{x}} \langle \vec{\kappa}' s'_1 s'_2 | \tilde{U}_2 | \vec{\kappa} s_1 s_2 \rangle e^{-i\vec{\kappa} \cdot \vec{x}} &= \\ &\equiv \langle \vec{x}' s'_1 s'_2 | \tilde{U}_2 | \vec{x} s_1 s_2 \rangle. \end{aligned} \quad (5.13)$$

Our requirement on the kernel of (5.6) is fulfilled if $\langle \vec{x}' s'_1 s'_2 | \tilde{U}_2 | \vec{x} s_1 s_2 \rangle$ is such that $\int d^3 x \int d^3 x' |\langle \vec{x}' s'_1 s'_2 | \tilde{U}_2 | \vec{x} s_1 s_2 \rangle|$ exists and is finite: i.e., if the \tilde{U}_2 -matrix has finite range in x -space.

Under the two weak requirements (i) and (ii) the spectrum $u_s(K)$ will, therefore, be discrete⁹).

The spectrum $u_s(\vec{K})$ of \tilde{U}_2 plays a central role in our method. $u_s(\vec{K})$ in (5.4) takes the place of the expression $e^{-\alpha E_s(\vec{K})}$ which one would write down for true bosons. It is indeed the spectrum $u_s(\vec{K})$ of the \tilde{U}_2 -matrix rather than the spectrum $E_s(\vec{K})$ of the two-particle Hamiltonian which is relevant for the quasichemical equilibrium approximation. In Appendix 3 we discuss a semi-classical approach to the calculation of the spectrum $u_s(\vec{K})$ which throws some light onto the physical meaning of $u_s(\vec{K})$. We interpret the eigenvalues $u_s(K)$ as describing the energy spectrum of "pseudomolecules" whose internal structure is given by the corresponding wave-function $\varphi_{s\vec{K}}(\vec{\kappa})$ in k -space, or by its Fourier transform

$$\psi_{s\vec{K}}(\vec{x}) = \frac{1}{(2\pi)^{3/2}} \int d^3 \vec{\kappa} \varphi_{s\vec{K}}(\vec{\kappa}) e^{-i\vec{\kappa} \cdot \vec{x}} \quad (5.13')$$

in x -space.

We are now in a position to give conditions for the validity of our basic assumption I.

I. A first and obvious condition is that collisions of the pseudomolecules (i) with atoms, and (ii) with each other shall be unimportant.

II. A second condition is that the three-, or four-, etc., particle correlations should not, by some special effect, be very much stronger than the two-particle correlation. (E.g., this condition is violated if the atoms (A) form a triatomic molecule A_3 which is more stable than the diatomic molecule A_2)

III. The third condition is best understood by comparison with Fierz's theory of condensation in classical dilute gases¹¹). Fierz treats the case of a classical gas of atoms which have a short-range attractive potential, and which is dilute enough so that one can omit any volume-exclusion effects. He then shows that at high temperatures practically no molecules of any kind are formed; at a sharply defined temperature, formation of molecules in large numbers occurs suddenly, but the equilibrium favours molecules with very high atomic weight n , i.e. liquid drops. Clearly, in this case, although condition I (and II for low n) hold, our approximation is inadequate. The third condition is, therefore, that no gas-liquid transition shall occur for the temperature region to which our treatment is applied.

IV. A fourth condition is necessary if the result (5.4) which states that the pseudomolecules obey Bose statistics is to have any meaning outside the region in which this reduces to Boltzmann statistics. The deviation of (5.4) from the Boltzmann result becomes noticeable when the K -space range K_1 of $u_s(\vec{K})$ becomes comparable with or smaller than the inverse of the intermolecular distance d_2 :

$$K_1 < d_2^{-1}. \quad (5.14)$$

In order for the Bose corrections to be meaningful at all, (5.14) must not contradict any of the conditions I—III. The crucial condition is I(ii). Since in all cases of interest I(ii) requires that the size a of the pseudomolecules, i.e., the range of $\psi_{s\vec{K}}(\vec{x})$ in (5.13), be small compared to d_2 , the possibility to fulfill (5.14) requires at the same time

$$K_1 \ll a^{-1}. \quad (5.15)$$

In appendix I it is shown that the same condition (5.15) also ensures the validity of the neglect of the terms in (4.19) which interchange single atoms between different molecules.

If the above conditions are satisfied, we expect our approximation to hold. In section 6 we shall show that the conditions are fulfilled for the case of chemical equilibrium in dilute gases. For quite different reasons, the same conditions are expected to be fulfilled in the electron gas in a metal: this case is treated in section 7.

6. True Chemical Equilibrium in Gases.

As a special case, we now consider the situation of true chemical equilibrium in a gas. We neglect the quenching factors from the start; the justification for this lies in the fact that, as we shall show, our result goes over into the thermodynamical theory of chemical equilibrium. It then follows from a remark in appendix I (Equation I. 13) that we can never reach the quenched region at all. Without the quenching factors, we have $\tilde{U}_2 = U_2 = e^{-\alpha H} - e^{-\alpha H_0}$. If we assume that the correlations are due entirely to the existence of bound states we can write

$$\langle \vec{\kappa} | U_2(\vec{K}) | \vec{\kappa}' \rangle = \sum_S e^{-\alpha E_S} e^{-\alpha(\hbar^2 K^2/4m)} \varphi_S^*(\vec{\kappa}) \varphi_S(\vec{\kappa}') \quad (6.1)$$

where the sum extends over all bound states S , E_S being the energy, $\varphi_S(\vec{\kappa})$ the (κ -space) wave function of state S . The assumption (6.1) is valid if the scattering is sufficiently weak; we are not going to deal with this question here. Inserting $u_S(\vec{K})$ from (6.1) into (4.21), we get

$$-\alpha \Omega'_M = \sum_S \sum_{\vec{K}} \log \left(1 - e^{2\alpha\mu} e^{-\alpha E_S} e^{-\alpha(\hbar^2 K^2/4m)} \right). \quad (6.2)$$

Measuring all energies from the lowest eigenvalue E_0 ,

$$E'_S = E_S - E_0 \quad (6.3)$$

(6.2) reads

$$-\alpha \Omega'_M = \sum_S \sum_{\vec{K}} \log \left(1 - e^{\alpha(2\mu - E_0)} e^{-\alpha(E'_S + (\hbar^2 K^2/4m))} \right). \quad (6.4)$$

This is indeed identical with the grand-canonical partition function for a Bose gas of particles with mass $2m$ and an internal degree of freedom, S , giving rise to energy levels E'_S , and with chemical potential $(2\mu - E_0)$. (6.4), together with (3.24), is identical with the thermodynamical result (1.7). In the limit of a very dilute gas, where $e^{\alpha(2\mu - E_0)} \ll 1$, we again get the Boltzmann result (2.22) with the difference, however, that this time the sum over S runs only over internal states with antisymmetrized wave function (Equation 4.18). The factor $\frac{1}{2}$ which we had to insert ad hoc in going from (2.22) to (2.22') is, therefore, automatically contained in our present result.

