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Abstract

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On the Problem of Calculating the Free Energy for a Gas of Low Density

(Presented by Academician N. N. Bogolyubov, January 22, 1960)

In the work of N. N. Bogolyubov and S. V. Tyablikov (^{1}), an approximate method was proposed for solving problems of statistical physics, based on the use of two-time retarded and advanced Green functions depending on temperature, and of their spectral representations of the Lehmann–Källén type (^{2,3}). Spectral representations of this type had been used earlier ($^{4-9}$).

In the present work, the method proposed by N. N. Bogolyubov and S. V. Tyablikov is applied to the study of the properties of a Fermi system with interaction in the low-density approximation. The second correlation function of the system is found and, with its aid, the free energy and the distribution of particles over momenta are determined.

The Hamiltonian of the system under consideration in the second-quantization representation has the form

$$H=\sum_{f}T(f)a_f^+a_f+\frac{1}{2}\sum_{f_1f_2f_1'f_2'}U(f_1f_2\mid f_2'f_1')a_{f_1}^+a_{f_2}^+a_{f_2'}a_{f_1'}. \tag{1}$$

Here

$$U(f_1f_2\mid f_2'f_1')=\frac{1}{V}\,\frac{\delta_{\sigma_1\sigma_1'}\delta_{\sigma_2\sigma_2'}-\delta_{\sigma_1\sigma_2'}\delta_{\sigma_2\sigma_1'}}{2}\,\delta(p_1+p_2-p_1'-p_2')\,\frac{v(p_1-p_1')+v(p_2-p_1')}{2}; \tag{1'}$$

$T(f)=p^2/2m-\lambda$, where λ is the chemical potential of the system; p and σ are, respectively, the momenta and spins of the particles. The operators a_f and a_f^+ obey Fermi anticommutation relations.

Following (^{1,9}), we shall consider a single analytic function $G_{f_1f_2g_1g_2}(E)$ of the complex variable E, which is the Fourier transform of the two-particle Green function

$$
\begin{aligned}
G_{f_1 f_2 g_1 g_2}(t-t') = \langle\langle a_{f_1}(t) a_{f_2}(t) a^+_{g_2}(t') a^+_{g_1}(t')\rangle\rangle = \\
= \theta(t-t')\langle[a_{f_1}(t) a_{f_2}(t),\, a^+_{g_2}(t') a^+_{g_1}(t')]\rangle \\
- \theta(t'-t)\langle[a_{f_1}(t) a_{f_2}(t),\, a^+_{g_2}(t') a^+_{g_1}(t')]\rangle.
\end{aligned} \tag{2}
$$

Here $\langle A\rangle = Q^{-1}\,\mathrm{Sp}(Ae^{-H/\theta})$; $Q = \mathrm{Sp}\, e^{-H/\theta}$; $\theta = kT$; $a_f(t)$ are operators in the Heisenberg representation; $[A,B] = AB - BA$; $\theta(t) = 0$ for $t < 0$, $\theta(t) = 1$ for $t > 0$.

The second correlation function of the system that is of interest to us, $F_{2 g_1 g_2 f_1 f_2} = \langle a^+_{g_2} a^+_{g_1} a_{f_1} a_{f_2}\rangle$, is connected with $G_{f_1 f_2 g_1 g_2}(E)$ by the relation

$$
F_{2 g_1 g_2 f_1 f_2} = \int_{-\infty}^{+\infty} d\omega\, \frac{G_{f_1 f_2 g_1 g_2}(\omega + i\varepsilon) - G_{f_1 f_2 g_1 g_2}(\omega - i\varepsilon)}{e^{\omega/\theta} - 1}. \tag{3}
$$

