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Evaluations of the Equations of State and Thermodynamic Quantities of Fluid Metal at High Temperatures and Densities

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Abstract

We have applied the temperature dependent Thomas-Fermi theory to evaluate the equations of state, chemical potentials, entropies, % ionizations, total energies and kinetic energies of an atom, and several thermodynamic quantities of one of metallic substance, Na, for a density range of $0.1\rho_0 \sim 10\rho_0$, where ρ_0 is the normal density of Na at its melting point, and for a temperature range of $60.88 \text{ Ryd.} \sim 0.0216 \text{ Ryd.}$, where the system is expected to be in a gaseous or liquid state.

The main interest of present work lies in physical quantities at high temperatures and high densities, however, we have included those quantities of Na at sufficiently low temperatures and low densities to show that the approximation is not so crude as one might expect.

Particularly, at high temperatures, the calculated equations of state, kinetic energies of an atom, chemical potentials and entropies are compared with those of an ideal Fermi gas. The results show that, at high temperatures, the agreement seems good for chemical potentials. However, the differences in entropy, kinetic energy of an atom, and equation of state are not negligible even at such high temperature as $kT = 60.88 \text{ Ryd.}$

요 약

溫度從屬 Thomas-Fermi 理論을 適用하여 金屬의 一種인 Na에 對한 狀態方程式, chemical potential, % ion化度, 엔트로피, 原子當運動에너지 및 總에너지 등을 包含한 諸熱力學的의 量을 算出하였다. ρ_0 를 Na의 沸騰點에서의 正常密度라 할 때 $0.1\rho_0 \sim 10\rho_0$ 까지의 密度領域에서, 또한 Na이 氣體 또는 液體狀態로 存在할 것으로 期待되는 $kT = 60.88 \text{ Ryd.} \sim 0.0216 \text{ Ryd.}$ 까지의 溫度領域에 對하여 이들 量을 算出하였다.

本 研究에서는 高溫 및 高壓狀態에서의 物理量을 算出하는 것을 主目的으로 하고 있으나 Thomas-Fermi 近似가 期待되는 것처럼 그렇게 조잡하지 않음을 보이기 위하여 極低溫 및 極低密度에서의 物理量들도 算出하였다.

특히 高溫에서의 狀態方程式, 運動에너지, chemical potential 및 엔트로피를 ideal Fermi gas의 이들 量과 比較하였다. 그 結果, 算出한 chemical potential은

서로 잘 一致하나 엔트로피, 原子當運動에너지 및 狀態方程式은 $kT = 60.88 \text{ Ryd.}$ 의 高溫에서도 相當한 差異가 있음을 發見하였다.

I. Introduction

Thomas¹⁾ and Fermi²⁾ suggested the Thomas-Fermi theory for calculations of the Self-Consistent-Central-Field potentials and electron density distribution functions of the ground state isolated atoms. Since then, the theory has been developed to include the exchange effect³⁾ and to treat systems of non-ground state finite atoms⁴⁾.

Even though the precise structure of shells is not present in the approximation, qualitative behavior of the electron density distribution function about a specific nucleus seems to be acceptable. Especially, the theory yields excellent S. C. F. potentials⁵⁾. The approximation is expected to be improved as temperature and density of a system increases⁶⁾.

Due to its simple and fast numerical procedures, the theory has a definite advantage over the other theories when we are to evaluate physical quantities at high temperatures and high densities.

Throughout present work, we have developed a computer program to solve the Thomas-Fermi equation and to calculate physical quantities of a given system. Effort has been made to minimize the size of program so as to be adequate to small computers.

II. Thomas-Fermi Theory

a) Thomas-Fermi equation

If we let $\bar{V}(r)$ be the average electrostatic potential felt by an electron at a distance r from any specific nucleus, then Poisson's equation gives

$$\nabla^2 \bar{V}(r) = -\frac{e}{\epsilon_0} \rho(r). \quad (1)$$

where ϵ_0 is the dielectric constant in vacuum, e is the charge of an electron, $\rho(r)$ is the electron density distribution function about a given nucleus. The Thomas-Fermi theory approximates $\rho(r)$ by

$$\rho(r) = \frac{8\pi}{h^3} \int_0^\infty \frac{P^2}{\exp\left\{\beta\left(\frac{P^2}{2m} - e\bar{V}(r) - \alpha\right)\right\} + 1} dP. \quad (2)$$

Where h is Planck constant, β is $\tau^{-1} = (kT)^{-1}$, and $\beta\alpha$ is the chemical potential of a system. Since as $r \rightarrow 0$, $\bar{V}(r) \rightarrow \frac{Ze}{4\pi\epsilon_0 r}$, and when r is at ion-sphere radius, R_s , $\bar{V}(r)$ is expected to be constant, the boundary conditions may be written, as

$$\begin{aligned} r\bar{V}(r) &= \frac{Ze}{4\pi\epsilon_0} & \text{at } r=0, \\ \frac{d\bar{V}(r)}{dr} &= 0 & \text{at } r=R_s, \end{aligned} \quad (3)$$

where Z is the atomic number of a given system. The ion-sphere radius is determined by the average electron density ρ of $\frac{4}{3}\pi R_s^3 \rho = Z$, since Z electrons are located inside the ion-sphere.

