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Уравнение самосогласования в термодинамической задаче электронного газа

Целью работы является вычисление термодинамических характеристик классического плотного электронного газа, заключенного в сосуд сферической формы. Искомые величины представляются в виде функционалов от решения интегрального уравнения типа Гаммерштейна. В первом приближении и численно вычислено самосогласованное поле как функция радиуса. Определены значения свободной энергии, кинетической и потенциальной энергий, плотность числа электронов как функция радиуса, давление, получено уравнение состояния. Результаты являются асимптотически точными в пределе высоких плотностей. Показано, что для рассматриваемой системы термодинамического в обычном смысле предела не существует.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Self-Consistent Equations in Thermodynamic Problem of Classical Electron Gas

The purpose of the paper is the calculation of thermodynamic characteristics of classical dense electron gas contained in a vessel of spherical form. The quantities to be found are represented in the form of functionals of the solution of an equation of Hammerstein form. The self-consistent field as a function of radius is calculated in the first approximation and numerically. The free energy, the kinetic and the potential energies, the density of electrons as a function of radius, and the pressure are determined, the thermodynamic state equation is obtained. The results are asymptotically exact in the limit of high densities. It is shown that the thermodynamic in the usual sense of the limit does not exist for the system under consideration.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1979

In the present paper we shall give interpretation of the results obtained in ref.1 for classical electron gas in terms of self-consistent field. On the basis of these results we shall determine the thermodynamic parameters of the system.

It has been proved in ref.1 that asymptotically exact in the limit of high dencities expression for the free energy of electron gas is

$$F[N,V,\beta] = -\frac{1}{\beta}\ln\frac{1}{N!}\left[\left(\frac{2\pi m}{\beta}\right)^{3/2}V\right]^{N} - \frac{1}{2}N\frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}}\times$$

$$\times\frac{\int\limits_{\mathbb{E}^3}\bar{\Psi}(\underline{\xi})\,e^{-\beta\frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}}\bar{\Psi}(\underline{\xi})}\,d\underline{\xi}}{\int\limits_{\mathbb{E}^3}e^{-\beta\frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}}\bar{\Psi}(\underline{\xi})}\,d\underline{\xi}} - N\frac{1}{\beta}\ln\frac{3}{4\pi}\int\limits_{\mathbb{E}^3}e^{-\beta\frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}}\bar{\Psi}(\underline{\xi})}\,d\underline{\xi}, \qquad (1)$$

where the function $\bar{\Psi}(\underline{\xi})$ satisfies the equation

$$\Psi(\underline{\xi}) = \frac{\int\limits_{\mathbb{E}^3}\frac{1}{|\underline{\xi}-\underline{\eta}|}\,e^{-\beta\frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}}\Psi(\underline{\eta})}\,d\underline{\eta}}{\int\limits_{\mathbb{E}^3}e^{-\beta\frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}}\Psi(\underline{\eta})}\,d\underline{\eta}}. \qquad (2)$$

The equation (2) is that of the Hammerstein type[2]

$$\psi(\underline{\xi}) = \int_V \mathcal{K}(\underline{\xi},\underline{\zeta})\, f(\underline{\zeta},\psi(\underline{\zeta}))\, d\underline{\zeta} \qquad (3)$$

with

$$\mathcal{K}(\underline{\xi},\underline{\zeta}) = \frac{1}{|\underline{\xi}-\underline{\zeta}|}\,, \quad V = E^3,$$

$$f(\underline{\zeta},\psi(\underline{\zeta})) = \frac{e^{-\beta \frac{KN}{(\frac{3}{4\pi}V)^{1/3}}\psi(\underline{\zeta})}}{\int_V e^{-\beta \frac{KN}{(\frac{3}{4\pi}V)^{1/3}}\psi(\underline{\zeta})}\, d\underline{\zeta}}\,. \qquad (4)$$

Note that the equation (3) for infinite volume $V = R^3$ in the case

$$f(\underline{\zeta},\psi(\underline{\zeta})) = \lambda e^{\psi(\underline{\zeta})}\,, \quad \lambda \in R^1$$

was considered earlier by A.A.Vlasov[3], S.V.Tiablikov[4], and other authors.

