The Pressure of a Non-interacting Electron System of a Finite Number of Particles at Zero-Temperature

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Abstract

The pressure of a non-interacting electron system of a finite number of particles is calculated with the basis on quantum theory and "semi-classical" theory at zero-temperature. The result is compared with the pressure of a free electron gas of an infinite number of particles given by statistical mechanics. It is found that the result approaches the one of statistical mechanics when the particle number is enormously increased, keeping the particle number per unit volume constant.

§ 1. Introduction

Generally, equation of state of a gas can be calculated by

$$PV = k_B T \ell n Z_G, \tag{1.1}$$

where Z_G is the grand partition function. In statistical mechanics the pressure of a free electron gas at zero-temperature is easily obtained from equation (1.1):

$$P = \frac{2}{5}(3\pi^2)^{\frac{2}{3}} \frac{\hbar^2}{2m}\left(\frac{N}{V}\right)^{\frac{5}{3}} \tag{1.2}$$

The above equation is applicable to the case when both the number of particles N and the volume V are enormous[1]

When N and V are finite, however, we can not use equation (1.2) since statistical mechanics is invalid in such a finite system. In order to obtain the pressure of a finite system, we must abandon statistical mechanics and stand on the microscopic point of view.

In this paper, we introduce a new definition of the pressure of a finite system and calculate the pressure by making use of a microscopic theory, namely, quantum theory and "semi-classical" theory. We will find the pressure obtained approaches the equation (1.2) asymptotically in the limit N and $V \to \infty$, keeping the number density N/V constant, i.e., in the thermodynamic limit.

We will give the definition and calculate by quantum theory in section 2 and by "semi-classical" theory in section 3. In the both sections the system of one electron is treated, and the results are found to coincide with each other. In section 4, a

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non-interacting electron system of a finite number of particles at zero-temperature will be discussed and, by making use of the idea of section 3, numerical calculations will be made. We will also compare our result with the one by statistical mechanics. In the last section some conclusions are given.

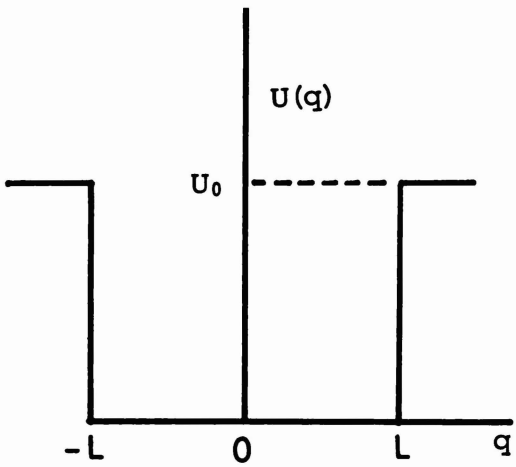

Fig. 1. Square well potential with finite potential step.

§ 2. Quantum theoretical calculations of the pressure

Let us consider one electron to be confined in a cube of side $2L$ or in a spherical shell of radius L. Inside the container, the electron is free so that the potential vanishes. On the other hand, outside the container, the potential becomes infinite since the electron is not permitted to exist. Then there exists an infinite step of the potential at the wall of the container. For simplicity, however, we assume first the potential to take a finite value U_0 as shown in Fig. 1. After the final calculation we will take $U_0 \to \infty$.

We define the pressure to be a force on a unit area of the wall of the container exerted by the electron. The force on the wall perpendicular to the q_1-axis is

$$-\dot{p}_1 = \partial H/\partial q_1 \,, \qquad (2.1)$$

where p_1 is the q_1-component of the momentum and H is the Hamiltonian of the electron, $H=(p_1^2+p_2^2+p_3^2)/2m+U(q_1,q_2,q_3)$. Equation (2.1) is the canonical equation of Hamilton. Quantum mechanical expectation value of this equation is[2)]

$$\langle F^{q_1}\rangle \equiv \langle -\dot{p}_1\rangle = \langle \partial H/\partial q_1\rangle \qquad (2.2)$$