Since it is more convenient to transform Eqs. (1), (2), and (3) into a dimensionless equations, we will transform the above equations by letting

$$\phi(r) = \frac{4\pi\epsilon_0(e\bar{V}(r) + \alpha)}{Ze^2} r \quad (4)$$

and

$$x = \frac{r}{R_s} \quad (5)$$

After the above substitutions, Eqs. (1), (2), and (3) are written as

$$\frac{d^2\phi(x)}{dx^2} = ax I_{\frac{1}{2}}\left(b \frac{\phi(x)}{x}\right), \quad (6)$$

$$\phi(0) = 1 \quad (7)$$

and

$$\phi(x) = -\frac{d\phi(x)}{dx} \quad \text{at } x=1, \quad (8)$$

where

$$I_{\frac{M}{2}}(y) = \int_0^{\infty} \frac{t^{\frac{M}{2}}}{\exp(t-y)+1} dt \quad (9)$$

When we employ the Bohr unit, the constants a and b in the Eq. (6) is

$$\begin{aligned} a &= \frac{3\tau^{1.5}}{2\pi^2\rho}, \\ b &= \frac{2Z}{R_s\tau}. \end{aligned} \quad (10)$$

Integrating Eq. (6) from x to 1, we get

$$\frac{d\phi(x)}{dx} = \frac{d\phi(x)}{dx} \Big|_{x=1} - a(G(1) - G(x)) \quad (11)$$

where

$$G(x) = \int_x^1 t I_{\frac{1}{2}}\left(b \frac{\phi(t)}{t}\right) dt. \quad (12)$$

Again integrating Eq. (11) from 0 to x , and replacing $\phi'(1)$ by $\phi(1)$

$$\begin{aligned} \phi(x) &= \phi(0) + \phi(1)x - a(xG(1) \\ &\quad - \int_0^x G(t) dt). \end{aligned}$$

The last term in the above equation is integrated by parts to yield

$$\begin{aligned} \phi(x) &= \phi(0) + \phi(1)x - ax \int_x^1 t I_{\frac{1}{2}}\left(b \frac{\phi(t)}{t}\right) dt \\ &\quad - a \int_0^1 t^2 I_{\frac{1}{2}}\left(b \frac{\phi(t)}{t}\right) dt \\ &\quad + a \int_x^1 t^2 I_{\frac{1}{2}}\left(b \frac{\phi(t)}{t^2}\right) dt. \end{aligned} \quad (13)$$

If we put $x=1$ into the above equation, we get

$$\phi(0) = a \int_0^1 t^2 I_{\frac{1}{2}}\left(b \frac{\phi(t)}{t}\right) dt. \quad (14)$$

It seems worthwhile to discuss the significance of the above relation. Since the electron density distribution function is proportional to $I_{\frac{1}{2}}\left(b \frac{\phi(t)}{t}\right)$, one of the boundary conditions, $\phi(0)$ is identical with the normalization condition. This point is particularly important when we attempt to solve the Thomas-Fermi equation for a system of ions and electrons. Unlike the chemical potential, the ionic core size or the percentage ionization can not be self-determined. Once percentage ionization or ionic core size is determined, then we may proceed to solve the Thomas-Fermi equation for the system of ions

and electrons.

From Eqs. (13) and (14) we get

$$\phi(x) = \phi(1)x + a \int_x^1 t(t-x) I_{\frac{1}{2}}\left(b \frac{\phi(t)}{t}\right) dt \quad (15)$$

The above equation is the Thomas-Fermi equation expressed in an integral equation. Since the average electrostatic potential varies rapidly near nuclei, we will transform the above equation by letting

$$\begin{aligned} x &= u^2, \\ t &= v^2, \end{aligned}$$

to write

$$\begin{aligned} \phi(u) &= \phi(1)u^2 + 2a \int_u^1 v^3(v^2-u^2) \\ &\quad I_{\frac{1}{2}}\left(b \frac{\phi(v)}{v^2}\right) dv. \end{aligned} \quad (16)$$

The above integral equation is to be solved numerically starting from $u=1$.

