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Giant Cluster Expansion Theory and Its Application to High Temperature Plasma*

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The conventional virial expansion of thermodynamic functions is converted into a new expansion scheme, similar to the former but more powerful. The new method is particularly suitable to dealing with the interaction of long-range character, such as Coulomb potential, since it suffers from no divergence difficulties contrary to the conventional one. As an application of the method, the equilibrium properties of high temperature plasma is studied and the term of next higher orders than the Debye-Hückel limiting law is obtained exactly. The order estimation indicates that the Debye-Hückel law is accurate within the error of a few per cent in this case. A possible extension of the present method to the theory of non-equilibrium properties of plasma or to quantum statistics is suggested.

§ 1. Introduction

In classical statistical mechanics, thermodynamic functions of an imperfect gas are expanded in a form of power series of particle number density ρ, and coefficients are known to be expressed in terms of irreducible cluster integrals[1]. In some cases, however, these expansion formulae are no longer valid, because of the divergence difficulties of cluster integrals. For instance, in an ionic solution or classical plasma, the interaction potentials between particles are of long-range character and all cluster integrals diverge to infinity. Mathematically speaking, this implies that the point $\rho=0$ is a singular point of thermodynamic functions, since these functions cannot be expanded in powers of ρ. Therefore, according to the theory of functions of complex variables, the point $\rho=0$ should be one of the following three cases: the pole, the essentially singular point and the branch point. In any case, the thermodynamic functions are expected to have some singular properties at low densities. Then it is quite clear that the usual virial expansion method cannot afford to describing the low density behaviour of the system.

So far, there have been several attempts to overcome the difficulties mentioned above. Among them, Mayer[2] has shown that the long-range interaction can be reduced to the short-range one, if the integral over the intermediate particles of a chain is performed for a given type of prototype graph. Thus, the expansion formula in terms of prototype graphs is free from the divergence difficulties arising from the long-range correlation. In fact, Mayer has proved that the Debye-Hückel limiting law is derived by a summation procedure over the clusters of ring type.

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However, it is important to note that Mayer's procedure brings about new difficulties owing to the short-range correlation. One may encounter with these difficulties if he investigates into the contributions of the complex prototype graphs beyond the ring type. In Mayer's theory, the existence of hard-core potential is assumed and each term corresponding to one prototype graph is calculated without any divergence difficulties. However, if one makes the core radius approach zero, some terms considered by Mayer are shown to diverge to infinity. Thus, the development in terms of prototype graphs is not applicable to the pure Coulomb potential without a hard-core.

The purpose of this paper is to develop a systematic expansion procedure without suffering from difficulties arising from both long- and short-range correlations. In § 2 we shall briefly account for Mayer's expansion method in terms of prototype graphs and discuss how the divergence difficulties arise from the short-range correlation. In § 3 we shall discuss how to avoid these difficulties, taking a simple example of graphs of watermelon type[3),4)]. Generalizing this procedure to the more complex graphs, we shall obtain an expansion formula which has a form similar to the usual one. Each term of new series corresponds to an aggregate of all usual clusters of a given type, and therefore the expansion developed here will be called "giant cluster expansion." The giant cluster integrals corresponding to the usual irreducible cluster integrals are defined and shown to have topological properties similar to the usual one but dependent on ρ. Then § 4 is devoted to an application of the method to an electron gas in a uniform positive ion background and the term corresponding to the usual second virial coefficient is calculated. Calculations are carried out in two different ways: the one based on the use of Bessel functions and the other which will clarify how the lowest order term of giant cluster can be obtained by a summation of the most highly divergent terms of prototype graphs. In § 5 the contributions of higher order giant clusters are briefly discussed and it is verified that the thermodynamic functions are exact up to and including the order considered in this paper. The orders of magnitude are estimated for the high temperature plasma and it is shown that the Debye Hückel law is accurate within the error of a few per cent. It is suggested that the thermodynamic functions of plasma are written as a double power series of λ and $\log \lambda$, with λ the characteristic non-dimensional parameter for plasma. In § 6 is discussed a discrepancy between the results obtained by Ichikawa[5)] and ours. A possible generalization of the present method to the study of non-equilibrium properties of plasma or to quantum statistics is suggested, and these matters will be the subjects of forthcoming papers.