Hence, dividing equation (2.2) by the area of the wall, the pressure is given by

$$P_q^{q_1} \equiv \langle F^{q_1}\rangle/(\text{the area of the wall}). \qquad (2.3)$$

Similarly, the pressures $P_q^{q_2}$ and $P_q^{q_3}$ on the wall parpendicular to the q_2-axis and the q_3-axis are obtained, respectively.

a) the case of a cube of side *2L*

First we treat with the case when the container is a cube of side $2L$. The pressure P_q^x on the wall parpendicular to the x-axis is given by

$$P_q^x = \langle \partial H/\partial x\rangle/(2L)^2 = \int_0^\infty |\psi(x)|^2 \partial H/\partial x \, dx/(2L)^2$$

$$= U_0 |\psi(L)|^2/(2L)^2 \qquad (2.4)$$

where $\psi(x)$ is a normalized eigenfunction belonging to an eigenvalue ε of the Hamiltonian H. As seen from equation (2.4), we need the absolute value of $\psi(x)$ at $x=L$ which is given by

$$|\psi(L)|^2=\left[\frac{2\,\alpha L\pm\sin 2\,\alpha L}{\alpha\,(1\pm\cos 2\,\alpha L)}+\frac{1}{\beta}\right]^{-1}, \qquad (2.5)$$

$$\alpha^2=2\,m\varepsilon/\hbar^2,\ \beta^2=2\,m(U_0-\varepsilon)/\hbar^2,$$

after simple calculations. Here the upper(lower) sign corresponds to the case when $\psi(x)$ is an even(odd) function. Because of the boundary condition at $x=L$ satisfied by $\psi(x)$, we have

$$\tan\alpha L=\frac{1}{2}\left[\frac{\beta^2-\alpha^2}{\alpha\beta}\pm\frac{\beta^2+\alpha^2}{\alpha\beta}\right] \qquad (2.6)$$

In the limit $U_0\to\infty$, by using equations (2.5) and (2.6), we obtain

$$\lim_{U_0\to\infty} U_0|\psi(L)|^2=\varepsilon_{n_1}/L, \qquad (2.7)$$

where $\varepsilon_{n_1}=\hbar^2\pi^2 n_1^2/(8\,mL^2)$, $(n_1=1,\ 2,\ 3,\cdots)$. ε_{n_1} is the energy eigenvalue when an electron is closed in a cube of side $2L$. From equations (2.4) and (2.7),

$$P_q^x=2\varepsilon_{n_1}/V.$$

Similarly, we get

$$P_q^y=2\varepsilon_{n_2}/V \text{ and } P_q^z=2\varepsilon_{n_3}/V.$$

The pressure averaged over three directions (x,y and z) is

$$P_q\equiv(P_q^x+P_q^y+P_q^z)/3=2\,{}_{n_1,n_2,n_3}/3\,V, \qquad (2.8)$$

where $\varepsilon_{n_1,n_2,n_3}=(\hbar^2/2\,m)(\pi/2\,L)^2(n_1^2+n_2^2+n_3^2)$.
Equation (2.8) is the pressure that the electron with the quantum number (n_1,n_2,n_3) exerts on the wall of a cube of side $2L$.

b) the case of a spherical shell of radius L

Next we consider the case in which the container is a spherical shell of radius L. The pressure that an electron acts on the wall can be obtained in the same manner as described above. We adopt a polar coordinate system. From the equation (2.3),

$$P_q=\langle F_r\rangle/(4\,\pi L^2)=\langle\partial H/\partial r\rangle/(4\,\pi L^2)$$

$$=U_0 R_{n,l}^2(L)/(4\,\pi L^2), \qquad (2.9)$$

where $R_{n,l}(r)$ is the normalized radial wave function, and $n(\ell)$ is the radial(angular-momentum) quantum number. We obtain, at $r=L$,

$$R_{n,l}^2(L)=\frac{2}{L^3}\left[2-\frac{j_{l-1}(\alpha L)j_{l+1}(\alpha L)}{j_l(\alpha L)}-\frac{h_{l-1}^{(1)}(i\beta L)h_{l+1}^{(1)}(i\beta L)}{h_l^{(1)}(i\beta L)}\right]^{-1} \qquad (2.10)$$

where j_l is the spherical Bessel function and $h_l^{(1)}$ is the spherical Hankel function. The boundary condition at a surface $(r=L)$, on which there is a finite potential step, leads to

$$\alpha L j_l'(\alpha L)/j_l(\alpha L)=i\beta L\, h_l^{(1)\prime}(i\beta L)/h_l^{(1)}(i\beta L). \tag{2.11}$$