Detailed numerical procedures for the above equation have been reported⁷⁾, we will not discuss here the numerical procedures.

b) Equations of state and thermodynamic quantities of a system by the Thomas Fermi approximation

Once the self consistent solution of the Thomas-Fermi equation is obtained, the electron density distribution function, $\rho(x)$, is readily calculated from the following equation,

$$\rho(x) = \frac{1}{3} a I_{\frac{1}{2}}\left(b \frac{\phi(x)}{x}\right) \quad (17)$$

When $\tau \rightarrow \infty$, or for the system of ideal Fermi gas, $\rho(x)$ is expected to approach to the average electron density ρ . Thus,

$$I_{\frac{1}{2}}(b\phi(1)) = \frac{3}{a} \rho \quad (18)$$

The above relation is used to determine the chemical potential, $\mu = b\phi(1)$, of the ideal Fermi gas and asymptotic behavior of the chemical potential of actual system at high temperatures.

The kinetic energy and total energy of an atom can be evaluated from the following equations⁴⁾.

$$E_k = \frac{1}{3} Z a \tau I_{\frac{3}{2}}(b\phi(1)) + \frac{1}{2} a b Z \tau \int_0^1 u^3 (1 + \phi(u)) I_{\frac{1}{2}}\left(b \frac{\phi(u)}{u^2}\right) du - \frac{1}{4} b Z \tau \phi(1) \quad (19)$$

$$E_t = E_k - a b Z \tau \int_0^1 u^3 (1 + \phi(u)) I_{\frac{1}{2}}\left(b \frac{\phi(u)}{u^2}\right) du + \frac{1}{2} b Z \tau \phi(1) \quad (20)$$

At a sufficiently high temperature where the electron density distribution is considered to be uniform, $\phi(u)_{TF}$ is

$$\phi(u)_{TF} = 1 + \phi(1)u^2 - \frac{3}{2}u^2 + \frac{1}{2}u^6. \quad (21)$$

On the other hand, $\phi(u)_F$ for the system of ideal Fermi gas is

$$\phi(u)_F = \phi(1)u^2 \quad (22)$$

Thus, as $u \rightarrow 0$, $\phi(0)_{TF} \rightarrow 1$, while $\phi(0)_F \rightarrow 0$.

Since $|\phi(1)|$ is very large at high temperature, for the most range of u , $0 \leq u \leq 1$, $\phi(u)_{TF} \doteq \phi(u)_F$. However, as $u \rightarrow 0$, $\phi(u)_{TF} \rightarrow 1 + \phi(u)_F$. The value '1' in the right hand side of Eq. (21) accounts for the short range Coulomb interaction which is missing in an ideal Fermi gas. Therefore, at sufficiently high temperature, E_{kTF} is given by

$$E_{kTF} = \frac{1}{3} Z a \tau I_{\frac{3}{2}}(b\phi(1)) + \frac{9}{20} b Z \tau \quad (23)$$

while, the kinetic energy of an ideal Fermi gas, E_{kF} , is given by

$$E_{kF} = \frac{1}{3} Z a \tau I_{\frac{3}{2}}(b\phi(1)) + \frac{3}{8} b Z \tau \quad (24)$$

Thus, ΔE_k , the difference in the kinetic energy of an atom between actual Coulomb system and ideal Fermi system is

$$\Delta E_k = E_{kTF} - E_{kF} = \frac{3}{40} b Z \tau \quad (25)$$

which is due to short range Coulomb interaction. Since $pV = \frac{2}{3}E_k + \frac{1}{3}E_p$, the expression for the equation of state is obtained to write⁴⁾

$$PV/kT = \frac{2}{9} Z a I_{\frac{3}{2}}(b\phi(1)) \quad (26)$$

where V is the ion-sphere volume. Since $I_{\frac{3}{2}}(b\phi(1)) \rightarrow \frac{3}{2}I_{\frac{1}{2}}(b\phi(1))$, as $\tau \rightarrow \infty$ ⁸⁾, $PV/kT \rightarrow Z$ as $\tau \rightarrow \infty$.

Finally, the entropy, S , is evaluated by the following equation⁴⁾.

$$S/k = \frac{5}{3\tau} E_k - 2abZ \int_0^1 \phi(u) u^3 I_{\frac{1}{2}}\left(b \frac{\phi(u)}{u^2}\right) du \quad (27)$$

At sufficiently high temperature where the electron density distribution is considered to be uniform, ΔS , the difference in entropies between actual Coulomb system and ideal Fermi system, is expected to be

$$\Delta S/k = S_{TF}/k - S_F/k = -\frac{7}{40} b Z \quad (28)$$

When the electron density distribution is uniform, the chemical potential and the equation of state of the Thomas-Fermi theory will approach to those of the ideal Fermi gas. The entropy and kinetic energy of an atom by the Thomas-Fermi theory, on the contrary, will not approach to those of the ideal Fermi gas. However, the difference in the entropy will eventually approach to 0 at infinite temperature, while the difference in the kinetic energy will persist to exist.