As shown in ref.5 for $\mathcal{K}(\underline{\xi},\underline{\zeta}) > 0$ the equation (3) has unique solution. That is the solution $\bar{\psi}(\underline{\xi})$ of the equation (2) is unique, therefore, our system, as expected, does not undergo any phase transitions.

Let us make in (2) the change of variables

$$R\underline{\xi} = \underline{x}\,, \quad R\underline{\zeta} = \underline{y}\,; \qquad (6)$$

$$\frac{KN}{R}\psi\left(\frac{1}{R}\underline{x}\right) = U(\underline{x})\,, \qquad (7)$$

where

$$R = \left(\frac{3}{4\pi}V\right)^{1/3} \qquad (8)$$

is the radius of the sphere, the electron gas is contained in. We have

$$U(\underline{x}) = N\,\frac{\int_V \frac{K}{|\underline{x}-\underline{y}|}\, e^{-\beta U(\underline{y})}\, d\underline{y}}{\int_V e^{-\beta U(\underline{y})}\, d\underline{y}}\,, \qquad (9)$$

This is exactly the Vlasov equilibrium self-consistent field equation. The free energy in terms of the new variables is

$$F[N,V,\beta] = -\frac{1}{\beta}\ln\frac{1}{N!}\left[\left(\frac{2\pi m}{\beta}\right)^{3/2} V\right]^N -$$

$$-\frac{1}{2}N\,\frac{\int_V U(\underline{x})\, e^{-\beta U(\underline{x})}\, d\underline{x}}{\int_V e^{-\beta U(\underline{x})}\, d\underline{x}} - N\frac{1}{\beta}\ln\frac{1}{V}\int_V e^{-\beta U(\underline{x})}\, d\underline{x}\,. \qquad (10)$$

In the expressions (9) and (10) the quantity

$$\rho(\underline{x}) = \frac{e^{-\beta U(\underline{x})}}{\int_V e^{-\beta U(\underline{x})}\, d\underline{x}} \qquad (11)$$

represents the one-particle distribution function.

The calculation of the thermodynamic parameters of the system proceeding from the free energy (10) as the corresponding derivatives is embarrassed by the fact that besides the explicit dependece of F on N , V , β there is the implicit one through the function $U(\underline{x})$, which we do not know. To overcome this difficulty, we consider the functional

$$\tilde{F}[U;N,V,\beta] = -\frac{1}{\beta}\ln\frac{1}{N!}\left[\left(\frac{2\pi m}{\beta}\right)^{3/2}V\right]^{N} -$$

$$-\frac{1}{2}N\int_V U(\underline{x})\,\rho_U(\underline{x})\,d\underline{x} - N\frac{1}{\beta}\ln\frac{1}{V}\int_V e^{-\beta U(\underline{x})}\,d\underline{x}\,, \tag{12}$$

where $\rho_U(\underline{x})$ is to be determined from the integral equation

$$U(\underline{x}) = N\int_V \frac{K}{|\underline{x}-\underline{y}|}\,\rho_U(\underline{x})\,d\underline{x}\,. \tag{13}$$

We shall show that for $U(\underline{x}) = \bar{U}(\underline{x})$, where $\bar{U}(\underline{x})$ is the solution of the equation (9), the equality holds

$$\delta\tilde{F}[U;N,V,\beta] = 0$$

and that $\tilde{F}[\bar{U};N,V,\beta]$ is the value of the free energy to be found

$$F = \tilde{F}[\bar{U};N,V,\beta]\,. \tag{14}$$

Varying $\tilde{F}$, we have

$$\delta\tilde{F}[\bar{U};N,V,\beta] = -\frac{1}{2}N\int_V \delta U(\underline{x})\,\rho_{\bar{U}}(\underline{x})\,d\underline{x} - \frac{1}{2}N\int_V \bar{U}(\underline{x})\,\delta\rho_{\bar{U}}(\underline{x})\,d\underline{x} +$$

$$+N\frac{\int_V \delta U(\underline{x})\,e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}}{\int_V e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}}\,. \tag{15}$$

From the other hand, according to (13)

$$\delta\bar{U}(\underline{y}) = N\int_V \frac{K}{|\underline{x}-\underline{y}|}\,\delta\rho_{\bar{U}}(\underline{x})\,d\underline{x}\,. \tag{16}$$