We see now clearly under what conditions the thermodynamical theory of chemical equilibrium is correct:

I. Condition I must hold. (I i) is fulfilled if the average distance d_1 between atoms is large compared to the size a of the molecule (which is, strictly, different for each state S , and equal to the range of $|\psi_S(\vec{x})|^2$). (I ii) is fulfilled when the average distance d_2 between molecules is large compared to a . Comprehensively, this requires

$$\frac{N}{V} a^3 \ll 1. \quad (6.5)$$

II. Condition II must hold, i.e. the diatomic molecule must be much more stable than higher molecules; i.e. the lowest energy E'_0 of any higher molecule must fulfill

$$E'_0 - E_0 \gg kT. \quad (6.6)$$

III. The validity of this condition is ensured by the saturation property of chemical forces; once the molecule is formed, the higher correlation functions are essentially repulsive. This ensures that molecules are formed before the atoms form a liquid, if molecules exist at all. (The ultimate condensation of the molecular gas into a liquid depends on the remaining *intermolecular* correlations and is outside our scope.)

IV. This condition ensures simultaneously the validity of (6.4) in the region where the effects of Bose statistics set in and (as shown in appendix II) the permissibility of neglecting the statistical interchange of single atoms between molecules. The range K_1 of $u_S(\vec{K})$ is, here, given by

$$K_1 = \lambda^{-1} \quad (6.7)$$

where

$$\lambda = \left(\frac{2 \pi \hbar^2}{2 m kT} \right)^{\frac{1}{2}} \quad (6.8)$$

is the mean thermal wave length of a molecule. At low enough temperatures (5.15) holds automatically:

$$\lambda \gg a. \quad (6.9)$$

Therefore we can reach the degeneracy region at molecule densities which do not violate (I ii).

V. (6.1) must hold. It can be shown that when the interaction is such as to produce bound states but negligible scattering phases, this assumption is equivalent to (6.9). We are not going to prove this in detail. Rather, we take the attitude: Chemical (and quasichemical) equilibrium is not determined by the *interaction* between

atoms, but by the \tilde{U}_2 -matrix which is the primary concept. (6.2) holds exactly, when the \tilde{U}_2 -matrix is determined by the bound states only; that this is true for vanishing scattering phases, is of secondary interest. The presence of strong scattering would be incompatible with condition I, since the range of the corresponding correlation would become of order λ^{10} .

VI. The neglect of the quenching factors is quite justified by (1.13). In principle, inclusion of these factors would lead to a slight modification of the \tilde{U}_2 -matrix, i.e. to a small shift of the eigenvalues E_s . However, the magnitude of this shift would be of the same order as other things which have been neglected, namely of order $(a/\lambda)^3$, and therefore it is not consistent to include this effect.

7. Speculations on Superconductivity.

The main application we have in mind for the present method is to the electron gas in metals, as a new approach to the problem of superconductivity. This will require a detailed study of the quenched \tilde{U}_2 -matrix for electrons in metals, which has not yet been undertaken. No theory of superconductivity is, therefore, contained in this paper; however, some general results of the method seem promising enough to warrant a few speculations on the nature of this phenomenon, subject to later confirmation by a study of \tilde{U}_2 . The main task at present is to give a justification for the applicability of the present method to electrons in metals under the influence of their interactions. We investigate separately the conditions stated in section 5.

I. (i) Collisions between pseudomolecules and electrons have to be unimportant. Unlike the case of true chemical equilibrium, this cannot be justified by the low density of the system. Indeed, from this viewpoint, already the free electron theory of metals would be unjustified: the mean free path for electron-electron scattering under the influence of a *screened* Coulomb repulsion would only be of the order of a lattice distance! The justification for the free electron theory of metals has to be sought in the "quenching" effect of the Pauli principle: when the gas is highly degenerate, most scattering processes between electrons are forbidden, since the final states are already occupied. This same argument applies for collisions between electrons and pseudomolecules, and, therefore, in the case of high quenching, we can expect our approximation to hold.

Indeed, the quasichemical approximation appears as a first-order correction to the free-electron theory of metals. In a systematic way, one might imagine an expansion of the partition function of the interacting electron gas in terms of two-, three-, ... n -particle U -matrices, each of them properly "quenched" by the purely statistical correlations. In such an expansion, the free-electron theory would be the zeroth approximation, whereas the "quasichemical approximation" represents the systematic first-order correction to it.

(ii) Collisions of pseudomolecules among each other will in general, also be affected by the quenching, but this effect is more involved and at present rather obscure. One would, therefore, expect the applicability of our method to require a low density of pseudomolecules, although this might eventually turn out to be a too stringent requirement. Since we expect the condensed pseudomolecules to be the superconducting particles, even this stringent condition will always be fulfilled in the neighbourhood of the superconducting transition.

II. A formation of higher pseudomolecules in preference to diatomic ones is too unlikely a possibility to need any special comment. Even if this were so, our approximation should give reliable qualitative results, unless exclusively molecules with an odd number of electrons are formed, which would then have a Fermi-type behaviour.

III. The validity of the third condition cannot be established rigorously. Imagine the programme outlined above, of expanding the partition function of an interacting electron gas into n -particle U -matrices, carried through. For a classical gas, this is just the "cluster"-expansion¹²); for a degenerate gas, it would involve a careful sorting out of dynamical and statistical correlations, as was carried through in section 3 for the two-particle correlations, and has not, to our knowledge, been attempted so far. As discussed in conjunction with condition I, the quenching effect of the Pauli principle will greatly reduce the importance of the higher terms — as can be seen on the two-particle correlation, Equation (3.22); in fact, only through the quenching effect can this expansion have any meaning at all. Even then, however, it can happen that at low temperatures, the equilibrium suddenly shifts to very high n , giving rise to a liquid-condensation. The question which is of interest here is whether or not this effect sets in before the presence of two-electron pseudomolecules is felt. Physically, this leaves the alternative: either our theory can be applied, or the electron gas undergoes a liquid condensation. Since it is very hard to see how such a condensation

could occur without separation of phases, and, furthermore, how superconductivity could result from it, we assume that the formation of pseudomolecules is the dominant feature.

To sum up, therefore, excluding the possibility of the formation of an electron liquid in metals, it seems that the quasichemical approximation represents a consistent extension of the free electron theory of metals and should be highly suited for the discussion of superconductivity.