Using the equations of motion for the operators a_f in the form

$$
i\hbar \frac{\partial a_f(t)}{\partial t} = [a_f, H] = T(f) a_f + \sum_{f' f'_1 f'_2} U(f f' \mid f'_2 f'_1) a^+_{f'} a_{f'_2} a_{f'_1},
$$

we obtain the equation of motion for the function $G_{f_1 f_2 g_1 g_2}(t-t')$

$$
\begin{aligned}
i\hbar \frac{\partial}{\partial t} \left\langle\left\langle a_{f_1}(t) a_{f_2}(t) a^+_{g_2}(t') a^+_{g_1}(t')\right\rangle\right\rangle = {} & -i\hbar\delta(t-t')\left(1 - \langle a^+_{f_1} a_{f_1}\rangle - \langle a^+_{f_2} a_{f_2}\rangle\right)\left(\delta_{f_1 g_1}\delta_{f_2 g_2} - \delta_{f_1 g_2}\delta_{f_2 g_1}\right) \\
& + \{T(f_1) + T(f_2)\} \left\langle\left\langle a_{f_1}(t) a_{f_2}(t) a^+_{g_2}(t') a^+_{g_1}(t')\right\rangle\right\rangle \\
& + \sum_{f' f'_1 f'_2} U(f_1 f' \mid f'_2 f'_1) \left\langle\left\langle a^+_{f'}(t) a_{f'_2}(t) a_{f'_1}(t) a_{f_2}(t) a^+_{g_2}(t') a^+_{g_1}(t')\right\rangle\right\rangle \\
& + \sum_{f' f'_1 f'_2} U(f_2 f' \mid f'_2 f'_1) \left\langle\left\langle a_{f_1}(t) a^+_{f'}(t) a_{f'_2}(t) a_{f'_1}(t) a^+_{g_2}(t') a^+_{g_1}(t')\right\rangle\right\rangle .
\end{aligned} \tag{4}
$$

We shall consider the problem in the low-density approximation $N/V \ll 1$. This means that the limiting Fermi momentum is small, i.e. there exists only an insignificant number of states f for which the mean occupation numbers $\bar{n}_f = \langle a^+_f a_f\rangle$ are close to unity.

In this approximation equation (4) takes the form

$$
\left(i\hbar \frac{\partial}{\partial t} - H_{12}\right) \left\langle\left\langle a_{f_1}(t) a_{f_2}(t) a^+_{g_2}(t') a^+_{g_1}(t')\right\rangle\right\rangle = -i\hbar\delta(t{-}t')\left(\delta_{f_1 g_1}\delta_{f_2 g_2} - \delta_{f_2 g_1}\delta_{f_1 g_2}\right), \tag{5}
$$

where H_{12} is the Hamiltonian operator for the two-body problem:

$$H_{12}\left\langle\left\langle a_{f_1}(t)a_{f_2}(t)a^{+}_{g_2}(t')a^{+}_{g_1}(t')\right\rangle\right\rangle = \{T(f_1)+T(f_2)\}\left\langle\left\langle a_{f_1}(t)a_{f_2}(t)a^{+}_{g_2}(t')a^{+}_{g_1}(t')\right\rangle\right\rangle + \sum_{f_1'f_2'} U(f_1f_2 \mid f_2'f_1')\left\langle\left\langle a_{f_1'}(t)a_{f_2'}(t)a^{+}_{g_2}(t')a^{+}_{g_1}(t')\right\rangle\right\rangle .$$

Performing a Fourier transformation, we obtain

$$(E-H_{12})G_{f_1f_2g_1g_2}(E) = \frac{i}{2\pi}\left(\delta_{f_1g_1}\delta_{f_2g_2} - \delta_{f_1g_2}\delta_{f_2g_1}\right),$$

i.e. we can write, as usual,

$$\frac{2\pi}{i}G_{f_1f_2g_1g_2}(E) = \sum_{\nu}\frac{F^*_\nu(f_1,f_2)F_\nu(g_1,g_2)}{E-E_\nu}, \tag{6}$$

where $\{F_\nu(f_1,f_2)\}$ is the complete system of eigenfunctions of the Hamiltonian H_{12}, and E_ν are its eigenvalues,

$$(E_\nu - H_{12})F_\nu(f_1,f_2) = 0. \tag{7}$$

The functions $F_\nu(f_1,f_2)$ are normalized so that

$$\sum_\nu F^*_\nu(f_1,f_2)F_\nu(g_1,g_2) = \delta_{f_1g_1}\delta_{f_2g_2} - \delta_{f_1g_2}\delta_{f_2g_1}.$$

Using (3) and (6), we now write $F_{2g_1g_2f_1f_2}$ in the form

$$F_{2g_1g_2f_1f_2} = \sum_\nu \frac{F^*_\nu(f_1,f_2)F_\nu(g_1,g_2)}{e^{E_\nu/\theta}-1}. \tag{8}$$

It is interesting to note that the use of the spectral representation leads us immediately to an expression in which we can interpret the resulting bound states as Bose molecules.