§ 2. Mayer's expansion scheme

In order to deal with the thermodynamic properties of an imperfect gas, it is convenient to introduce a function S defined by

$$S=\sum_{n=1}^{\infty}\beta_n\rho^{n+1}/(n+1) \tag{1}$$

where β_n is the irreducible cluster integral, ρ is the particle number density given by N/V, N being the particle number and V the volume of the system. Then the Helmholtz free energy and the equation of state are given respectively by,[1]

$$A/N\kappa T=\log(h^2/2\pi m\kappa T)^{3/2}\rho/e-S/\rho, \tag{2}$$

$$P/\kappa T=\rho+S-\rho\partial S/\partial\rho. \tag{3}$$

Here m stands for the mass of particle, κ Boltzmann's constant, h Planck's constant, T the absolute temperature. All other thermodynamic functions are derived from the S, therefore the investigation of equilibrium properties of an imperfect gas reduces to calculating the function S. In this section we shall give a brief account of Mayer's expansion scheme in terms of prototype graphs.

If we set the potential function between the i-th and j-th particles to be ϕ_{ij} and substitute an explicit expression for β_n in Eq. (1), we have

$$S=\sum_{n=2}^{\infty}\frac{\rho^n}{n!}\frac{1}{V}\int\cdots\int\sum_{n\geq i>j\geq 1}\Pi f_{ij}\,d\tau_1\cdots d\tau_n. \tag{4}$$

All products in which all particles are more than singly connected

Here f function is given, as usual, by

$$f_{ij}=\exp(-\beta\phi_{ij})-1 \tag{5}$$

with $\beta=1/\kappa T$. Usually, each term in Eq. (4) is represented by a bond diagram composed of n points and of bonds representing the f function. Hereafter we shall call this bond the f-bond. If the f is expanded in powers of $-\beta\phi_{ij}$ and if we take the term $(-\beta\phi_{ij})^k/k!$, the f-bond is splitted into k ϕ-bonds as shown in Fig. 1. Then each term in Eq. (4) will be represented by diagrams composed of ϕ-bonds. The difference between the diagrams composed of f and ϕ-bonds is clear: in the former case one and only one bond is permitted to connect the points directly, while in the latter an arbitrary number of bonds are permitted.

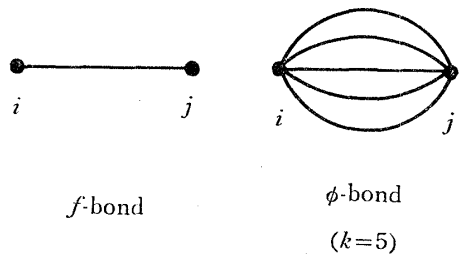

Fig. 1

The diagrams of ϕ-bonds constructed in this way may be classified according to their topological properties. For this purpose, we introduce the terminology "junction," which is defined as a point to which three or more bonds are connected[3], and let us consider the diagram of which all points are junctions. Mayer has called such a diagram "prototype graph." Then it is clear that all the diagrams are constructed by adding the points on the bonds between junctions of prototype graphs (except for the diagrams of ring type of which contribution should be calculated separately). Therefore, if we first select one prototype graph and then sum up the terms of all the diagrams derived by this prototype graph, the S is expanded in terms of prototype graphs. In fact, as Mayer[2] has proved, S is written as

$$S=S_0+\sum_{m=2}^{\infty}\frac{\rho^m}{m!}\frac{1}{V}\int\sum_{m\geqq i>j\geqq 1}{}'\prod\frac{(-\beta q_{ij})^{k_{ij}}}{k_{ij}!}d(m). \tag{6}$$

Here S_0 is the contribution of clusters of ring type, and is given by

$$S_0=-(\rho^2\beta/2)\nu(0)+(1/2V)\sum_{\boldsymbol{k}}\{-\log[1+\rho\beta\nu(\boldsymbol{k})]+\rho\beta\nu(\boldsymbol{k})\} \tag{7}$$

with $\nu(\boldsymbol{k})$ the Fourier component of ϕ defined by

$$\nu(\boldsymbol{k})=\int\phi(\boldsymbol{x})\,e^{-i\boldsymbol{k}\cdot\boldsymbol{x}}\,d\boldsymbol{x}. \tag{8}$$

Furthermore, $\sum'$ in Eq. (6) implies the summation over prototype graphs, k_{ij} the number of bonds between the i-th and j-th junctions, $d(m)$ the integrations over m junctions, and q_{ij} is given by

$$q_{ij}=(1/V)\sum_{\boldsymbol{k}}\nu(\boldsymbol{k})\exp[i\boldsymbol{k}\cdot(\boldsymbol{x}_i-\boldsymbol{x}_j)]/[1+\rho\beta\nu(\boldsymbol{k})]. \tag{9}$$