The recurrence formula valid for both j_l and $h_l^{(1)}$ is written as

$$f_l'(z)=\frac{\ell}{z}f_l(z)-f_{l+1}(z)=f_{l-1}(z)-\frac{\ell+1}{z}f_l(z) \tag{2.12}$$

where f_l is j_l or $h_l^{(1)}$. From (2.10), (2.11) and (2.12),

$$R_{n,l}^2(L)=\frac{2}{L^2}\left[2+\left(\frac{U_0-\varepsilon}{\varepsilon}-1\right)\frac{h_{l-1}^{(1)}(i\beta L)h_{l+1}^{(1)}(i\beta L)}{h_l^{(1)}(i\beta L)^2}\right]^{-1} \tag{2.13}$$

In the limit $U_0\to\infty$, we can see

$$\lim_{U_0\to\infty} U_0 R_{n,l}^2(L)=2\,\varepsilon_{n,l}/L^3, \tag{2.14}$$

where $\varepsilon_{n,l}$ is the eigenvalue of energy of an electron which is captured in a spherical shell of radius L. From (2.9) and (2.14), we get

$$P_q=2\,\varepsilon_{n,l}/3\,V. \tag{2.15}$$

The above equation is the pressure that the electron with the quantum number (n, ℓ) exerts on the wall of the container.

§ 3. "Semi-classical" calculations of the pressure

In the previous section, we have calculated the pressure by use of quantum mechanics, when there is one electron in a container. By the way quantum mechanics offers the information of the energy levels of the electrons in the container and of the probability functions of the electrons in it, but it never gives us the informations how an electron moves in the container. Furthermore, it does not have any answer on the question what the passage is when an electron transfers from the point A to B in the container[3]. It will be natural to consider that quantum mechanics is essentially constructed by the probability theory[4].

For a while, we neglect that quantum mechanics has a probability theoretic property. We assume the electron in the container has an orbital motion with the energy given by quantum mechanics. We call this assumption "semi-classical". The pressure based on such an assumption may be defined as follows;

$$P_c\equiv\lim_{t\to\infty}(\text{the force on the wall})/(\text{the area of the wall}), \tag{3.1}$$

where t is a time interval of motion. From this definition, we try to calcuate the pressure in the same manner as section 2, when the electron is confined **a)** in a cube of side $2L$ and **b)** in a spherical shell of radius L.

a) the case of a cube of side $2L$.

When the energy level of an electron is given, one can determine the momentum corresponding to it. Once the electron that has the x-component of the momentum p_x collides with the wall parpendicular to the x-axis, the x-component of the momentum changes to $-p_x$. The force exerted on the wall by the electron is obtained by multipling the momentum change $2|p_x|$ by the collision number of times per unit time. The collision number of times per unit time is not constant for the finite time interval because there is a fluctuation. In the limit $t \to \infty$, however, it becomes constant, namely, $|p_x|/4mL$. Thus from equation (3.1),

$$P_c^x = p_x^2/8mL^3 = 2\varepsilon_{n_1}/V.$$

The eigenvalue ε_{n_1} is the energy, when an electron is closed in a cube of side $2L$. Similarly, we have

$$P_c^y = 2\varepsilon_{n_2}/V \text{ and } P_c^z = 2\varepsilon_{n_3}/V.$$

Therefore,

$$P_c \equiv (P_c^x + P_c^y + P_c^z)/3 = 2\varepsilon_{n_1,n_2,n_3}/3V, \qquad (3.2)$$

where $\varepsilon_{n_1,n_2,n_3} = (\hbar^2/2m)(\pi/2L)^2(n_1^2 + n_2^2 + n_3^2)$.

b) the case of a spherical shell of radius L

We can proceed in the same manner as **a**). If the momentum of an electron is p, we obtain the force on the wall by multipling the number of times by which an electron collides with the wall in a unit time, $p/(2mL\cos\theta)$, by the momentum change per unit time. Here θ is the angle between the direction to the wall of the electron and the direction connecting the center of a container to the collision point. Then equation (3.1) is calculated as

$$P_c = (p^2/mL)/4\pi L^2 = 2\varepsilon_{n,\ell}/3V. \qquad (3.3)$$

Equation (3.3) is the pressure exerted on the wall of the spherical shell by an electron inside it.