Let us concider now the second term in (15). In view of (9)

$$-\frac{1}{2}N\int_V \bar{U}(\underline{x})\,\delta\rho_{\bar{U}}(\underline{x})\,d\underline{x} = -\frac{1}{2}N^2\frac{\iint_{VV}\frac{K}{|\underline{x}-\underline{y}|}\,e^{-\beta U(\underline{y})}\,\delta\rho_{\bar{U}}(\underline{x})\,d\underline{x}\,d\underline{y}}{\int_V e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}}\,; \tag{17}$$

whence by virtue of (16)

$$-\frac{1}{2}N\int_V \bar{U}(\underline{x})\,\delta\rho_{\bar{U}}(\underline{x})\,d\underline{x} = -\frac{1}{2}N\,\frac{\int_V \delta\bar{U}(\underline{x})\,e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}}{\int_V e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}}\,, \qquad (18)$$

In this case

$$\delta\tilde{F}[\bar{U};N,V,\beta] =$$

$$= -\frac{1}{2}N\int_V \delta\bar{U}(\underline{x})\,\rho_{\bar{U}}(\underline{x})\,d\underline{x} + \frac{1}{2}N\,\frac{\int_V \delta\bar{U}(\underline{x})\,e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}}{\int_V e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}}\,, \qquad (19)$$

but according to (9)

$$\rho_{\bar{U}}(\underline{x}) = \frac{e^{-\beta\bar{U}(\underline{x})}}{\int_V e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}}\,, \qquad (20)$$

therefore

$$\delta\tilde{F}[\bar{U};N,V,\beta] = 0. \qquad (21)$$

In view of (20) the equality (14) is evident.

Thus, according to (21), in calculating the derivatives of the free energy $F = \tilde{F}[\bar{U};N,V,\beta]$ with respect to N , V ,

β we are able not to take into consideration the implicit dependence of the function $\bar{U}(\underline{x})$ on these quantities.

Differentiation yields

$$E = \frac{\partial}{\partial\beta}\left(\beta F[N,V,\beta]\right) = \frac{\partial}{\partial\beta}\left(\beta\tilde{F}[\bar{U};N,V,\beta]\right) =$$

$$= N\cdot\frac{3}{2}\frac{1}{\beta} - \frac{1}{2}N\int_V \bar{U}(\underline{x})\,\rho_{\bar{U}}(\underline{x})\,d\underline{x} + N\,\frac{\int_V \bar{U}(\underline{x})\,e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}}{\int_V e^{-\beta\bar{U}(\underline{x})}\,d\underline{x}} =$$

$$= N\left[\frac{3}{2}\frac{1}{\beta} + \frac{1}{2}\int_V \bar{U}(\underline{x})\,\rho_{\bar{U}}(\underline{x})\,d\underline{x}\right] = E_{\text{кин.}} + E_{\text{пот.}}\,, \qquad (22)$$

where

$$E_{\text{кин.}} = N\cdot\frac{3}{2}\cdot\frac{1}{\beta}\,, \qquad (23)$$

$$E_{\text{пот.}} = N\cdot\frac{1}{2}\int_V \bar{U}(\underline{x})\,\rho_{\bar{U}}(\underline{x})\,d\underline{x}\,. \qquad (24)$$

The potential energy coincides naturally with that of self-consistent field. The energy $E_{\text{пот.}}$ expressed in terms of the self-cosistent field reduced to the unit sphere $\bar{\Psi}(\underline{\xi})$ has the form

$$E_{\text{пот.}} = K \frac{N^2}{\left(\frac{3}{4\pi}V\right)^{1/3}} \frac{\int\limits_{E^3} \bar{\Psi}(\underline{\xi})\, e^{-\beta \frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}} \bar{\Psi}(\underline{\xi})}\, d\underline{\xi}}{\int\limits_{E^3} e^{-\beta \frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}} \bar{\Psi}(\underline{\xi})}\, d\underline{\xi}} . \tag{25}$$