In the case of electron gas in a uniform positive ion background, $\nu(\boldsymbol{k})$ is given by

$$\nu(\boldsymbol{k})=4\pi\varepsilon^2/k^2\quad(\boldsymbol{k}\neq 0),\quad \nu(0)=0, \tag{10}$$

where ε is the absolute value of eletronic charge. Then q_{ij} is shown to be

$$q(r)=\varepsilon^2\exp(-\kappa_0 r)/r \tag{11}$$

with $\kappa_0=\sqrt{4\pi\beta\rho\varepsilon^2}$. Furthermore from Eqs. (7) and (10) it follows that

$$S_0=2\sqrt{\pi}\,\varepsilon^3\beta^{3/2}\rho^{3/2}/3, \tag{12}$$

in this case. From Eqs. (3) and (12), we have

$$P/\rho\kappa T=1-\sqrt{\pi}\,\varepsilon^3\beta^{3/2}\rho^{1/2}/3, \tag{13}$$

which is the Debye-Hückel limiting law.

§ 3. Contributions of prototype graphs and giant cluster expansion

We have calculated in § 2 the term S_0 which is the contribution of clusters of ring type, i.e., clusters without junctions. We now proceed in this section to discuss the more complicated clusters with some junctions. As we have mentioned in § 2, the contributions of these clusters can be expressed in terms of prototype graphs, and we shall first consider the graphs with 2 junctions. The simplest one of these is shown in Fig. 2, i.e., the graph with 3 bonds. Its contribution to S is given by

$$\frac{\rho^2}{2!}\frac{1}{V}\int\frac{(-\beta q_{12})^3}{3!}d\tau_1 d\tau_2=-\frac{2\pi\rho^2\beta^3\varepsilon^6}{3}\int_0^{\infty}\frac{\exp(-3\kappa_0 r)}{r}dr, \tag{14}$$

from Eqs. (6) and (11). Obviously, this integral is divergent at $r=0$. In a similar manner, it is shown that the contributions of graphs with 4,5,6,$\cdots$bonds are

all divergent. In Mayer's theory, however, the corresponding results are convergent, since the assumed existence of hard-core potential makes the lower limit of integration the finite value, thus preventing the divergence at $r=0$. However, if we make the core radius tend to zero, the integrals become ∞ as mentioned above. This is the main reason why the development in terms of prototype graphs is not satisfactory for dealing with the pure Coulomb potential without a core.

Fig. 2. The simplest prototype graph with 2 junctions.

Let us now discuss how to avoid this divergence difficulty. For this purpose, it may be instructive to consider the procedure in which the f-bond is expanded in powers of ϕ-bonds, as we have done in § 2. If the function ϕ has a dependence $1/r$ near $r=0$, the integration for ϕ-bonds may be divergent at $r=0$, in spite of the convergence of the integral for the f-bond. This in turn suggests that the divergence arising from the short-range character can be avoided by summing up the graphs over the number of bonds. Keeping this in mind, let us sum up all the prototype graphs with 2 junctions as shown in Fig. 3. If we set the contributions of these graphs to S to be S_2, we obtain

$$S_2=\frac{\rho^2}{2}\frac{1}{V}\int\sum_{k=3}^{\infty}\frac{(-\beta q_{12})^k}{k!}d\tau_1 d\tau_2$$

$$=2\pi\rho^2\int_0^{\infty}\left[e^{-\beta q(r)}-1+\beta q(r)-\frac{\beta^2 q^2(r)}{2}\right]r^2dr. \tag{15}$$

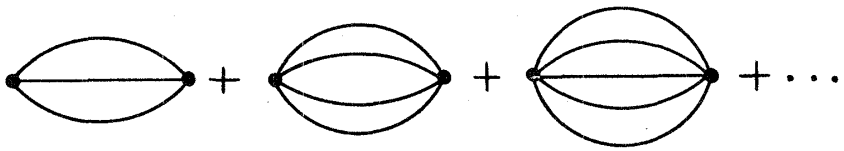

Fig. 3. All the prototype graphs with 2 junctions. The contribution of these graphs to S is S_2.