The results of **a**) and **b**) coincide with those in section 2.

§ 4. Numerical calculations (comparison with statistical mechanics)

Let us calculate the pressure of a non-interacting electron system of a finite number of particles at zero-temperature by employing the results obtained in sections 2 and 3. As seen in those sections, an electron exerts the pressure, expressed as

$$P_i = 2\varepsilon_i/3V,$$

on the wall of the container. Here the suffix i represents quantum numbers (n_1, n_2, n_3) or (n, ℓ), and ε_i is the one-particle energy of the electron in the state i. For N electrons move independently with each other in the container, the total pressure P

of the system is the summation of P_i's and is given by

$$P=\frac{2}{3V}\sum \varepsilon_i n_i, \qquad (4.1)$$

where n_i is the occupation number of the state i. Since we treat with the finite system at zero-temperature and electrons obey the Pauli exclusion principle, $n_i=0$ or 1 and then the summation over i in the above equation should be taken in such a way that $\sum n_i=N$ and the total energy $E=\sum \varepsilon_i n_i$ becomes minimum.

In order to investigate how the pressure P varies as the particle number N changes, we performed the numerical calculation. Fig. 2 shows the relationship

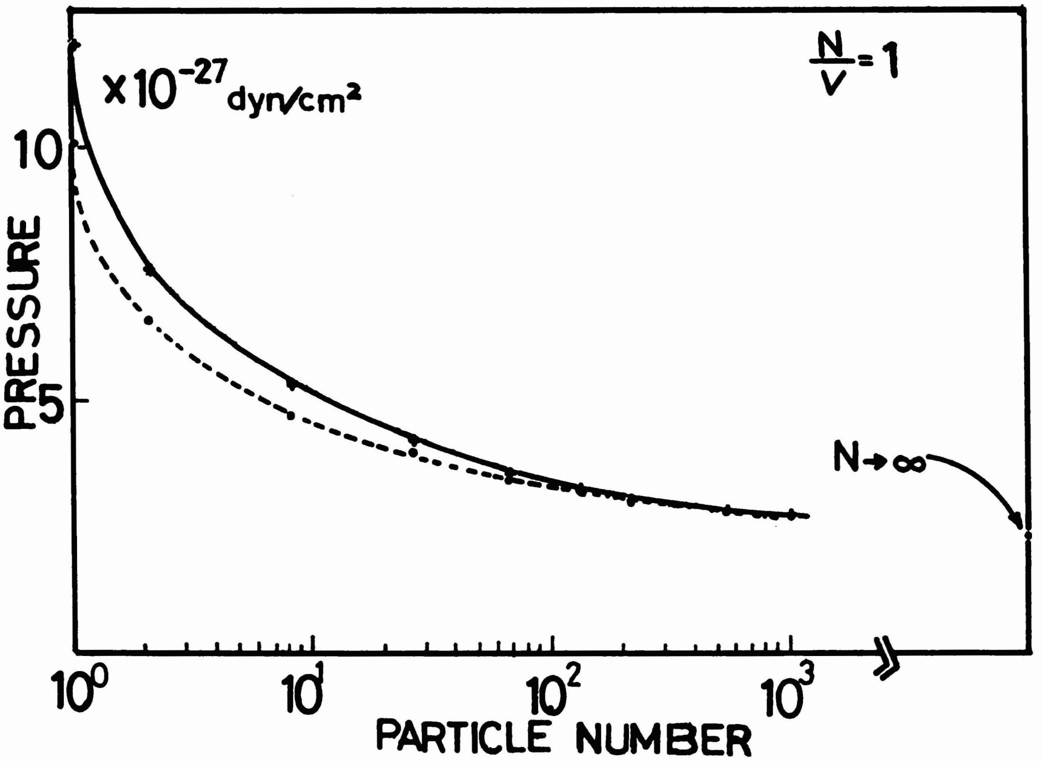

Fig. 2. Relationship between the pressure and the particle number for the value of $N/V=1$; full line corresponds to the case of a cube of side $2L$ and broken line to the one of the spherical shell of radius L. The point of the right-hand side represents the result by statistical mechanics.