III. Equations of State and Thermodynamic Quantities

The equations of state and several thermodynamic quantities of Na at various temperatures and densities are evaluated. Present calculation covers the density range of $0.1\rho_0 \sim 10\rho_0$, where ρ_0 is the normal density of Na at its melting point, and temperature range of $60.88 \text{ Ryd.} \sim 0.0216 \text{ Ryd.}$ Throughout those temperature and density range, the system is expected to be in a gaseous or liquid state.

Particularly, at high temperatures, the equations of state and several thermodynamic quantities of Na by the Thomas-Fermi theory are compared with those of an ideal Fermi system. All the units in this report are expressed by Bohr unit.

Fig. 1. shows the chemical potentials which

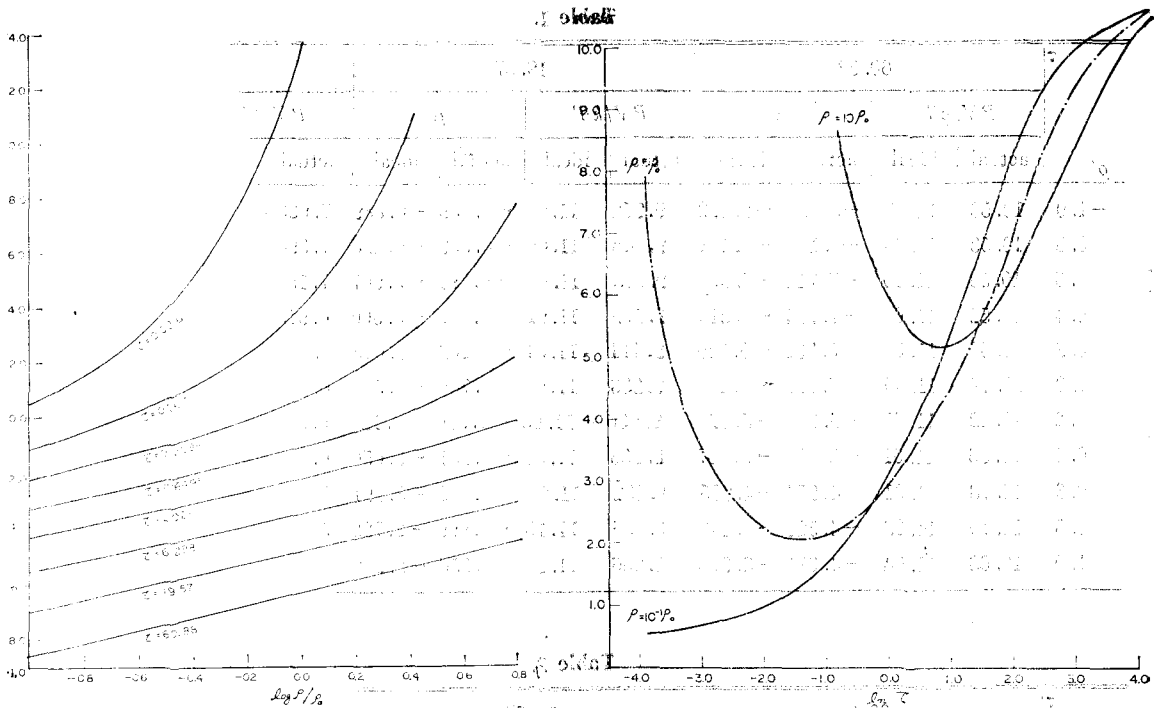


Fig. 1. Chemical potentials

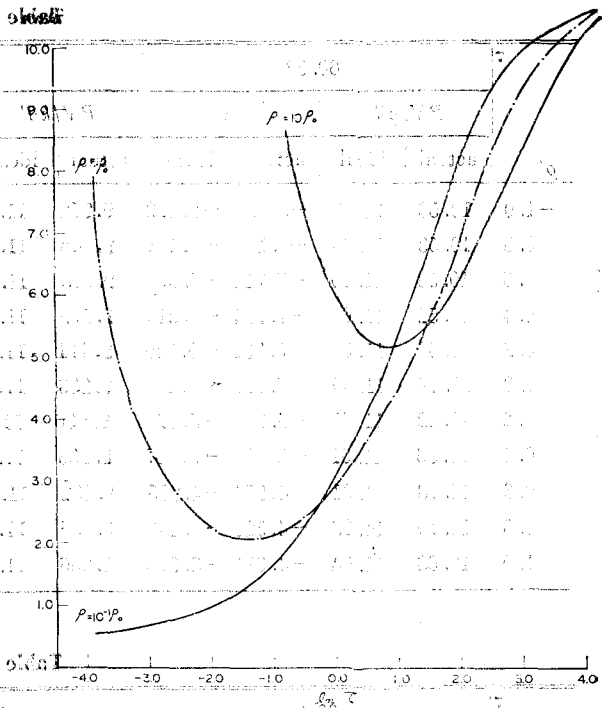


Fig. 2. τ, kT in Rydberg

yield the self consistent solutions of the Thomas-Fermi equation at various temperatures and densities. The evaluated chemical potentials are in good agreement with those by Latter⁴ even though his results are not for actual systems. When temperature of a system is sufficiently high so that an electron density distribution is considered to be uniform, the chemical potential approaches to $\ln\left(\frac{4\pi^{3/2}\rho}{\tau^{1.5}}\right)$. Thus, as $\tau \rightarrow \infty, \mu \rightarrow -\infty$ as $-1.5 \ln \tau$.

The equations of state, PV/kT , at typical densities are shown in Fig. 2. The behavior of PV/kT at lower temperatures is quite different from the one of ideal Fermi gas. At lower temperatures, PV/kT increases as average density of a system increases. While at higher temperatures, it decreases as average density of a system increases.