The question remains, whether condition IV of section 5 is fulfilled, i.e. whether the Bose statistics ever come into play. For the quenched \tilde{U}_2 -matrix (5.11), the range K_1 in center-of-gravity momentum is, in general, of the order of the Fermi momentum k_0 , i.e. equal to the range in $\vec{\kappa}$. This is certainly so for any Galilean invariant interaction, where the dependence of (5.11) on \vec{K} is entirely contained in the factors $n(\vec{K}/2 + \vec{\kappa})$. In a metal, however, we expect the correlation between electrons to be due to two causes:

(a) The Coulomb interaction. This is purely repulsive. (The exchange terms, which serve to compensate an overestimated repulsion, are already contained in the symmetrized correlation matrix!) It will, therefore, produce only negative eigenvalue of the \tilde{U}_2 -matrix. For each of them, the range in \vec{K} of $u_s(\vec{K})$ is of the same order as the range in $\vec{\kappa}$ of the wave function, and, therefore, the contribution from these eigenvalues can only be taken seriously in the Boltzmann case, i. e.

$$z^2 |u_s| \ll 1. \quad (\text{A})$$

(b) The Fröhlich interaction will in general be much weaker than the Coulomb interaction, but it has attractive parts and will, if strong enough, be able to produce one or more positive eigenvalues $u_s(\vec{K})$ of \tilde{U}_2 . Furthermore, these eigenvalues will have the required property of a short range in \vec{K} , as can be seen from the following simple argument: The Fröhlich interaction is produced by the exchange of sound waves between the two electrons. If the two electrons move with a center-of-gravity velocity exceeding the velocity of sound, the waves emitted by one will not be able to reach the other, and the interaction must vanish. We are, therefore, led to expect that the positive $u_s(\vec{K})$ contributed by the Fröhlich interaction will have the property required by condition IV, namely a short range in \vec{K} ; the range of the corresponding wave-function in $\vec{\kappa}$ will still be of order k_0 , the Fermi momentum. This being so, we can go

into the region where the Bose corrections in (5.5) become important, i.e. where

$$z^2 u_s \cong 1. \quad (\text{B})$$

Of course, strictly (B) contradicts (A), except in the case where all the negative eigenvalues due to the Coulomb repulsion are smaller in absolute value than the positive eigenvalues produced by the Fröhlich interaction. The semi-classical model of Appendice III indicates that this is the probable situation at low enough temperatures. However, even if this were not so, the contradiction is not very serious; it means that, once we enter the region (B) where the Bose effects on the positive eigenvalues set in, the terms in (5.5) contributed by the negative eigenvalues can no longer be trusted. That is, we miss certain effects of the repulsive forces which are quite noticeable, but which have nothing to do with the Bose-condensation of the positive eigenvalues in which we are, after all, mainly interested.

For the purpose of the following discussion we shall, therefore, assume, that the quasichemical equilibrium approximation is applicable to metals. The grand canonical partition function of the electron gas without external forces neglecting the spin is then given by (3.24) and (4.21), viz.

$$\begin{aligned} \Omega(\mu) = & -kT \sum_{\vec{K}} \log (1 + \exp [\alpha(\mu - \varepsilon(\vec{k}))]) + \\ & + kT \sum_s \sum_{\vec{K}} \log (1 - e^{2\alpha\mu} u_s(\vec{K})). \end{aligned} \quad (7.1)$$

The first term is the usual expression for Ω from the Fermi statistics of the free electrons, the second term arises from the effect of the two-particle correlations: $u_s(\vec{K})$ are the eigenvalues of \tilde{U}_2 :

$$\begin{aligned} e^{2\alpha\mu} \langle \vec{\kappa}' | \tilde{U}_2(\vec{K}) | \vec{\kappa} \rangle &= \left[n\left(\frac{\vec{K}}{2} + \vec{\kappa}'\right) n\left(\frac{\vec{K}}{2} - \vec{\kappa}'\right) \right]^{\frac{1}{2}} \times \\ \times \langle \vec{\kappa}' | e^{\alpha/2 H_0} e^{-\alpha H} e^{\alpha/2 H_0} - 1 | \vec{\kappa} \rangle &\left[n\left(\frac{\vec{K}}{2} + \vec{\kappa}\right) n\left(\frac{\vec{K}}{2} - \vec{\kappa}\right) \right]^{\frac{1}{2}}. \end{aligned} \quad (7.2)$$

For weak correlations, we expect the $u_s(\vec{K})$ to be small compared to unity. Different situations now arise according to the sign of $u_s(\vec{K})$: If all $u_s(\vec{K}) < 0$, i.e. if the correlation matrix is negative-definite, we call the correlation "purely repulsive". One would expect a purely repulsive interaction among electrons to lead to such

a purely repulsive correlation (cf. the semi-classical treatment in appendix III). In this case, the second term in (7.1) is regular for all α and μ and does not, therefore, produce a transition. For other than purely repulsive correlations, however, where one of the eigenvalues $u_S(\vec{K})$ is positive, at low enough temperatures the pseudo-molecular contribution in (7.1) will always become noticeable, namely when $e^{2\alpha\mu} u_S(\vec{K})$ becomes comparable to unity. The chemical potential will be limited to $\mu < \mu_0$, where

$$e^{2\alpha\mu_0} [u_S(\vec{K})]_{\max} = 1. \quad (7.3)$$

Exactly what happens upon approaching the limit (7.3) depends on the detailed nature of the largest eigenvalue $u_0(\vec{K})$. Assuming that $u_0(\vec{K})$ reaches its maximum for $\vec{K}=0$, and that $|u_0(\vec{K}) - u_0(0)| > c \cdot \vec{K}^3$ for small $|\vec{K}|$, a phenomenon similar to Bose-condensation occurs: Roughly speaking, when replacing sums by integral in (7.1) the maximum number of particles which can be accommodated by the integral, for $\mu = \mu_0$, becomes

$$N = \frac{V}{(2\pi)^3} \int d^3 \vec{k} \frac{1}{e^{\alpha(\varepsilon(\vec{k}) - \mu)} + 1} + \frac{V}{(2\pi)^3} \sum_S \int d^3 \vec{K} \frac{u'_S(K)/u_S(K)}{e^{-2\alpha\mu}[u_S(K)]^{-1} - 1} \quad (7.4)$$

which is finite under the conditions mentioned. The remaining electrons have to be accommodated, paired into pseudomolecules, into the pseudomolecular ground state, which forms a condensed phase pervading the whole system. Under the application of an inhomogeneous magnetic field, which is small enough not to mix the different eigenvalues $u_S(\vec{K})$, the pseudomolecules behave similarly to simple charged bosons: they show a Meissner effect. (This does *not* depend on the dependence of $u_S(\vec{K})$ on \vec{K} , once the existence of the condensed state is established.) We therefore identify tentatively the transition given by (7.3) with the transition to the superconducting state. Thermodynamically, this is a transition without latent heat; the behaviour of the specific heat at the transition again depends on the detailed dependence of $u_S(\vec{K})$ on \vec{K} . The penetration depth will be related directly to the number of condensed pseudomolecules which plays the role of the "number of superconducting particles" in the usual interpretation; to get order-of-magnitude agreement with experiment this number must increase strongly with decreasing temperature. In the simple picture of reference 1,

the transition was given by a formula similar to (7.3) with a $u_s(\vec{K})$ of the form

$$u_s(\vec{K}) = e^{-\alpha E_0} e^{-\alpha \hbar^2 \vec{K}^2 / 4m}; \quad E_0 > 0. \quad (7.5)$$