between the pressure and the particle number, for the value of $N/V=1$, in two cases when the container is a cube of side $2L$ and a spherical shell of radius L. We can see from Fig. 2 that P decreases monotonously as N increases and that it approaches asymptotically the pressure obtained by statistical mechanics in the thermodynamic limit (N and $V\to\infty$, keeping N/V constant). The reason why the pressure increases with the decrease of small N can be interpreted by the uncertainty principle. For example, when $N=1$, the position uncertainty of order $2L$ implies a momentum uncertainty at least of order $\hbar/2L$. This is also compelled that the momentum of an electron is not smaller than $\hbar/2L$ when an electron is closed in the range $2L$[5]. It is also found that the difference of the pressures between in two cases of the shape of the container becomes smaller as N (and V) becomes larger. This implies that the container does not depend on the shape for relatively large volume.

In Fig. 2, we examined only for the value of $N/V=1$. Naturally it occurs a question how P behaves when N/V takes the other values. The pressure of a free electron gas in statistical mechanics is proportional to $(N/V)^{5/3}$, as seen from equation (1.2). Therefore, our result (4.1) is expected to behave as $(N/V)^{5/3}$ when N(and V) is infinity large. In Fig. 3, the behaviour of P against N/V is plotted. According to Fig. 3, when the volume V increases to infinity, the dependence of P on N/V is the same as equation (1.2) as expectedly.

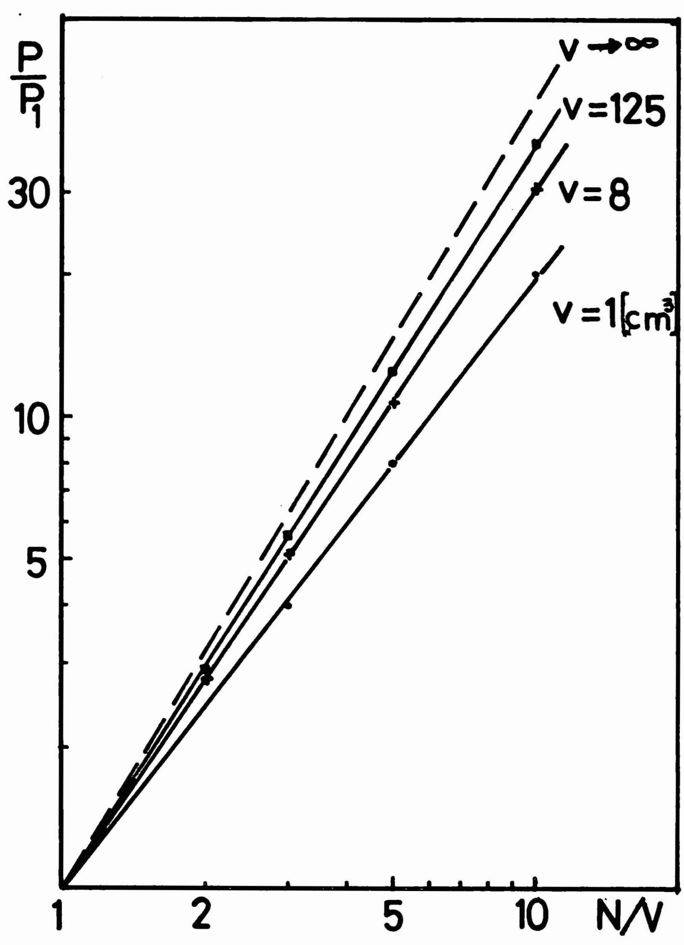

Fig. 3. A plot of P/P_1 vs. N/V for a free electron gas of a finite number of particles. P_1 is the pressure when $N/V=1$; broken line is the result given by statistical mechanics.