We shall next find the correction ΔF to the free energy of the unperturbed system by means of the formula

$$\frac{\partial \Delta F}{\partial g} = \operatorname{Sp} UF_2(g), \tag{9}$$

where $F_2(g)$ is the second correlation function of the system with Hamiltonian $T+gU$. Carrying out in equation (7) the separation of the motion of the center of inertia and splitting the sum in (8) into sums over the discrete and continuous spectra of the eigenvalues of the Hamiltonian of the relative motion of a pair of particles, we write

$$\frac{\partial \Delta F}{\partial g} = \sum_{Qmnl} \frac{\left(F^*_{Qmnl}, UF_{Qmnl}\right)}{e^{E_{Qmnl}/\theta} - 1} + \sum_{Qml} \int dE_q \, \frac{\left(F^*_{Qqml}, UF_{Qqml}\right)}{e^{E_{Qqml}/\theta} - 1},$$

or, using the fact that $(\psi^*_{mnl}, U\psi_{mnl}) = \partial E_{nl}/\partial g$ for the discrete spectrum and $(\psi^+_{qlm}, U\psi^+_{qlm}) = -\frac{1}{\pi}\frac{\partial \delta_l(q)}{\partial g}$ for the continuous spectrum,

$$\frac{\partial \Delta F}{\partial g} = \sum_{Qmnl} \frac{\partial E_{Qmnl}}{\partial g} \frac{1}{e^{E_{Qmnl}/\theta} - 1} - \frac{1}{\pi} \sum_{Qml} \int dE_q \, \frac{\partial \delta_l(q)}{\partial g} \frac{1}{e^{E_{Qlm}/\theta} - 1}$$

(the particle spins have been set equal to 1/2).

Thus,

$$\begin{aligned} \Delta F = {} & \frac{4\pi V\theta}{(2\pi\hbar)^3} \sum_{nl} (2l+1) \int_0^\infty P^2 \, dP \, \ln \left| 1 - e^{-P^2/4m\theta - \varepsilon_{nl}/\theta + 2\lambda/\theta} \right| \\ & - \frac{8V}{(2\pi\hbar)^3} \sum_{l} (2l+1) \int_0^\infty \frac{p\, dp}{m} \int_0^\infty P^2 \, dP \, \frac{\delta_l(p)}{e^{P^2/4m\theta + p^2/m\theta - 2\lambda/\theta} - 1}. \end{aligned} \tag{10}$$

The first term of this expression may be interpreted as the free energy of an ideal Bose gas of molecules with mass $2m$; the second term represents the energy of interacting individual particles. Consideration of the next approximation would lead to accounting for the interaction between atoms and molecules and molecules with one another.

Since the potential was chosen by us in the form (1′), antisymmetric in the spins, the summation in (10) is carried out only over even l. In the most general case we would have obtained ΔF in the form of a sum over even l with weight 1/4 and over odd l with weight 3/4.

Writing formula (9) in the form

$$\frac{\partial \Delta F}{\partial g} = \frac{i}{2\pi} \operatorname{Sp} U \int_{-\infty}^{+\infty} d\omega \, \frac{1}{e^{\omega/\theta} - 1} \times$$

$$\times \left\{ \frac{1}{T_{p_1} + T_{p_2} + gU - (\omega - i\varepsilon)} - \frac{1}{T_{p_1} + T_{p_2} + gU - (\omega + i\varepsilon)} \right\},$$

one can also obtain the occupation numbers $\bar{n}(\mathbf{p}) = \bar{n}_0(\mathbf{p}) + \Delta\bar{n}(\mathbf{p})$, where $\Delta\bar{n}(\mathbf{p}) = \delta\Delta F/\delta T(\mathbf{p})$.