This gave a constant chemical potential for the system below the transition temperature and a much too small increase of condensed bosons with decreasing temperature. In order to get a large enough amount of condensed pseudomolecules, μ_0 must actually decrease with decreasing temperature; from (7.3) it then follows that $u_0(0)$ should have a slower temperature dependence than (7.5). Now it is known¹⁴⁾ that for the case of simple interactions through an x -space potential quantum mechanical effects have just the effect of damping the temperature-dependence of the U_2 -matrix, so that it is not a far-fetched assumption that this will be fulfilled in general. In reference ²⁾ it was shown that the critical magnetic field in a perfect Bose gas is simply related to the penetration depth δ by

$$H_c = \frac{\hbar c}{2e\delta^2}. \quad (7.6)$$

This result depends essentially on the fact that the spectrum $u_0(\vec{K})$ for the perfect gas is quadratic in \vec{K} for small \vec{K} . The coefficient of \vec{K}^2 , the mass, drops out in (7.6). We may, therefore, expect that the same law (7.6) will follow from the present model if $u_0(\vec{K}) - u_0(0) = \text{const. } \vec{K}^2$ for small K . For a different \vec{K} -dependence, a different relation would be expected. Since (7.6) gives quite good order-of-magnitude agreement, we presume that the eigenvalue $u_s(\vec{K})$ has to have a quadratic dependence on \vec{K} for small \vec{K} , or very nearly so.

Summing up, one sees that under quite weak assumptions about the largest eigenvalue $u_0(\vec{K})$ of the \tilde{U}_2 -matrix, we can expect to obtain the following properties of the system described by (7.1):

1. A thermodynamic transition without latent heat; the behaviour of the specific heat depends on details. The condition for the occurrence of this transition is that the attractive parts of the Fröhlich interaction be strong enough to produce a positive eigenvalue.

2. A Meissner effect in magnetic fields, below the transition.

3. A strong increase of the number of condensed particles with decreasing temperature.

4. The relation (7.6) for the critical field.

It seems, therefore, very plausible that the mechanism of two-particle correlations which leads to (7.1) is the agent of superconductivity. Two further facts deserve attention in this context:

a) Non-equilibrium properties, like steady currents, are outside the scope of the quasichemical approximation method, which is fundamentally restricted to thermal equilibrium.

b) The fact that the pseudomolecules presumably undergo a true Bose condensation will lead to unphysical properties wherever the fact that the condensed state extends over the whole volume enters, as discussed in reference ²⁾. In other words, the method will presumably give an infinite correlation length $\Lambda^{15)16)}$. This unphysical result stems from the fact that the quasichemical approximation method totally ignores dynamical correlation between pseudomolecules; the statistical correlations which are included in the model in principle are discussed in appendix II and shown to be insufficient to lead to a finite correlation length. A refined treatment which takes the interactions between pseudo-molecules into account would be expected to replace the Bose condensation by a "quasi-condensation" into a state with finite correlation length. As a first approximation, a theory with infinite correlation length is certainly satisfactory, since the effects of the finiteness of Λ are always small¹⁶⁾. The effects discussed in reference¹⁶⁾ would, however, not follow from a theory along the lines proposed here.

If the speculations contained in this section are correct, the next task would be to investigate the largest eigenvalue $u_0(\vec{K})$ of the quenched \tilde{U}_2 -matrix of electrons in a solid. This correlation matrix will be due to the combined effect of a) the screened Coulomb interaction between electrons, and b) the Fröhlich interaction due to the scattering of electrons by the lattice vibrations⁵⁾. The determination of $u_0(\vec{K})$ is then a problem which has yet to be solved.

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APPENDIX I.

Thermodynamical Theory of Chemical Equilibrium.

The thermodynamical theory of chemical equilibrium in perfect gases is well-known. In the simple case of an equilibrium between atoms (A) and diatomic molecules (A_2) with binding energy $-\varepsilon$ ($\varepsilon < 0$) one proceeds as follows: Since for perfect gases the free energies are additive upon mixing, the free energy of the system at temperature T , volume V and with N_1 atoms and N_2 molecules present ($N_1 + 2 N_2 = N$ being the total number of atoms), is

$$F(T, V, N_1 N_2) = F_1(T, V, N_1) + F_2(T, V, N_2) + N_2 \varepsilon \quad (\text{I.1})$$

where F_1 and F_2 are the free energies of the free atomic resp. molecular gas. The stability condition

$$\delta F = 0 \quad (\text{I.2})$$

when

$$\delta V = \delta T = 0 \quad (\text{I.2a})$$

and

$$\delta N = \delta N_1 + 2 \delta N_2 = 0 \quad (\text{I.2b})$$

yields

$$2 \mu_1 = \mu_2 + \varepsilon \quad (\text{I.3})$$

where

$$\mu_i = \left(\frac{\partial F_i}{\partial N_i} \right)_{T, V} \quad (i = 1, 2)$$

are the chemical potentials of the atomic and molecular gas respectively. F_1, F_2 (resp. μ_1, μ_2) can be calculated from statistical mechanics, and (1.3) then determines the equilibrium curve.

An equivalent formulation of this procedure is: Let the free energy of the total system *in equilibrium* be $F(T, V, N)$, and consider the "grand canonical potential"

$$\Omega(T, V, \mu) = F - \mu N \quad (\text{I.4})$$

in terms of which one has

$$N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T, V}$$

$$\left(\frac{\partial F}{\partial T} \right)_{N, V} = \left(\frac{\partial \Omega}{\partial T} \right)_{\mu, V}; \quad \left(\frac{\partial F}{\partial V} \right)_{T, N} = \left(\frac{\partial \Omega}{\partial V} \right)_{T, \mu}. \quad (\text{I.5})$$

For the individual gases, we have similarly

$$\Omega_i(T, V, \mu_i) = F_i - \mu_i N_i. \quad (\text{I.6})$$

Then the chemical equilibrium property is expressed by

$$\Omega(T, V, \mu) = \Omega_1(T, V, \mu) + \Omega_2(T, V, 2\mu - \varepsilon). \quad (\text{I.7})$$

(Since quite generally Ω is related to the pressure p by

$$\Omega = -pV. \quad (\text{I.8})$$

Equation (1.7) expresses directly the additivity of partial pressures.) Ω_1 and Ω_2 are to be taken from statistical mechanics; for Fermi atoms one has

$$\Omega_1(\mu_1) = -kT \sum_s \log(1 + e^{\alpha(\mu_1 - E_s)}) \quad (\text{I.9})$$

where s runs over all single-particle states, E_s being the energy in state s , $\alpha = 1/kT$. For the molecules one has to take Bose statistics:

$$\Omega_2(\mu_2) = +kT \sum_s \log(1 - e^{\alpha(\mu_2 - E_s)}) \quad (\text{I.10})$$

with equivalent notation. In the limiting case of Boltzmann statistics, which is valid at high temperatures, the two statistics merge in the formula

$$\Omega(\mu) = -kT \sum_s e^{\alpha(\mu - E_s)}. \quad (\text{I.11})$$

The crucial assumptions of the thermodynamical theory of chemical equilibrium are (i) the validity of the perfect-gas approximation for atoms and for molecules, and (ii) the additivity of free energies of the atomic and molecular gas upon mixing. Physically, these mean a neglect of interactions between all particles. On the other hand, this same interaction is responsible for the formation of the bound state of the molecule! A more careful investigation of the approximation involved is needed to remove this apparent paradox. This is done in section 6.