At $\tau = 60.88, 19.57,$ and 6.288 Ryd., the equations of state, chemical potentials, entropies, and kinetic energies of an atom calculated by

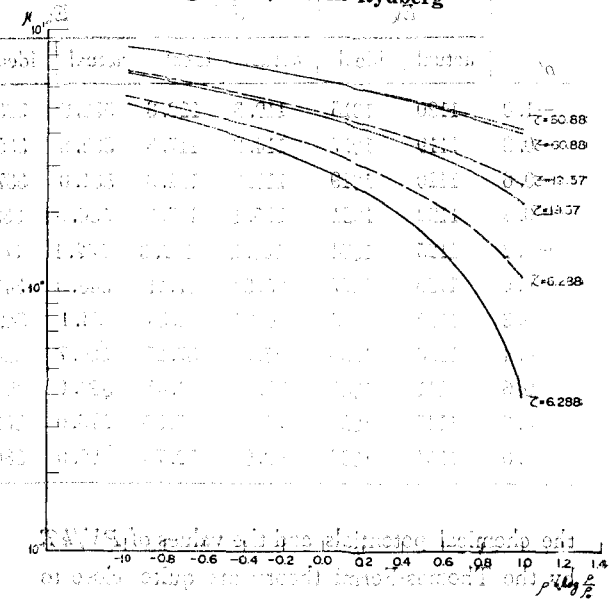


Fig. 3. Chemical potentials of actual system and ideal Fermi gas. The Thomas-Fermi theory are compared with those of ideal Fermi gas. As we may notice from Table 1 and Fig. 3, at high temperatures,

Table 1.

$$\rho' = \log \frac{\rho}{\rho_0}$$

ρ'	τ											
	60.88				19.57				6.288			
	PV/kT		μ		PV/kT		μ		PV/kT		μ	
	actual	ideal	actual	ideal	actual	ideal	actual	ideal	actual	ideal	actual	ideal
-1.0	10.53	11.00	-8.638	-8.592	9.958	11.00	-6.989	-6.889	7.633	11.01	-5.551	-5.184
-0.8	10.53	11.00	-8.176	-8.131	9.848	11.00	-6.539	-6.428	7.394	11.02	-5.122	-4.723
-0.6	10.53	11.00	-7.714	-7.670	9.723	11.01	-6.091	-5.967	7.152	11.03	-4.694	-4.260
-0.4	10.52	11.00	-7.254	-7.210	9.579	11.01	-5.645	-5.506	6.913	11.04	-4.267	-3.797
-0.2	10.50	11.00	-6.796	-6.749	9.414	11.01	-5.202	-5.045	6.683	11.07	-3.839	-3.332
0.0	10.47	11.00	-6.338	-6.288	9.233	11.02	-4.760	-4.583	6.470	11.11	-3.409	-2.864
0.2	10.42	11.01	-5.882	-5.828	9.036	11.03	-4.320	-4.120	6.283	11.17	-2.974	-2.392
0.4	10.36	11.01	-5.428	-5.367	8.833	11.05	-3.881	-3.656	6.133	11.27	-2.533	-1.913
0.6	10.28	11.01	-4.974	-4.905	8.632	11.08	-3.442	-3.191	6.032	11.43	-2.082	-1.424
0.8	10.19	11.02	-4.520	-4.443	8.436	11.13	-2.999	-2.722	5.999	11.68	-1.612	-0.9176
1.0	10.08	11.04	-4.071	-3.980	8.266	11.20	-2.556	-2.248	6.062	12.08	-1.124	-0.3851

Table 2.