Making transformations similar to those performed in calculating the free energy of the system, one can obtain

$$\frac{\partial \Delta\bar{n}(\mathbf{p}_0)}{\partial g} = -\frac{1}{\theta}\,\mathrm{Sp}\left[U\{\delta(\mathbf{p}_1-\mathbf{p}_0)+\delta(\mathbf{p}_2-\mathbf{p}_0)\}\frac{\exp\left[\dfrac{T_{p_1}+T_{p_2}+gU}{\theta}\right]}{\left(\exp\left[\dfrac{T_{p_1}+T_{p_2}+gU}{\theta}\right]-1\right)^2}\right],$$

and, consequently,

$$\begin{aligned}\Delta\bar{n}(\mathbf{p}_0) = {}& \frac{2V}{(2\pi\hbar)^3}\int d\mathbf{Q}\sum_{nl}(2l{+}1)\left|R_{nl}\left(\left|\mathbf{p}_0-\frac{\mathbf{Q}}{2}\right|\right)\right|^2\frac{1}{\exp\left[\frac{Q^2}{4m\theta}+\frac{\varepsilon_{nl}}{\theta}-\frac{2\lambda}{\theta}\right]-1}+\\ &+\frac{V}{(2\pi\hbar)^3}\frac{4}{\pi m\theta}\int d\mathbf{Q}\int q\,dq\sum_{l}(2l{+}1)\left|R_{ql}\left(\left|\mathbf{p}_0-\frac{\mathbf{Q}}{2}\right|\right)\right|^2\delta_l(q)\frac{\exp\left[\frac{Q^2}{4m\theta}+\frac{q^2}{m\theta}-\frac{2\lambda}{\theta}\right]}{\left(\exp\left[\frac{Q^2}{4m\theta}+\frac{q^2}{m\theta}-\frac{2\lambda}{\theta}\right]-1\right)^2}.\end{aligned}\tag{11}$$

(the summation here is still carried out only over even l).

Let us now consider the limiting case of low temperatures. In our approximation, at low temperatures the principal role is played by bound states (the first term in expression (10) is proportional to N/V, whereas the second term of this expression is proportional to $(N/V)^2$). Retaining in the sum over bound states the principal term corresponding to the energy $\Delta=(\varepsilon_{nl})_{\min}$, we therefore write the free energy of the system in the form

$$\begin{aligned}F = {}&\lambda N_F-\theta\sum_q \ln\left|1+\exp\left[-\frac{q^2}{2m\theta}+\frac{\lambda}{\theta}\right]\right|+\\ &+\mu N_B+\theta\sum_Q \ln\left|1-\exp\left[-\frac{Q^2}{2M\theta}+\frac{\mu}{\theta}\right]\right|+\Delta N_B;\end{aligned}\tag{12}$$

$$\mu=2\lambda-\Delta;\qquad N_F+2N_B=N;\qquad M=2m.$$

Expression (12) shows that at low temperatures our system is a mixture of Fermi atoms and diatomic Bose molecules. The quantity Δ has the meaning of the binding energy of a molecule. The Bose component naturally possesses all the properties of an ideal Bose gas. The condition $2\lambda-\Delta=0$ determines the Bose-condensation temperature. Investigation of the conditions of chemical equilibrium in a system with the possible chemical reaction $2F \rightleftarrows B$ leads to the conclusion that, in the approximation under consideration, at very low temperatures the Fermi component completely disappears from the mixture. If the assumption of replacing the sum over discrete energies by its principal term had not been introduced, one could speak of the existence in these molecules of internal excitation levels.

Let us next consider the case of high temperatures. Now the chemical potential λ takes negative values large in absolute magnitude, so that

$$e^{\lambda/\theta} \ll 1.$$

Using for λ its classical expression, we obtain at high temperatures from (10)

$$\Delta F = -\frac{N^2\theta}{V}\left(\frac{4\pi\hbar^2}{m\theta}\right)^{3/2}\left\{\sum_{nl}(2l+1)e^{-\varepsilon_{nl}/\theta} + \sum_{l}(2l+1)\int_0^\infty dp\, e^{-p^2/m\theta}\frac{1}{\pi}\frac{d\delta_l(p)}{dp}\right\}, \tag{13}$$

which gives for the second virial coefficient an expression coinciding with those known earlier (10,11).

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Note: Figure translations are in progress. See original paper for figures.