It is important to realize that the atomic gas can never enter the Fermi degeneracy region. In fact, for a Bose gas the chemical potential is always negative

$$\mu_2 \leq 0 \quad (\text{I.12})$$

and this implies, together with (1.3)

$$\mu_1 \leq \frac{\varepsilon}{2} < 0 \quad (\text{I.13})$$

whereas the degenerate region of the atomic gas is defined by

$$\mu_1 > 0. \quad (\text{I.14})$$

Therefore, in the case of true chemical equilibrium, the "quenching factors" (1.2) will never be of any importance. This is a special feature of the true chemical equilibrium; the reason for this is that before the atomic gas even approaches the degeneracy region, a great number of molecules is formed and starts condensing, diminishing the density of the atomic gas very rapidly.

APPENDIX II.

General Evaluation of (4.19) and Discussion.

We want to evaluate (4.19) exactly, taking into account all permutations, in order to discuss the limits of validity of (4.21). Consider any pair of permuted states in (4.19), e.g. (k'_{2i-1}, k'_{2i}) . We shall call this pair a "natural pair" if it is equal to any pair (k_{2j-1}, k_{2j}) , disregarding the order. The terms included in (4.21) are then precisely the terms without "non-natural" pairs. We are going to generalize the evaluation of Φ_i by making essentially an expansion in terms of numbers of non-natural pairs.

In any permutation there will be certain sequences of natural pairs which perform part of a cyclic permutation among themselves, say

$$(k_{i_1}, k_{i_1+1}) \rightarrow (k_{i_2}, k_{i_2+1}) \rightarrow \dots \rightarrow (k_{i_n}, k_{i_n+1}) \quad (\text{II.1})$$

such that, under P , $(k'_{i_j}, k'_{i_j+1}) = (k_{i_{j+1}}, k_{i_{j+1}+1})$, disregarding the order within the pair, for $j = 1, 2, \dots, n$. Such a sequence will be called a "complete sequence of natural pairs of length n ",

a) if (k_{i_1}, k_{i_1+1}) is different from all (k'_{2i}, k'_{2i+1}) , i.e. is not itself a natural pair in the permutation P , and if also (k'_{i_n}, k'_{i_n+1}) is not a natural pair: i.e., if the sequence (I.1) breaks off at both ends; or

b) if $(k'_{i_n}, k'_{i_n+1}) = (k_{i_1}, k_{i_1+1})$, i.e. if the sequence (I.1) closes by $(k_{i_n}, k_{i_n+1}) \rightarrow (k_{i_1}, k_{i_1+1})$. Since we only consider irreducible permutations, this case can only happen if the sequence (I.1) contains all pairs, i.e., for $n = l$. The permutations which give rise to this case are, therefore, just the ones we took into account in (4.21).

Consider now the contribution to (4.19) of a permutation containing (among others) a complete sequence of natural pairs of length n ,

*

(II.1). It will read:

$$\begin{aligned} & \frac{1}{2^l l!} (-1)^P \sum_{\sigma_{i_1} \cdots \sigma_{i_n}} \sum_{\hat{\sigma}_{n+1} \cdots \hat{\sigma}_l} (u_{\sigma_{i_1}} u_{\sigma_{i_2}} \cdots u_{\sigma_{i_n}}) (u_{\hat{\sigma}_{n+1}} \cdots u_{\hat{\sigma}_l}) \times \\ & \times \sum_{(k_{i_1} \cdots k_{i_{n+1}+1})} \langle [k_{i_1} k_{i_1+1}] | \sigma_{i_1} \rangle \langle \sigma_{i_1} | [k_{i_2} k_{i_2+1}] \rangle \cdots \langle [k_{i_n} k_{i_n+1}] | \sigma_{i_n} \rangle \times \\ & \times \langle \sigma_{i_n} | [k_{i_{n+1}} k_{i_{n+1}+1}] \rangle \times \sum_{(\hat{k}_{2n+2} \cdots \hat{k}_l)} \langle [k_{2n+2} k_{2n+3}] | \sigma_{n+1} \rangle \cdots \quad (\text{II.2}) \end{aligned}$$

The summation over the pairs $(k_{i_2}, k_{i_2+1}), \dots, (k_{i_n}, k_{i_n+1})$ can readily be performed, using (4.18), and we get

$$\begin{aligned} & \frac{1}{2^l l!} (-1)^P \sum_{\sigma_{i_1}} \sum_{(\hat{\sigma}_{n+1} \cdots \hat{\sigma}_l)} (u_{\sigma_{i_1}})^{n+1} (u_{\hat{\sigma}_{n+1}} \cdots) \times \\ & \times \sum_{(\hat{k})} (\cdots) \times \sum_{k_{i_1} k_{i_1+1} k_{i_{n+1}} k_{i_{n+1}+1}} \langle [k_{i_1} k_{i_1+1}] | \sigma_{i_1} \rangle \langle \sigma_{i_1} | [k_{i_{n+1}} k_{i_{n+1}+1}] \rangle. \quad (\text{II.3}) \end{aligned}$$

The same process can be repeated for all complete sequences of natural pairs, and we get for the contribution of a permutation with s complete sequences of natural pairs with lengths n_1, \dots, n_s ($\sum_r n_r = l - s$):

$$\begin{aligned} & \frac{1}{2^l l!} (-1)^P \sum_{\sigma_1 \cdots \sigma_s} (u_{\sigma_1}^{n_1+1} u_{\sigma_2}^{n_2+1} \cdots u_{\sigma_s}^{n_s+1}) \times \sum_{(k_1 \cdots k_{2s})} \times \\ & \times \langle [k_1 k_2] | \sigma_1 \rangle \langle \sigma_1 | [k'_1 k'_2] \rangle \cdots \langle [k_{2s-1} k_{2s}] | \sigma_s \rangle \langle \sigma_s | [k'_{2s-1} k'_{2s}] \rangle. \quad (\text{II.4}) \end{aligned}$$

The same contribution (II.4) is given by all permutations which can be obtained by filling in the $(l - s)$ pairs we have integrated over into the appropriate places in all possible ways; this number is equal to

$$2^{l-s} \prod_{i=1}^s \binom{l-s}{n_i} n_i! = s^{l-s} (l-s)! \quad (\text{II.5})$$

The contribution to (4.19) from all permutations with s complete sequences of natural pairs with lengths n_1, \dots, n_s is, therefore, given by

$$\begin{aligned} & \Phi_l^{(s)}(n_1 \cdots n_s) = \frac{(l-s)!}{2^s l!} \sum_{(\sigma_1 \cdots \sigma_s)} \sum_P (u_{\sigma_1}^{n_1+1} \cdots u_{\sigma_s}^{n_s+1}) \times \\ & \times \sum_{(k_1 \cdots k_{2s})} \langle [k_1 k_2] | \sigma_1 \rangle \langle \sigma_1 | [k'_1 k'_2] \rangle \cdots \langle [k_{2s-1} k_{2s}] | \sigma_s \rangle \langle \sigma_s | [k'_{2s-1} k'_{2s}] \rangle \quad (\text{II.6}) \end{aligned}$$

where P runs over all irreducible permutations of the $2s$ states k_1, \dots, k_{2s} such that no (k'_{2i}, k'_{2i+1}) is a natural pair.