$$\rho' = \log \frac{\rho}{\rho_0}$$

ρ'	τ											
	60.88				19.57				6.288			
	E_k		S/k		E_k		S/k		E_k		S/k	
	actual	ideal	actual	ideal	actual	ideal	actual	ideal	actual	ideal	actual	ideal
-1.0	1120	1015	119.5	122.3	520.9	333.2	99.73	104.2	412.2	114.3	69.86	87.32
-0.8	1119	1017	114.8	117.3	525.8	335.0	93.61	99.24	416.2	116.1	65.09	82.72
-0.6	1120	1019	110.0	112.3	531.0	337.3	88.48	94.37	420.1	118.2	60.43	78.19
-0.4	1122	1021	105.1	107.3	536.5	339.6	83.34	89.49	423.9	120.6	55.89	73.73
-0.2	1125	1024	100.2	102.3	542.1	342.4	78.20	84.66	427.8	123.6	51.47	69.41
0.0	1128	1027	95.24	97.29	548.0	345.8	73.07	79.87	431.7	127.2	47.20	65.22
0.2	1132	1032	90.24	92.34	554.1	349.9	67.96	75.13	436.0	131.5	43.06	61.16
0.4	1136	1036	85.21	87.27	560.7	354.8	62.90	70.44	440.4	136.8	39.07	57.30
0.6	1141	1041	80.16	82.45	568.1	360.7	57.91	65.82	445.2	143.3	35.22	53.64
0.8	1147	1056	75.04	77.55	576.0	368.7	52.98	61.35	450.4	151.6	31.51	50.27
1.0	1154	1066	69.99	72.70	585.0	386.7	48.19	57.67	456.8	162.2	27.95	44.42

the chemical potentials and the values of PV/kT by the Thomas-Fermi theory are quite close to those of ideal Fermi gas.

As far as the electron density distribution is uniform, the chemical potentials and the equations of state of actual system should be in complete agreement with those of ideal Fermi system.

However, as we may notice from Table 2, the kinetic energies of an atom calculated by the Thomas-Fermi theory are significantly different from those of ideal Fermi gas. Even if we correct the kinetic energies of an atom by the amount of ΔE_k given in Eq. (25), disagreements between both theories are not negligible. This fact may be explained as fol-