From this equation, it is clear that the divergence at $r=0$ no longer appears. The similar equation to this has been obtained by Yukhnovsky[6], by the use of the method of collective variables. It is also possible to obtain the corresponding equation without expanding the f-bond in terms of ϕ-bonds, as we have shown previously in the theory of watermelon approximation for classical fluids.[3]

The generalization of the above procedure to the more complicated prototype graphs is straightforward. For example, let us consider the graphs with 3 junctions. The simplest one is that shown in Fig. 4 at the left end. If we sum up all the graphs in Fig. 4, keeping the number of bond between the junctions 1 and 2 to be one, we have from Eq. (6)

$$S_3^{(a)}=\frac{3\rho^3}{3!\,V}\int w_0(12)\,w_2(23)\,w_2(31)\,d\tau_1 d\tau_2 d\tau_3 \tag{16}$$

as a contribution to S. Here w function is generally defined by

$$w_n=\sum_{k=n}^{\infty}(-\beta q)^k/k!, \quad (n\neq 0) \tag{17}$$

i. e. $w_1=e^{-\beta q}-1$, $w_2=e^{-\beta q}-1+\beta q$ and $w_3=e^{-\beta q}-1+\beta q-\beta^2 q^2/2$,

and
$$w_0=-\beta q. \tag{18}$$

Furthermore, the factor 3 in front of the integral corresponds to the three types of graphs as shown in Fig. 5.

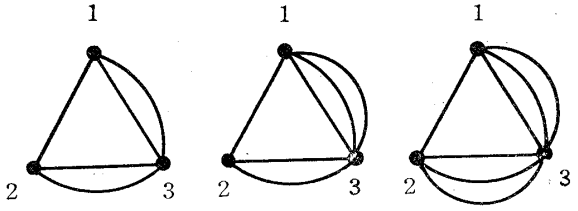

Fig. 4. Prototype graphs with 3 junctions, in which one bond is connected between the junctions 1 and 2. Their contribution to S is $S_3^{(a)}$.

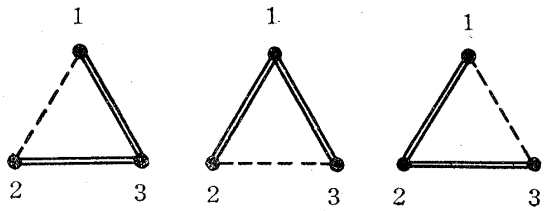

Fig. 5. Three types of graphs in which w_0 bond is connected between junctions. The dotted line is w_0 bond and the double bond is w_2 bond.

If we further consider the prototype graphs in which at least 2 bonds are connected between junctions as shown in Fig. 6, we have

$$S_3^{(b)}=\frac{\rho^3}{3!\,V}\int w_2(12)\,w_2(23)\,w_2(31)\,d\tau_1\,d\tau_2\,d\tau_3 \tag{19}$$

as a contribution to S.

It is obvious that the similar procedure can be carried out for prototype graphs with 4, 5, 6$\cdots$ junctions. In general, if we write

$$S=S_0+\sum_{m=1}^{\infty}\frac{\gamma_m}{m+1}\rho^{m+1} \tag{20}$$

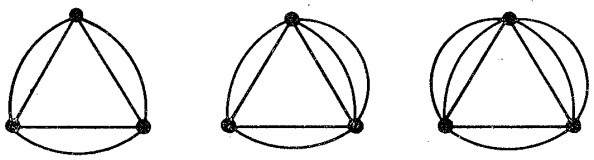

Fig. 6. Prototype graphs in which the number of bonds is larger than 2. Their contribution to S is $S_3^{(b)}$.

γ_m is expressed as an integral of a sum of products of w functions, i.e.,

$$\gamma_m=\frac{1}{m!\,V}\int\sum_{m+1\geq i>j\geq 1}\prod w_n(ij)\,d(m+1). \tag{21}$$

For example, γ_1 and γ_2 are given respectively by

$$\gamma_1=\frac{1}{V}\int w_3(12)\,d\tau_1\,d\tau_2,$$

$$\gamma_2=\frac{3}{2!\,V}\int w_0(12)\,w_2(23)\,w_2(31)\,d\tau_1\,d\tau_2\,d\tau_3$$

$$+\frac{1}{2!\,V}\int w_2(12)\,w_2(23)\,w_2(31)\,d\tau_1\,d\tau_2\,d\tau_3.$$

Comparing Eq. (20) with Eq. (1), one may easily see that γ_m is a counterpart of the usual irreducible cluster integral. However, γ_m corresponds not to a single cluster but to an aggregate of all the usual clusters of a given type. For example, γ_2 represents the contributions of usual clusters of ϕ-bonds shown in Fig. 7. For this reason, we shall call γ_m the giant cluster integral and the expansion given by Eq. (20) the giant cluster expansion. It is quite easy to see that this expansion scheme suffers neither from the divergence difficulty due to the long-range character nor from the one due to the short-range character.