We now define the functions linking the s complete sequences of natural pairs, by

$$\Psi_s(\sigma_1 \dots \sigma_s) = \frac{1}{2^s s!} \sum_P (-1)^P \sum_{(k_1 \dots k_{2s})} \langle [k_1 k_2] | \sigma_1 \rangle \langle \sigma_1 | [k'_1 k'_2] \rangle \dots \dots \langle [k_{2s-1} k_{2s}] | \sigma_s \rangle \langle \sigma_s | [k'_{2s-1} k'_{2s}] \rangle \tag{II.7}$$

where P runs over all irreducible permutations of (k_1, \dots, k_{2s}) without natural pairs. In particular, one has

$$\Psi_1(\sigma) = 1 \tag{II.7'}$$

and, e.g.

$$\begin{aligned} \Psi_2(\sigma_1 \sigma_2) = \frac{1}{8} \sum_{k_1 k_2 k_3 k_4} \{ & \langle [k_1 k_2] | \sigma_1 \rangle \langle \sigma_1 | [k_1 k_4] \rangle \langle [k_3 k_4] | \sigma_2 \rangle \langle \sigma_2 | [k_2 k_3] \rangle + \\ & + \langle [k_1 k_2] | \sigma_1 \rangle \langle \sigma_1 | [k_2 k_3] \rangle \langle [k_3 k_4] | \sigma_2 \rangle \langle \sigma_2 | [k_1 k_4] \rangle - \\ & - \langle [k_1 k_2] | \sigma_1 \rangle \langle \sigma_1 | [k_1 k_3] \rangle \langle [k_3 k_4] | \sigma_2 \rangle \langle \sigma_2 | [k_2 k_4] \rangle - \\ & - \langle [k_1 k_2] | \sigma_1 \rangle \langle \sigma_1 | [k_2 k_4] \rangle \langle [k_3 k_4] | \sigma_2 \rangle \langle \sigma_2 | [k_1 k_3] \rangle \}. \end{aligned}$$

Then (II.6) becomes:

$$\Phi_l^{(s)}(n_1, \dots, n_s) = \frac{(l-s)! s!}{l!} \sum_{\sigma_1 \dots \sigma_s} u_{\sigma_1}^{n_1+1} u_{\sigma_2}^{n_2+1} \dots u_{\sigma_s}^{n_s+1} \Psi_s(\sigma_1 \dots \sigma_s). \tag{II.8}$$

We can now perform the sum over the (n_1, \dots, n_s) . Defining

$$F_l^{(s)}(x_1, \dots, x_s) \equiv \sum_{\substack{(n_1, n_2, \dots, n_s)=1 \\ (\sum n_s = l-s)}}^{l-1} x_1^{n_1+1} \dots x_s^{n_s+1} \tag{II.9}$$

we get for the contribution of all permutations with s complete sequences of natural pairs.

$$\Phi_l^{(s)} \equiv \sum_{n_1 \dots n_s} \Phi_l^{(s)}(n_1 \dots n_s) = \frac{(l-s)! s!}{l!} \sum_{(\sigma_1 \dots \sigma_s)} F_l^{(s)}(u_{\sigma_1}, \dots, u_{\sigma_s}) \Psi_s(\sigma_1 \dots \sigma_s) \tag{II.10}$$

(II.9) is a higher difference quotient:

$$F_l^{(s)}(x_1, \dots, x_s) = (x_1 x_2 \dots x_s) \Delta^{s-1}(x^{l-1}) [x_1 \dots x_s] \tag{II.11}$$

where

$$\Delta^{s-1}(f(x)) [x_1, \dots, x_s] \equiv \sum_{i=1}^s \frac{f(x_i)}{\prod_{k \neq i} (x_i - x_k)} \tag{II.12}$$

Inserting now (II.10) into (4.12) we get

$$\begin{aligned} -\alpha \Omega_M = & \sum_{l=1}^{\infty} \sum_{s=1}^l \frac{(l-s)! s!}{l!} \sum_{(\sigma_1 \dots \sigma_s)} \Psi_s(\sigma_1 \dots \sigma_s) \times \\ & \times (u_{\sigma_1} u_{\sigma_2} \dots u_{\sigma_s}) \Delta^{s-1} \left(\frac{(z^2 u_{\sigma})^l}{u_{\sigma}} \right) [u_{\sigma_1}, \dots, u_{\sigma_s}] \end{aligned} \tag{II.13}$$

and, since Δ^{s-1} is a linear operator independent of l , we can perform the sum over l at fixed s . The result is

$$\Omega_M = \sum_{s=1}^{\infty} \Omega_M^{(s)} \quad (\text{II.14})$$

with

$$\begin{aligned} -\alpha \Omega_M^{(s)} = & s! \sum_{\sigma_1 \cdots \sigma_s} \Psi_s(\sigma_1, \cdots, \sigma_s) (u_{\sigma_1} \cdot u_{\sigma_2} \cdots u_{\sigma_s}) \times \\ & \times \Delta^{s-1} \left(\frac{1}{x} f_s(z^2 x) \right) [u_{\sigma_1}, u_{\sigma_2}, \cdots, u_{\sigma_s}] \end{aligned} \quad (\text{II.15})$$

where

$$f_s(x) \equiv \sum_{l=s}^{\infty} \frac{(l-s)!}{l!} x^l. \quad (\text{II.16})$$

Equation (II.14) is the required expansion of Ω_M in terms of the number $(s-1)$ of non-natural pairs. The first two terms read:

$$-\alpha \Omega_M' = \sum_{\sigma} f_1(z^2 u_{\sigma}) = - \sum_{\sigma} \log(1 - z^2 u_{\sigma}) \quad (\text{II.17})$$

which is identical to the result (4.21), and

$$-\alpha \Omega_M'' = 2 \sum_{\sigma_1 \sigma_2} \Psi_2(\sigma_1 \sigma_2) \frac{u_{\sigma_1} f_2(z^2 u_{\sigma_2}) - u_{\sigma_2} f_2(z^2 u_{\sigma_1})}{u_{\sigma_2} - u_{\sigma_1}} \quad (\text{II.18})$$

which is the first-order correction to (4.21).