The chemical potential μ is given by

$$\mu = \frac{\partial F}{\partial N} = -\frac{1}{\beta} \ln\left[\left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{V}{N} e\right] + \frac{1}{\beta} - \frac{1}{2}\int\limits_{V} \bar{U}(\underline{x})\, \rho_{\bar{U}}(\underline{x})\, d\underline{x} -$$

$$- \frac{1}{\beta} \ln \frac{1}{V} \int\limits_{V} e^{-\beta \bar{U}(\underline{x})}\, d\underline{x} = \tag{26}$$

$$= -\frac{1}{\beta} \ln\left[\left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{V}{N} e\right] + \frac{1}{\beta} - \frac{1}{2} \frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}} \frac{\int\limits_{E^3} \bar{\Psi}(\underline{\xi})\, e^{-\beta \frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}} \bar{\Psi}(\underline{\xi})}\, d\underline{\xi}}{\int\limits_{E^3} e^{-\beta \frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}} \bar{\Psi}(\underline{\xi})}\, d\underline{\xi}} -$$

$$- \frac{1}{\beta} \ln \frac{3}{4\pi} \int\limits_{E^3} e^{-\beta \frac{KN}{\left(\frac{3}{4\pi}V\right)^{1/3}} \bar{\Psi}(\underline{\xi})}\, d\underline{\xi} . \tag{27}$$

To calculate the pressure

$$p = -\frac{\partial F}{\partial V} \tag{28}$$

we make use of the law of corresponding states

$$\lambda^{-7/3} \tilde{F}\left[U_\lambda ; \lambda N, \lambda^{-1} V, \lambda^{-4/3}\beta\right] = \tilde{F}\left[U; N, V, \beta\right] , \tag{29}$$

where

$$U(\underline{x}) = \lambda^{-4/3}\, U_\lambda\left(\lambda^{-1/3} \underline{x}\right). \tag{30}$$

Let us prove it. We have

$$\lambda^{-7/3} \tilde{F}\left[U_\lambda ; \lambda N, \lambda^{-1} V, \lambda^{-4/3}\beta\right] = -\frac{1}{\beta} \ln \frac{1}{N!}\left[\left(\frac{2\pi m}{\beta}\right)^{3/2} V\right]^N -$$

$$- \lambda^{-7/3}\left[\frac{1}{2} \lambda N \int\limits_{\lambda^{-1}V} U_\lambda(\underline{x})\, \rho^{(\lambda)}_{U_\lambda}(\underline{x})\, d\underline{x} + \lambda^{7/3} N \frac{1}{\beta} \ln \frac{1}{V} \int e^{-\lambda^{-4/3}\beta U_\lambda(\underline{x})}\, d\underline{x}\right] \tag{31}$$

Making the change of variable

$$\underline{x} = \lambda^{-1/3} \underline{\xi} , \tag{32}$$

for the second term in the square braces we obtain the expression

$$\lambda^{7/3} N \frac{1}{\beta} \ln \frac{1}{V} \int\limits_{\lambda^{-1}V} e^{-\lambda^{-4/3}\beta U_\lambda(\underline{x})}\, d\underline{x} = \lambda^{7/3} N \frac{1}{\beta} \ln \frac{1}{V} \int\limits_{V} e^{-\beta U(\underline{\xi})}\, d\underline{\xi} . \tag{33}$$

To calculate the first term we find before the function $\rho^{(\lambda)}_{U}(\underline{x})$.

by the definition of which

$$U_\lambda(\underline{y}) = \lambda N \int\limits_{\lambda^{-1}V} \frac{K}{|\underline{x}-\underline{y}|}\, \rho_{U_\lambda}^{(\lambda)}(\underline{x})\, d\underline{x}\,, \tag{34}$$

Making the change (32) we find

$$U_\lambda(\lambda^{-1/3}\underline{y}) = \lambda^{1/3} \int\limits_{V} \frac{K}{|\underline{x}-\underline{y}|}\, \rho_{U_\lambda}^{(\lambda)}(\lambda^{-1/3}\underline{x})\, d\underline{x}\,. \tag{35}$$

whence

$$U(\underline{y}) = \int\limits_{V} \frac{K}{|\underline{x}-\underline{y}|} \cdot \frac{1}{\lambda}\, \rho_{U_\lambda}^{(\lambda)}(\lambda^{-1/3}\underline{x})\, d\underline{x}\,. \tag{36}$$

Comparing (36) with (13) we obtain

$$\frac{1}{\lambda}\, \rho_{U_\lambda}^{(\lambda)}(\lambda^{-1/3}\underline{x}) = \rho_U(\underline{x})\,. \tag{37}$$

Then

$$\frac{1}{2}\lambda N \int\limits_{\lambda^{-1}V} U_\lambda(\underline{x})\, \rho_{U_\lambda}^{(\lambda)}(\underline{x})\, d\underline{x} = \frac{1}{2} N \int\limits_{V} U_\lambda(\lambda^{-1/3}\underline{x})\, \rho_{U_\lambda}^{(\lambda)}(\lambda^{-1/3}\underline{x})\, d\underline{x} =$$

$$= \lambda^{7/3}\, \frac{1}{2} N \int\limits_{V} U(\underline{x})\, \rho_U(\underline{x})\, d\underline{x}\,, \tag{38}$$

that in view of (33) leads to (29).