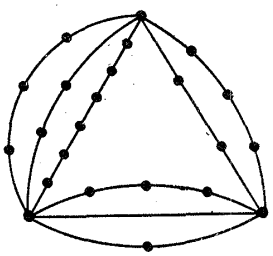

Fig. 7. Clusters of ϕ-bonds contributing to γ_2.

Just as in the usual cluster expansion, the giant cluster integral is represented by the bond diagram composed of w-bonds. For example, the bond diagrams of γ_1 and γ_2 are given in Fig. 8. Furthermore, those of γ_3 are shown in Fig. 9.

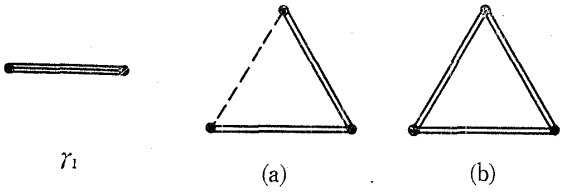

Fig. 8. Bond diagrams of γ_1 and γ_2. The triple bond is w_3. (a) and (b) correspond to $S_3^{(a)}$ and $S_3^{(b)}$, respectively.

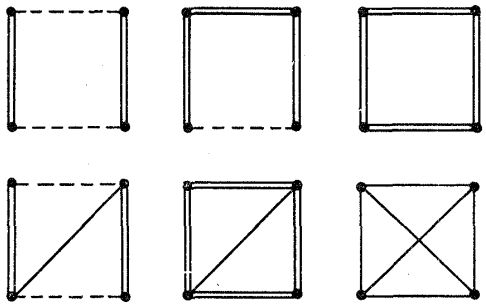

Fig. 9. Some type of bond diagrams contributing to γ_3. The single bond is w_1.

From these figures one may see that the bond diagrams representing the giant cluster integrals are quite similar to the usual one. However, the essential difference lies in the fact that they should be drawn so that all the points are junctions in this case. For example, the bond diagrams shown in Fig. 10 do not appear, since these are not consistent with this requirement. As long as this is satisfied, there are several ways in which w-bonds are connected for a given type of bond diagram, as being shown in Fig. 9. Accordingly, there appears, so to speak, the fine structure of usual bond diagram in our case.

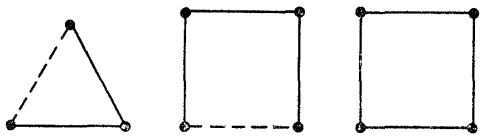

Fig. 10. Bond diagrams not appearing in the giant clusters.

Furthermore, it should be noted that γ_m is dependent on density, contrary to β_n, so that the giant cluster expansion is not a simple power series of density but a more complicated one. But, as will be shown in the next section, it enables one to study the low density behaviour of the system for which β_n diverges.

Before closing this section, we should like to mention that the similar procedure to the present one was discussed by Meeron[7] in his theory of nodal expansion for the potential of average force and for the distribution function. Furthermore, Morita[4] has succeeded in a partial summation of giant clusters in his theory of hyper-netted chain approximation. However, it seems that these authors stayed in a rather formal stage. We shall give an actual application of the method to the electron gas in the next section.

§ 4. Application to electron gas

In this section we shall calculate the function S_2 given by Eq. (15) for the electron gas. As can be seen from Fig. 8, this function corresponds to the usual second virial coefficient. In the following, we shall give two different ways of calculating the S_2: the one based on the use of Bessel functions and the other on the summation of the most highly divergent terms of prototype graphs.