In order to discuss the correction terms (II.18) and the terms with $s \geq 3$ in (II.14), we again restrict ourselves to the case of free particles in a volume V which is at the basis of the discussion in section 5. σ then stands for (\vec{K}, S) , where \vec{K} is the center-of-gravity momentum, S the internal state of the pseudomolecule. $\Psi_2(\sigma_1 \sigma_2)$ is an "interaction" between two molecular states σ_1 and σ_2 . Its range in \vec{K} is roughly equal to the range of the wave-function $\varphi_{S\vec{K}}(\vec{\kappa})$ in relative-momentum space, i.e. the inverse of the size a of the pseudomolecule. Provided that $a^{-1} \gg K_1$, where K_1 is the \vec{K} -space range of $u_S(\vec{K})$, (II.18) will be smaller than (II.17) by a factor of the order of $(aK_1)^3$. Indeed, since the range K_1 of u_{σ_1} and u_{σ_2} is very much smaller than the range of Ψ_2 , Ψ_2 in (II.18) can be replaced by a constant Ψ° . The two summations over σ_1 and σ_2 then give a result of the order of $(V K_1^3)^2 \Psi^{\circ}$. Ψ° , on the other hand, is of order a^3/V , as can be seen from (II.7); this can also be inferred from the dimensional argument that (1) the volume factors V must turn out correctly, i.e., Ω_M'' must be proportional to V , and (2) no other volume enters into Ψ_2 except V and a^3 . $-\alpha \Omega_M''$, therefore, becomes

of order $(V K_1^3) \cdot (a K_1)^3$ and is smaller than $-\alpha \Omega'_M$ by a factor $(a K_1)^3$. By a similar argument, for arbitrary s ,

$$\Omega_M^{(s)} / \Omega'_M = O[(a^3 K_1^3)^{s-1}]. \quad (\text{II.19})$$

These orders of magnitude can be understood qualitatively. For the case of true molecular binding, as treated in section 6, Bose statistics for the molecules stems from the fact that two molecules can be exchanged as a whole; this produces noticeable effects when the mean thermal wave length λ of the molecules (6.8) is comparable to the intermolecular distance d_2 ; the range K_1 of u_σ , in this case, is equal to λ^{-1} . The terms with $s = 2$, say, are corrections to the pure Bose statistics of the molecules arising from the effect of exchanging one single atom out of each of a pair of molecules. For such an exchange to happen, the wave-functions of the two molecules have to overlap; the molecules have, therefore, to be within a range a of each other, whereas the exchange of two molecules is possible when they are a distance of order λ apart: this argument leads one to expect a factor $(a/\lambda)^3$ between the two contributions. For pseudomolecules everything is the same, except that the range K_1 of $u_s(\vec{K})$ is not, in general, given by (6.7).

The expansion parameter in the series (II.15) is, therefore, essentially

$$\gamma \equiv (a K_1)^3. \quad (\text{II.20})$$

Now, Bose statistics comes into play only when

$$d_2 K_1 \lesssim 1 \quad (\text{II.21})$$

where d_2 is the average distance between pseudomolecules. For $1 \ll d_2 K_1$, everything reduces to Boltzmann statistics. On the other hand, we cannot in general expect our basic assumptions to hold unless

$$a \ll d_2 \quad (\text{II.22})$$

where a is the size of the pseudomolecule. (II.21) and (II.22) together entail

$$K_1 a \ll 1 \quad (\text{II.23})$$

so that $\gamma \ll 1$, and, therefore, the higher terms in (II.15), are always small.

Still, we cannot dismiss the series (II.15) quite as lightly. Let us first mention that statistical mechanics does not guarantee that a series like (II.15) which proceeds in powers of a certain parameter γ actually converges. We know that the partition function for N -particles is a polynomial of N^{th} degree in γ . As regards the expres-

sion for Ω of such a system, we can only conclude that it allows an asymptotic expansion in terms of γ ; the convergence is left open. By the definition of an asymptotic series, we then know that, if we break it off at a particular value s_0 of s , the error will be at most of the order of the $(s_0 + 1)^{\text{th}}$ term. Neglecting the terms with $s > s_0$ in (II.15), therefore, involves an error of the order of $\Omega_M^{(s_0+1)}$. We have to check whether this error is uniformly small as a function of z for the range $0 \leq z \leq 1$ which is allowed in Ω'_M .

First, (II.15) shows that each term $\Omega_M^{(s)}$ has, as a function of z , a singularity only at the same point z_0 as Ω'_M , namely

$$z_0 [u_\sigma]_{\max} = 1. \quad (\text{II.24})$$

Furthermore, one can see from (II.15) that the singularity of $\Omega_M^{(s)}$ at $z = z_0$ gets weaker with increasing s : From these two remarks one concludes that

$$|\Omega_M^{(s_0+1)}(z) / \Omega'_M(z)| < C_{s_0} \gamma^{s_0} \quad (\text{II.25})$$

uniformly for all $0 \leq z \leq 1$.

If this were not so, if e.g. Ω''_M had a stronger singularity than Ω'_M at $z = z_0$, then for $z \rightarrow z_0$, Ω''_M would become larger than Ω'_M and would eventually win over. This would then mean that the nature of the condensation would be completely altered by the statistical effects due to interchanges of single atoms between molecules. This possibility is in itself quite plausible, but the result (II.25) shows that this is not so, $\Omega''_M \ll \Omega'_M$ always holds, even for $z \rightarrow z_0$, and, therefore, the molecular gas shows an ordinary Bose condensation. We conclude that the statistical corrections $\Omega_M^{(s)}$ ($s > 1$) are not strong enough to establish a finite correlation length¹⁵⁾ for the condensed molecular gas: this has to be achieved by the dynamical interactions between molecules.

The foregoing discussion shows, then, that for our purpose the terms with $s > 1$ can always be ignored.

APPENDIX III.

Semi-classical model for the two-particle U-matrix.

We wish to study the classical equivalent of the problem of finding the eigenvalues of the two-particle U -matrix (without quenching), for the simple one-dimensional case of two point-particles with a conservative interaction:

$$H = H_0 + V(q) \quad (\text{III.1})$$

where

$$H_0 = \frac{p^2}{2m}$$

m = reduced mass, p = relative momentum, q = relative coordinate.

We are, therefore, concerned with the quantity

$$U(p, q) = e^{-\alpha H} - e^{-\alpha H_0} = (e^{-\alpha V} - 1) e^{-\alpha H_0}. \quad (\text{III.2})$$

We interpret $U(p, q)$ as the Hamiltonian of an "effective" system whose motion we wish to study. We make use of the following theorem of classical mechanics: If H is the Hamiltonian of a system, then any function $G(H)$, when considered as a Hamiltonian, leads to the same motion as H itself, with a difference in time scale only. All quantities which are independent of time scale are, therefore, the same for H and for $G(H)$. This relieves us from having to worry whether to take U or, say, $\log U$, as the Hamiltonian. The motions are given by

$$U(p, q) = \text{const.} = s \cdot e^{-\alpha E} \quad (\text{III.3})$$

$$s = \pm 1 \quad (\text{III.4})$$

where E and s form a complete set of integrals of motion.