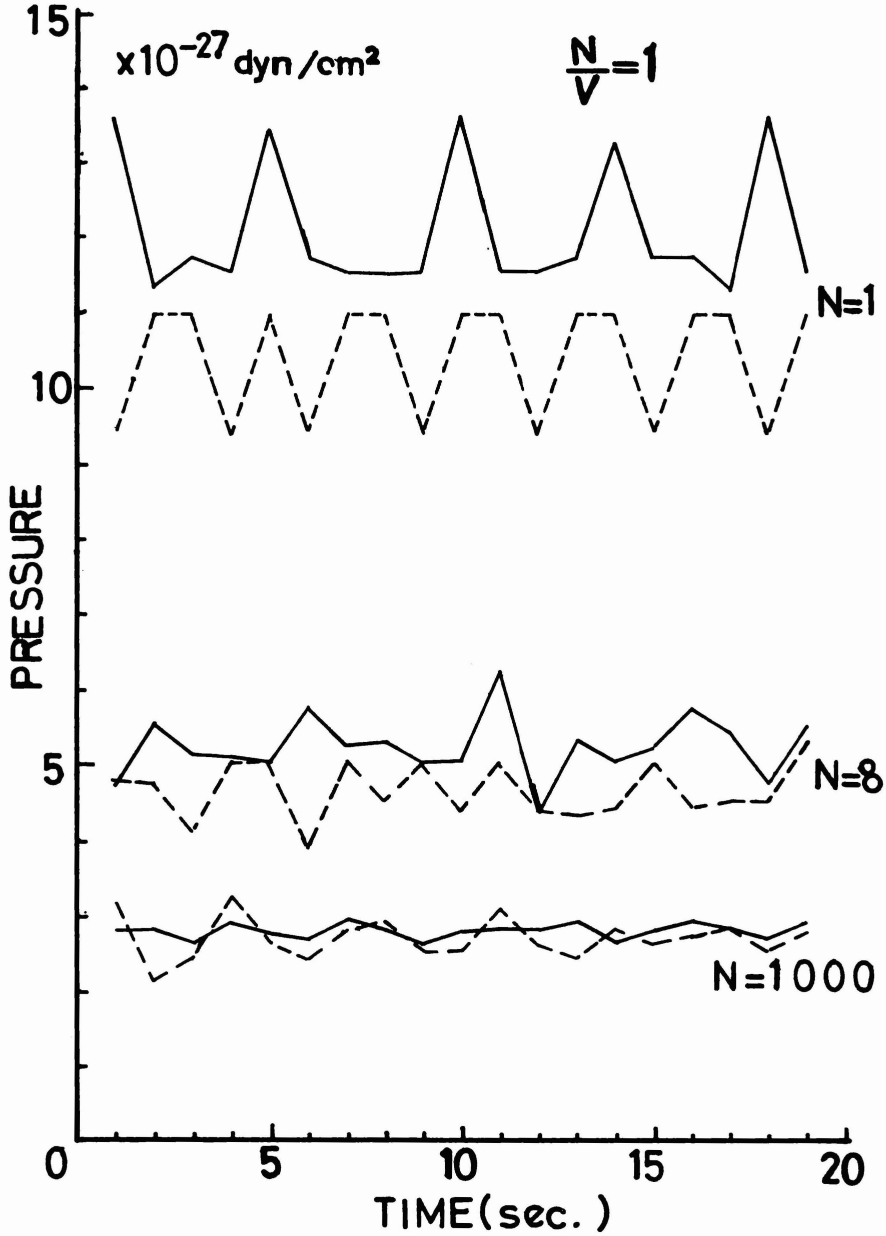

Fig. 4. Schematic view of the fluctuations in the pressures for each number of the particles in the containers; full line is the case of the cube of side $2L$ and broken line is the case of the spherical shell of radius L.