Differentiating (29) with respect to λ and making use of (21) we have

$$-\frac{7}{3}\lambda^{-10/3}\tilde{F}[\bar{U}_\lambda; \lambda N, \lambda^{-1}V, \lambda^{-4/3}\beta] + \lambda^{-7/3}\Big\{ N \frac{\partial \tilde{F}[\bar{U}_\lambda; \lambda N, \lambda^{-1}V, \lambda^{-4/3}\beta]}{\partial(\lambda N)} -$$

$$- \frac{1}{\lambda^2} V \frac{\partial \tilde{F}[\bar{U}_\lambda; \lambda N, \lambda^{-1}V, \lambda^{-4/3}\beta]}{\partial(\lambda^{-1}V)} - \lambda^{-7/3}\frac{4}{3}\beta \frac{\partial \tilde{F}[\bar{U}_\lambda; \lambda N, \lambda^{-1}V, \lambda^{-4/3}\beta]}{\partial(\lambda^{-4/3}\beta)}\Big\} = 0 \tag{39}$$

Setting here $\lambda = 1$ we obtain

$$-\frac{7}{3}F + pV - \frac{4}{3}(E-F) + \mu N = 0\,, \tag{40}$$

whence

$$pV = F + \frac{4}{3}E - \mu N = \Omega + \frac{4}{3}E\,. \tag{41}$$

Making use of the expression for the chemical potential (26) we find the pressure on the surface of the sphere

$$p = \frac{1}{3V}\left(4E - \frac{3N}{\beta}\right), \tag{42}$$

or

$$P = \frac{1}{3V}\left(4E_{\text{пот.}} + 2E_{\text{кин.}}\right). \tag{43}$$

Let us write the equation (9) in more convinient form. Note that in view of the symmetry of our problem we may restrict ourselves to spherically symmetric potentials $U(\underline{x})$ and dencities $\rho(\underline{x})$. Then, for the integrals over the shere of radius r' , appearing in the right-hand side of (9), are calculated **explicitly**

$$\int_{S_{r'}} \frac{1}{|\underline{x}-\underline{x}'|}\, dS_{r'} = \begin{cases} \frac{1}{|\underline{x}|}, & |\underline{x}| \geq |\underline{x}'| \\ \frac{1}{|\underline{x}'|}, & |\underline{x}| \leq |\underline{x}'| \end{cases} , \tag{44}$$

we have

$$U(\underline{x}) = N\kappa \frac{\int_0^R 4\pi r'^2 \left[\frac{\theta(r-r')}{r} + \frac{\theta(r'-r)}{r'}\right] e^{-\beta U(r')}\, dr'}{\int_0^R 4\pi r'^2 e^{-\beta U(r')}\, dr'} , \tag{45}$$

where

$$r = |\underline{x}| , \quad r' = |\underline{x}'| . \tag{46}$$

Similarly, the equation (2) takes the form

$$\psi(r) = \frac{\int_0^1 r'^2 \left[\frac{\theta(r-r')}{r} + \frac{\theta(r'-r)}{r'}\right] e^{-\beta \frac{KN}{R}\psi(r')}\, dr'}{\int_0^1 r'^2 e^{-\beta \frac{KN}{R}\psi(r')}\, dr'} . \tag{47}$$

As has already been mentioned before, the equations (45) and (47)have the unique solution. It is shown in ref.5 that this solution is the limit of sequential approximations.