The sign s is determined by the sign of U which, in turn, is determined by the sign of V . The possible motions are, therefore, all confined to regions of uniform sign of V . Let us take as an example

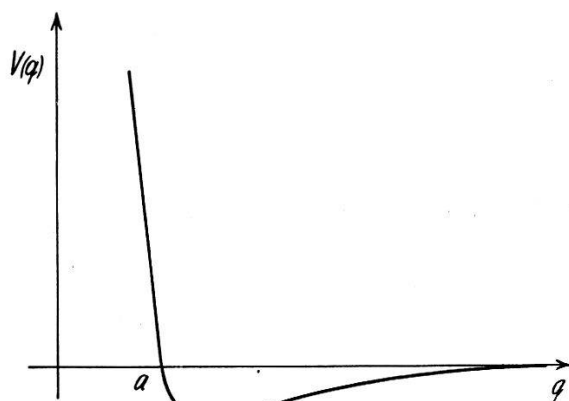


Fig. 1.

Typical Potential between two Particles.

a potential $V(q)$ of the shape shown in Fig. 1, i.e. with a strong repulsive region for $q < a$ and an attractive part for $q > a$. Then we get one set of motions for each of the two regions $q < a$ and $q > a$:

(i) $q < a$, i.e. $V(q) > 0$: $s = -1$. (III.3) reduces to:

$$U = -e^{-\alpha E} \quad (\text{III.3})$$

where

$$E = \frac{p^2}{2m} + V_{\text{eff}} \quad (\text{III.5})$$

and

$$V_{\text{eff}} = -kT \cdot \log(1 - e^{-\alpha V}) \quad (\text{III.6})$$

(ii) $q > a$, i.e. $V(q) < 0$: $s = +1$. (III.3) becomes

$$U = + e^{-\alpha E'} \quad (\text{III.3''})$$

where

$$E' = \frac{p^2}{2m} + V'_{\text{eff}} \quad (\text{III.5'})$$

and

$$V'_{\text{eff}} = -kT \cdot \log(e^{-\alpha V} - 1). \quad (\text{III.6'})$$

The repulsive and the attractive region give rise to separate troughs of "effective" potential in which the motion takes place according to (III.5) and (III.5'); in the trough corresponding to the repulsive region, the energy values give rise to negative values of U , in the attractive region, U is positive, as shown by (III.3') and

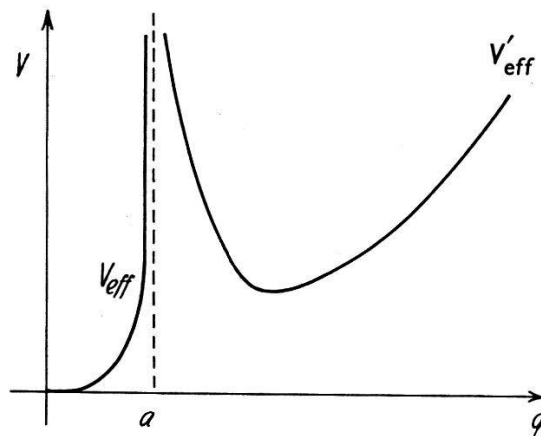


Fig. 2.

Effective Potential for the Potential of Fig. 1.

(III.3''). Fig. 2 shows the qualitative behaviour of V_{eff} and V'_{eff} for the potential shown in Fig. 1.

A quantization according to the correspondence principle can now be performed by requiring

$$\int p dq = (n + \frac{1}{2}) h. \quad (\text{III.7})$$

Indeed, the action integral $\int p dq$ is independent of the time scale and, therefore, according to the remark made above, only dependent on the motion, not the Hamiltonian. (III.7) gives rise to an infinite sequence of discrete energy eigenvalues E_n, E'_n in the two troughs respectively. These then generate two sets of eigenvalues of U :

$$\begin{aligned} u_{-n} &= - e^{-\alpha E_n} & (n = 1, 2, \dots) \\ u_{+n} &= + e^{-\alpha E'_n} & (n = 1, 2, \dots) \end{aligned} \quad (\text{III.8})$$

(III.8) gives the semiclassical spectrum of the "matrix" U , Equation (III.2). The following properties are obvious:

(i) U has a discrete spectrum, bounded on both sides, with a condensation point at 0.

(ii) Repulsive correlations give negative, attractive correlations positive eigenvalues.

(iii) For $T \rightarrow 0$, i.e. $\alpha \rightarrow \infty$, $V_{\text{eff}} \rightarrow 0$, $V'_{\text{eff}} \rightarrow V$, both limits being non-uniform. Therefore, at low temperatures, the "attractive" trough V'_{eff} becomes lower than the "repulsive" one, V_{eff} ; furthermore, V'_{eff} is also wider than V_{eff} : therefore, at low enough temperatures, the largest positive eigenvalue of U becomes larger than the largest negative one.

Of course, the classical model cannot be taken too literally for the cases of interest. It neglects not only the quenching, but also the wave-mechanical "smearing" of the correlation which is known to reduce considerably the peak of the factor $(e^{-\alpha V} - 1)$ near the minimum of V^{14}). Furthermore, a velocity dependence in the interaction may considerably change the results.

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- ⁷⁾ There is of course still an interdependence of the two systems contained in the quenching factors, which, however, is of a self-consistent form, only through the chemical potential, and leaves the two systems *formally* independent.
- ⁸⁾ B. KAHN and G. E. UHLENBECK, Physica **5**, 399 (1938).
- ⁹⁾ Strictly, some care is needed before inserting this result into (5.5). It may happen that in addition to the discrete spectrum found above in a finite volume V , there is a "pseudocontinuum" of eigenvalues u_S which are individually of order $(1/V)$, but whose density is proportional to V . Such a pseudocontinuum is lost when going over from (5.3) to (5.6). It can easily be seen that such a pseudocontinuum gives rise to a term of Boltzmann type in Ω'_M , to which only the sum of the eigenvalues of the pseudocontinuum contributes. The criterion for the existence of such an additional term in Ω'_M is that the difference between the trace of the \tilde{U}_2 -matrix in a finite volume V and in an infinite volume does not vanish in the limit $V \rightarrow \infty$. Since such a Boltzmann contribution in Ω'_M is of no interest to us, we are going to neglect this possibility; we only remark that it can never happen that the whole spectrum of the \tilde{U}_2 -matrix is a pseudoconti-

num, for otherwise the correlation matrix in infinite space would have to vanish identically. For the unquenched case, it is known¹⁰⁾ that the trace of the \tilde{U}_2 -function in infinite space gives the correct virial coefficient: therefore, there is no pseudocontinuum there.

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