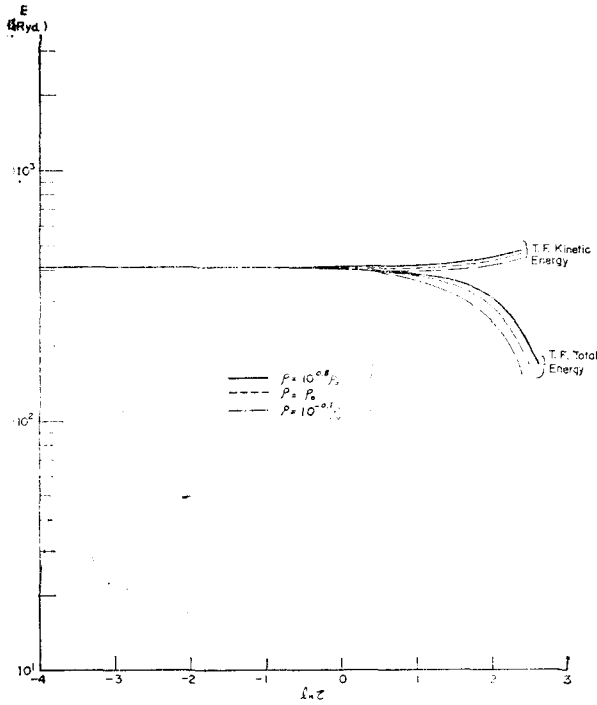


Fig. 4. T. F. Kinetic energy and total energy

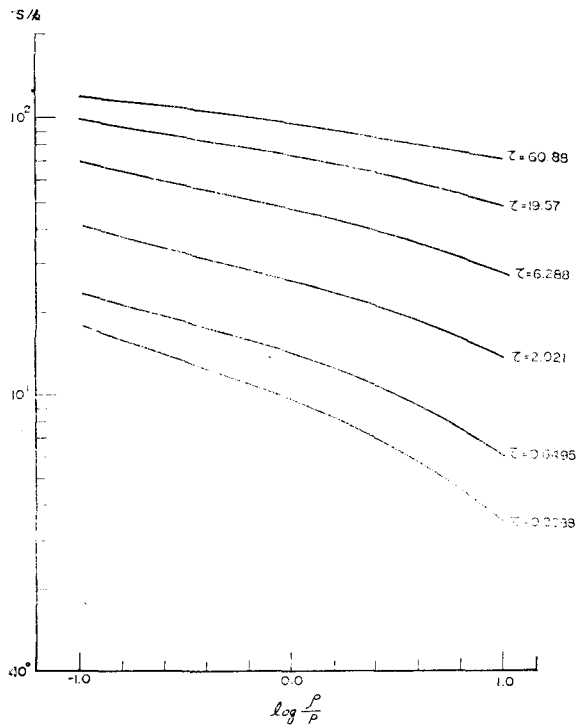


Fig. 5. Entropy

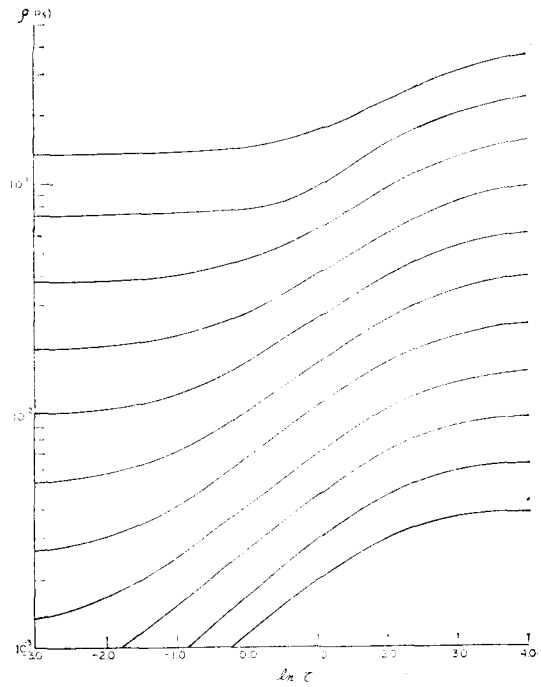


Fig. 6. Electron density at $r = R_0$

low: If temperature of a system is sufficiently high, the electron density distribution may be considered uniform. As the temperature of a system lowered, electrons will be built up near a nucleus. Overall, the electron density distribution might be still considered to be uniform. However, this electron build-up near nucleus will increase the kinetic energy considerably, since electrons near a nucleus have very large kinetic energy.

At sufficiently high temperatures, we may treat a real system as a system of ideal Fermi gas. This give an excellent approximation to the chemical potentials of a system, and a rather good approximation to the equations of state and entropies. However, this may results in a poor approximation to the kinetic energies of an atom.

The total energies and kinetic energies of an atom at various temperatures and densities are shown in Fig. 4. As temperature of a system decreases, the magnitude of the total energy

approaches to that of the kinetic energy. The difference in the magnitudes of the total energy and kinetic energy is due to the first term in the right hand side of Eq. (19) which is approximately proportional to $\left(\frac{\rho(R_s)}{\rho}\right)^{\frac{2}{3}}$ when the temperature of system is extremely low. We will see later that that is ionization ratio, η . Therefore, the difference in the magnitudes of the total energy and the kinetic energy will be proportional to $\eta^{\frac{2}{3}}$. At very high densities, where % ionization is not negligible even at ground state, the differences in the magnitudes of the total energies and kinetic energies are expected to exist.

The relation between the entropy of a system, S , and the relative density of a given system is shown in Fig. 5. At high temperatures, S/k is proportional to the logarithm of relative density as expected by Eq. (27).

The electron density distribution function at $r = R_s$ is shown in Fig. 6. If we decompose the electron density distribution function into two parts; the electron density distribution function due to electrons in continuum states and the one due to electrons in bound states. The electron density distribution function due to

electrons in continuum states is uniform throughout whole range of r . While, the electron density distribution function due to electrons in bound states should vanish at $r=R_s$, since the bound state electrons should stay inside of an atom. Thus, we may regard the electron density distribution function at $r = R_s$, $\rho(R_s)$, be the uniform electron density distribution function of the continuum states electrons. Therefore, % ionization, the percentile of electron in the continuum states, may be calculated by $\eta(\%) = \frac{\rho(R_s)}{\rho} \times 100(\%)$, where η is the % ionization.

Fig. 7 shows % ionizations at various densities. As the average density of electrons increases, dependence of % ionization on the temperature of a system becomes insignificant. At low temperatures, % ionization increases as density of a system increases. However, at high temperatures, the situation is reversed. This seems because, at high temperatures where a large portion of electrons is ionized, the decrease in ionsphere radius forces ionized electrons into bound states.