Substituting Eq. (11) in Eq. (15), we have

$$S_2=2\pi\rho^2\int_0^\infty\left[\exp\left(-\frac{\beta\varepsilon^2}{r}e^{-\kappa_0 r}\right)-1\right]r^2dr+\frac{\rho}{2}-\frac{\sqrt{\pi}\,\rho^{3/2}\beta^{3/2}\varepsilon^3}{4}.$$

In order to carry out further calculations, it is convenient to introduce a dimensionless parameter characteristic of the classical electron gas:

$$\lambda\equiv\kappa_0\beta\varepsilon^2=2\sqrt{\pi}\,\beta^{3/2}\rho^{1/2}\varepsilon^3. \tag{22}$$

Then we have

$$\frac{S_2}{\rho}=\frac{1}{2}-\frac{\lambda}{8}+\frac{\lambda^2}{2}\int_0^\infty\left[\exp\left(-\frac{e^{-\lambda t}}{t}\right)-1\right]t^2dt. \tag{23}$$

If we perform the partial integration, it follows that

$$S_2/\rho=1/2-\lambda/8-(\lambda^2/6)I(\lambda) \tag{24}$$

where $I(\lambda)$ is given by

$$I(\lambda)=\int_0^\infty(t+\lambda t^2)\exp\left(-\lambda t-\frac{e^{-\lambda t}}{t}\right)dt. \tag{25}$$

In calculating this function, we assume that λ is small, that is, we consider the low density and high temperature limit. In such a case, it may be possible to write $-\lambda t-e^{-\lambda t}/t$ as $-\lambda t-1/t+(1-e^{-\lambda t})/t$ and expand $\exp[(1-e^{-\lambda t})/t]$ as a power series of its exponent which is of the order of λ. Then we obtain

$$I(\lambda)=\sum_{n=0}^\infty I_n(\lambda)/n! \tag{26}$$

where

$$I_n(\lambda)=\int_0^\infty (t+\lambda t^2)\, e^{-\lambda t-1/t}\frac{(1-e^{-\lambda t})^n}{t^n}\,dt$$

$$=\sum_{r=0}^{n}\binom{n}{r}(-1)^r\int_0^\infty \frac{(t+\lambda t^2)}{t^n}e^{-\lambda(r+1)t-1/t}\,dt. \tag{27}$$

The integral in Eq. (27) can be expressed in terms of Bessel functions, if we notice the formula[8)]

$$K_n(z)=\int_0^\infty e^{-z\cosh\theta}\cosh n\theta\, d\theta.$$

In this way, we find

$$I_n=\sum_{r=0}^{n}\binom{n}{r}(-1)^r\lambda^{n/2}(r+1)^{n/2}\left[\frac{2}{\lambda(r+1)}K_{n-2}(2\sqrt{\lambda(r+1)})\right.$$

$$\left.+\frac{2}{(r+1)\sqrt{\lambda(r+1)}}K_{n-3}(2\sqrt{\lambda(r+1)})\right]. \tag{28}$$

If we substitute in this equation the explicit expression for $K_n(z)$:

$$K_n(z)=\frac{1}{2}\sum_{m=0}^{n-1}\frac{(-1)^m(n-m-1)!}{m!}\left(\frac{z}{2}\right)^{2m-n}+(-1)^{n+1}\sum_{m=0}^{\infty}\frac{(z/2)^{n+2m}}{m!\,(n+m)!}$$

$$\times\{\log(z/2)-1/2\cdot\psi(m)-1/2\cdot\psi(m+n)\}$$

$$\psi(m)=-\gamma+1+\frac{1}{2}+\cdots+\frac{1}{m},\quad \psi(0)=-\gamma,$$

(γ : Euler's constant $=0.57721566\cdots$),

we have

$$I_0=3/\lambda^2-2/\lambda+1/2-1/2\cdot\{\log\lambda-\psi(0)-\psi(2)\}+0(\lambda),$$

$$I_1=5/4\lambda-1/2-\log 2+0(\lambda),$$

$$I_2=2\log 2-\log 3+1/3+0(\lambda)$$

and

$$I_3=0(\lambda).$$

It is easily verified that I_n for $n\geqq 3$ can be ignored if we confine ourselves up to the order of λ^0. Substituting above equations in Eq. (26), we have from Eq. (24)

$$\frac{S_2}{\rho}=\lambda^2\left(\frac{\log 3}{12}+\frac{\gamma}{6}-\frac{11}{72}\right)+\frac{\lambda^2\log\lambda}{12}+0(\lambda^3). \tag{29}$$

On the other hand, the contribution of clusters of ring type, S_0, is written as

$$S_0/\rho=\lambda/3 \tag{30}$$

from Eqs. (12) and (22). Thus we see that the contribution of giant cluster with 2 junctions is of orders higher than that of clusters without junctions at low density limits. Furthermore, it should be noted that there appears the term $\log \lambda$ in Eq. (29). This implies that the point $\rho=0$ is a branch point of logarithmic character, while in Eq. (30) it is of algebraic one, [see Eq. (22)].