Setting in the zero approximation the function $\psi(r)$ equal to a constant, in the first approximation we obtain

$$\psi(r) = \frac{3}{2} - \frac{1}{2} r^2 , \tag{48}$$

$$U(r) = \frac{3}{2}\frac{KN}{R} - \frac{1}{2}\frac{KN}{R^3} r^2 . \tag{49}$$

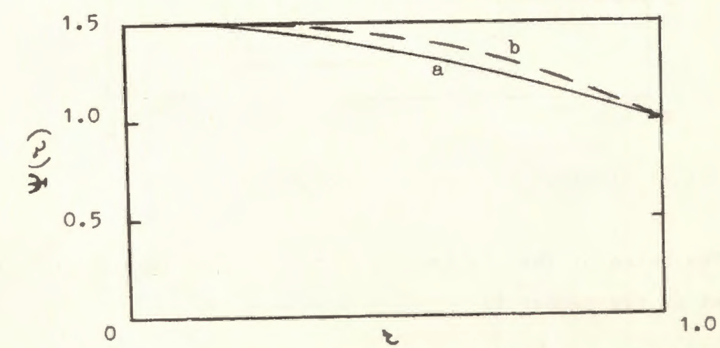

Fig.1. Self-consistent field $\Psi(r)$ vs radius.
a) The first approximation.
b) Numerical exact solution (broken line).

In Fig.1 we show the function $\Psi(\varkappa)$ in the first approximation (48) and, to compare with, its exact value for $\beta\frac{KN}{R}=1$ determined numerically. The difference between the two is within 5 %.

The electron dencity as a function of the distance from the center of the sphere is

$$n(r)=N\rho(r)=Ce^{\frac{1}{2}\beta\frac{KN}{R^3}r^2}, \tag{50}$$

where C is independent of r.

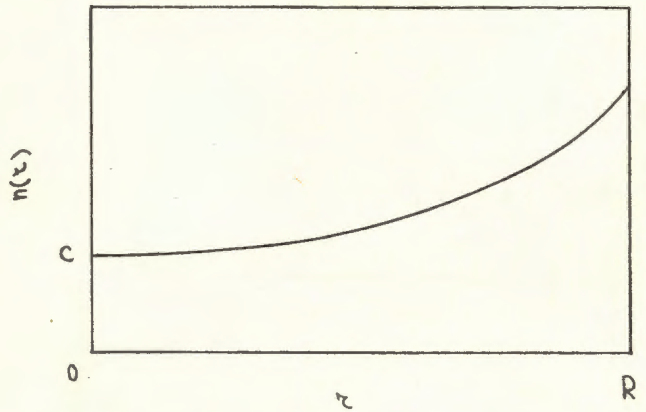

Fig.2. Electron dencity as function of radius.

The ratio of the electron dencity near the sphere surface to that in its center is

$$n(R)/n(0)=e^{\frac{1}{2}\beta\frac{KN}{(\frac{3}{4\pi}V)^{1/3}}}. \tag{51}$$

Thus, the classical electron gas cannot be considered as gas of constant dencity. The consideration of the electron gas in infinite volume is also impossible. The thermodynamic - in the common sence - limit for this problem does not exist.

Calculating on the basis of (47) the potential energy (25) we obtain

$$E_{\text{пот.}}=\frac{3}{5}\frac{KN^2}{(\frac{3}{4\pi}V)^{1/3}}, \tag{52}$$

whence we find the expression for the pressure

$$p=\frac{1}{3V}\left[\frac{2N}{\beta}+\frac{3}{5}\frac{KN^2}{(\frac{3}{4\pi})^{1/3}}\cdot\frac{1}{V^{1/3}}\right]. \tag{53}$$

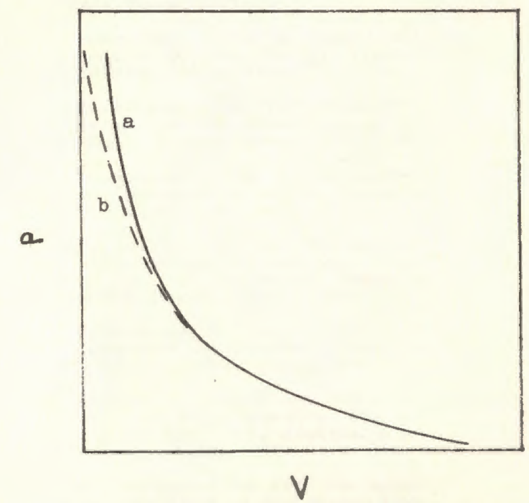

Fig.3. Isotherm of electron gas.
a) Electron gas.
b) Ideal gas (broken line).

R e f e r e n c e s

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