The ion-core radius, which is shown in Fig. 8, is determined as follows: There is a distance r from a given nucleus such that beyond this

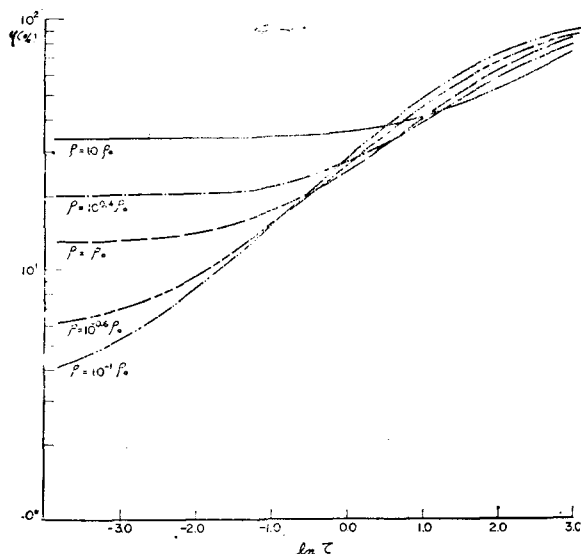


Fig. 7. % ionization

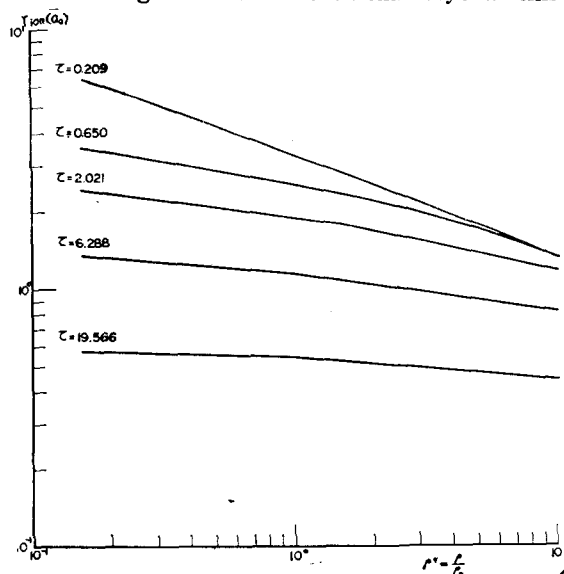


Fig. 8. Ion-core radius

distance the electron density distribution due to the bound states electrons can be neglected. Beyond this distance, $r^2\rho(r)$ behave like constant $\times r^2$. We determined the ion-core radius as a distance r from a nucleus from which $r^2\rho(r)$ starts to behave like $\text{const.} \times r^2$.

The calculated ion-core radius may provide helpful data, when we are interested in the size of the ion-core or when we are to apply the Thomas-Fermi theory to a system of ions and electrons.

IV. Conclusion

It has been shown that the Thomas-Fermi equation can be derived by using the W. K. B. wave functions.⁹⁾ The method approximates the electron density distribution function by using the W. K. B. wave functions. This fact may provide a helpful guidance when we are interested in the validity of the Thomas-Fermi approximation.

The W. K. B. approximation is useful when the potential changes so slowly that the momentum of a particle is considered to be constant over many de Broglie wavelengths. Thus the approximation breaks down near a nucleus where the potential varies rapidly. The same is true for case of the Thomas-Fermi approximation.

The most significant defect in the Thomas-Fermi approximation lies in the electron density distribution function. Especially, the short range defect of the Thomas-Fermi electron density distribution function seems to be disastrous. However, we must not overlook that the same approximation yields excellent S. C. F. potentials. The validity of the approximation seems to depend on which quantities we are interested in.

As the temperature and density of a system increases, the approximation is expected to be

improved.

The errors in the Thomas-Fermi quantities at extremely low temperature and density, where the approximation is expected to be worst, might provide criteria for maximum possible errors in the Thomas-Fermi quantities.

We have seen that the chemical potentials of ideal Fermi gas are very close to those of actual system. The density build-up near nucleus due to the electrostatic interaction seems to affect little on the chemical potentials of a system. On the contrary, it seems to affect significantly on the kinetic energies of an atom.

The S. C. F. potentials, chemical potentials, equations of state, and entropies of a given system seem to be rather insensitive to the electron density distribution function. However, the kinetic energies and total energies of an atom seem to be sensitive to the electron density distribution function.

We expect that the Thomas-Fermi approximation should give good approximations to the quantities which we have evaluated except for the electron density distribution functions and total energies and kinetic energies of an atom.

We have found that, at extremely low temperature and low density, the error in the Thomas-Fermi kinetic energy and total energy of an atom is about 100% even the order of the magnitude is correct. That is not disappointing if we consider the machine time consumed to evaluate those quantities. Overall, the temperature and density dependence of the energies of an atom seems to be acceptable. If we are to improve the physical quantities which depend strongly on the short range behavior of the electron density distribution function, we have to modify the electron density distribution function⁹⁾.

The machine time consumed to evaluate all the quantities presented here depends on the input chemical potential. When exact input

chemical potentials are known, it consumed about 2 minutes for calculating all the quantities at given temperature and density when a FACOM 230-35 are used. When the exact input chemical potentials are not given, it consumed about 12 minutes.

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