Let us now discuss to derive Eq. (29) in an alternative way. As we have mentioned in § 2, the contribution of each prototype graph diverges to ∞. However, if the existence of hard-core potential is assumed, it is convergent. Then the contribution of the prototype graph with 2 junctions and 3 bonds is given by

$$\frac{S_{2,3}}{\rho}=-\frac{\lambda^2}{2}\frac{1}{3!}\int_{\delta}^{\infty}\frac{e^{-3\lambda t}}{t}dt$$

where $\delta=a/\beta\varepsilon^2$, a being the diameter of hard-core.

Similarly, the contributions of the prototype graphs with 4, 5,$\cdots$bonds are given by

$$\frac{S_{2,4}}{\rho}=\frac{\lambda^2}{2}\frac{1}{4!}\int_{\delta}^{\infty}\frac{e^{-4\lambda t}}{t^2}dt,\quad \frac{S_{2,5}}{\rho}=-\frac{\lambda^2}{2}\frac{1}{5!}\int_{\delta}^{\infty}\frac{e^{-5\lambda t}}{t^3}dt,\ \text{etc.}$$

Though these terms become ∞ as $\delta\to 0$, we observe here the most highly divergent terms in this limit. They are given by

$$\frac{S_{2,4}}{\rho}\simeq\frac{\lambda^2}{2}\frac{1}{4!}\frac{1}{\delta}=\frac{\lambda^2}{2}\frac{1}{4!}\int_{\delta}^{\infty}\frac{dt}{t^2},$$

$$\frac{S_{2,5}}{\rho}\simeq-\frac{\lambda^2}{2}\frac{1}{5!}\frac{1}{2\delta^2}=-\frac{\lambda^2}{2}\frac{1}{5!}\int_{\delta}^{\infty}\frac{dt}{t^3},\quad \text{etc.}$$

Then summing up these terms, we obtain

$$\frac{S_2}{\rho}\simeq\frac{\lambda^2}{2}\int_{\delta}^{\infty}\left[e^{-1/t}-1+\frac{1}{t}-\frac{1}{2t^2}+\frac{1-e^{-3\lambda t}}{3!\,t^3}\right]t^2\,dt. \tag{31}$$

Now, this integral is finite as $\delta\to 0$, and then one may easily verify that the integration leads to the same result as is given by Eq. (29). Thus we see that the lowest order term of contribution of giant cluster can be calculated by summing up the most highly divergent terms of prototype graphs of which the giant cluster is composed. This situation seems somewhat analogous to the case of correlation energy of electron gas as was discussed by Gell-Mann and Brueckner.[9] We shall use this method in the next section for the order estimation of giant clusters with 3 junctions.

§ 5. Contribution of higher order giant cluster and equation of state of high temperature plasma

We have calculated in § 4 the contribution of giant cluster with 2 junctions. In this section we shall discuss the order estimation of more complicated giant clusters for small λ.

The term expected to be important besides S_0 and S_2 for small λ is $S_3^{(a)}$ given by Eq. (16). The bond diagram corresponding to this term is shown in Fig. 8, and is a counterpart of the usual third virial coefficient. Combining Eq. (16) with Eq. (17), we have

$$\frac{S_3^{(a)}}{\rho}=\frac{\rho^2}{2}\int(e^{-\beta q_{23}}-1+\beta q_{23})(e^{-\beta q_{13}}-1+\beta q_{13})(-\beta q_{12})\,d\tau_1\,d\tau_2. \tag{32}$$

Carrying out the change of variables and the integration for the angular part, we find

$$\frac{S_3^{(a)}}{\rho}=\frac{\lambda^3}{4}\left\{\int_0^\infty s\,e^{-\lambda s}\left[\exp\left(-\frac{e^{-\lambda s}}{s}\right)-1+\frac{e^{-\lambda s}}{s}\right]ds\right\}^2-\frac{\lambda^3}{4}A(\lambda) \tag{33}$$

where

$$A(\lambda)=2\int_0^\infty e^{\lambda s}\,s\left[\exp\left(-\frac{e^{-\lambda s}}{s}\right)-1+\frac{e^{-\lambda s}}{s}\right]ds\int_s^\infty e^{-\lambda t}\,t\left[\exp\left(-\frac{e^{-\lambda t}}{t}\right)-1+\frac{e^{-\lambda t}}{t}\right]dt. \tag{34}$$