Next we try to examine a fluctuation of the pressure which occurs when a time interval of motion is finite as explained in section 3. In doing so, we need to calculate the momentum of the electron and also the collision number of times in a unit time. The latter quantity depends on the former and on the position of the electron. In the "semi-classical" theoretical assumption discussed in section 3, the *momentum* is determined when the energy level is given. The position of the electron, however, can not be determined. Then we determine it by using the random number. In Fig. 4, we show schematicaly the result of the numerical calculation on the fluctuation of the presure per unit time for $N/V=1$. As a matter of fact, the fluctuation of the pressure is found to become smaller as the particle number N is increased. Of course, if the time interval of motion t is taken large enough, the fluctuation disappears. This situation is understood more clearly from Fig. 5 which shows, in case of $N=1$, how the fluctuation becomes smaller and smaller as the time interval increases, and that the pressure coincides with equation (3.2) and (3.3) in the limit $t \to \infty$.

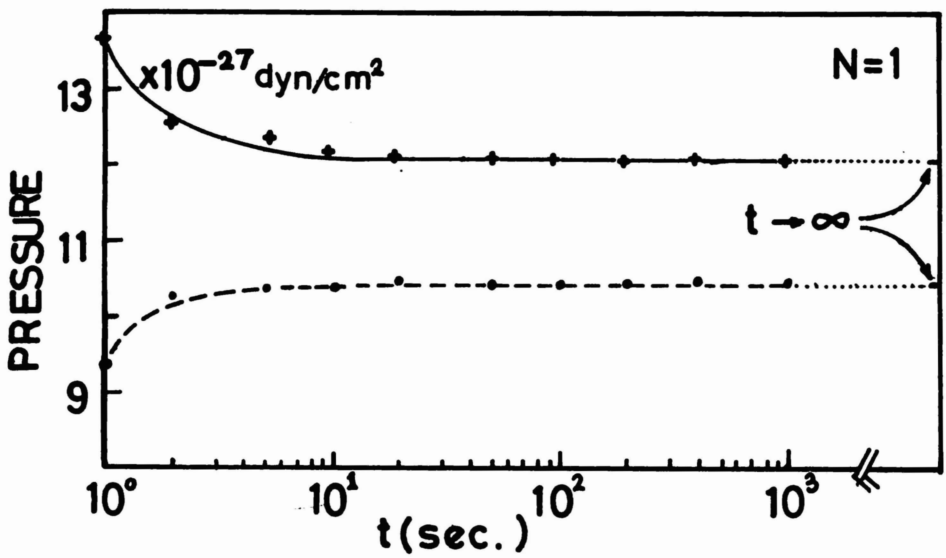

Fig. 5. Behaviour of the pressure against the time interval of motion. Full line is the case of the cube of side $2L$ and broken line is the case of the spherical shell of radius L. In the limit $t \to \infty$, each pressure coincides with equations (3.2) and (3.3).

§ 5. Conclusions

In the previous sections we have discussed the pressure for the non-interacting electron system of a finite number of particles with the basis on quantum theory and "semi-classical" theory, and also have performed numerical calculations to compare with statistical mechanics which is valid for the system of the infinite number of particles.

We have obtained important results as follows :

(1) The pressure for the finite particle number N given by equation (4.1) decreases monotonously with the increase of N.

(2) In the thermodynamic limit (N and $V \rightarrow \infty$, keeping the number density N/V constant), equation (4.1) reduces to the pressure for the free electron gas of the infinite number of particles given by statistical mechanics.

(3) And therefore it seems that new definitions of the pressure in sections 2 and 3 are valid.

It is more interesting to study the pressure for the interacting electron system of a finite number of particles at zero-temperature and also the dependence of the pressure on the temperature in the neighborhood of zero-temperature. We shall discuss on these problems elsewhere in a near future.

Acknowledgment

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References

1) A.L. Fetter and J.D. Walecka ; *Quantum Theory of Many-Particle Systems* (1971) chap. 2.
2) L.D. Landau and E.M. Lifshitz ; *Quantum Mechanics* (1964) chap. 3. §.22.
3) Ted Bastin ; *Quantum Theory and Beyond* (1971) chap. 5.
4) H.R. Post ; *ibid.* chap. 5.
5) L.I. schiff ; *Quantum Mechanics* (1955) chap. 2. §9.