The calculation of the first term on the right-hand side of Eq. (33) is straightforward, if we use the second method discussed in § 4. Then we obtain for this term

$$\frac{\lambda^3}{4}\left(-\gamma+\frac{3}{4}-\frac{1}{2}\log 3\lambda\right)^2 \tag{35}$$

for small λ. On the other hand, the second term in Eq. (33) is not calculated analytically, yet it is verified that its contribution for small λ is of the same order as is given by Eq. (35). In order to show this, we sum up the most highly divergent terms of prototype graphs, as was discussed in § 4. Then, after some manipulation, we have

$$A(\lambda)\simeq 2\int_0^\infty s\left(e^{-1/s}-1+\frac{1}{s}\right)ds\int_s^\infty\left(e^{-1/t}-1+\frac{1}{t}-\frac{1-e^{-3\lambda t}}{2!\,t^2}\right)t\,dt$$

$$-\frac{1}{2}\int_0^\infty\frac{1-e^{-\lambda s}}{s}\,ds\int_s^\infty\frac{e^{-3\lambda t}}{t}\,dt.$$

Differentiating this equation by λ, we find

$$\frac{dA}{d\lambda} \simeq -\frac{1}{\lambda}\int_0^\infty s\left(e^{-1/s}-1+\frac{1}{s}\right)e^{-3\lambda s}\,ds. \tag{36}$$

The right-hand side of Eq. (36) is equal to

$$-1/\lambda\cdot[2(3\lambda)^{-1}K_2(2\sqrt{3\lambda})-(3\lambda)^{-2}+(3\lambda)^{-1}].$$

Therefore, for small λ Eq. (36) becomes

$$\frac{dA}{d\lambda} \simeq \frac{1}{2\lambda}[\log(3\lambda)-\psi(0)-\psi(2)]+0(\lambda^0).$$

Integrating this equation, we have

$$A(\lambda) \simeq \text{const.}+1/2\cdot[\log 3-\psi(0)-\psi(2)]\log\lambda+1/4\cdot(\log\lambda)^2. \tag{37}$$

Comparing the above equation with Eqs. (33) and (35), we see that the contribution of the second term in Eq. (33) is of the order same as the first one. Though the value of constant in Eq. (37) is not determined by the above argument, it is clear that the order of $S_3^{(a)}/\rho$ is λ^3, if we consider the term $\log\lambda$ as if it were of the order λ^0. Under the same prescription, S_2/ρ is of the order of λ^2 as can be seen from Eq. (29). Thus, it is verified that the contribution of giant cluster of type (a) shown in Fig. 8 is of orders higher than γ_1 in the same figure.

The calculation of terms of type (b) and of more complex giant clusters is very difficult, and we shall not enter into this problem here. However, as was shown in the above calculation, it is quite probable that their contributions are of orders higher than that of γ_1. Then, up to the order of λ^2, we obtain from Eqs. (29) and (30)

$$S/\rho=\lambda/3+\lambda^2(\log 3\lambda/12+\gamma/6-11/72)+0(\lambda^3). \tag{38}$$

By the use of Eqs. (3) and (22), the equation of state is written as

$$P/\rho\,\kappa T=1-\lambda/2\cdot\partial/\partial\lambda\cdot(S/\rho).$$

Therefore, substituting Eq. (38) in the above equation, we have

$$\frac{P}{\rho\kappa T}=1-\frac{\lambda}{6}-\lambda^2\left(\frac{\log 3\lambda}{12}+\frac{\gamma}{6}-\frac{1}{9}\right)+0(\lambda^3). \tag{39}$$

The third term on the right-hand side is graphically shown in Fig. 11. As is seen from this figure, when λ is smaller than about 0.4, the third term makes the $P/\rho\kappa T$ larger than that calculated without this term. This situation is represented in Fig. 12.

In order to estimate orders of magnitude for the high temperature plasma, let us suppose $T\simeq 10^5\,^\circ$K and $\rho\simeq 10^{15}\text{cm}^{-3}$. Then we have $\lambda\simeq 10^{-2}$. If we set $\lambda=10^{-2}$, the Debye-Hückel term, $\lambda/6$, in Eq. (39) is 1.6667×10^{-3}. On the other hand, the correction term $\lambda^2(\log 3\lambda/12+\gamma/6-1/9)$ in Eq. (39) takes the value -0.0308×10^{-3}. Thus we see the latter amounts to only about 2% of the former. The higher the

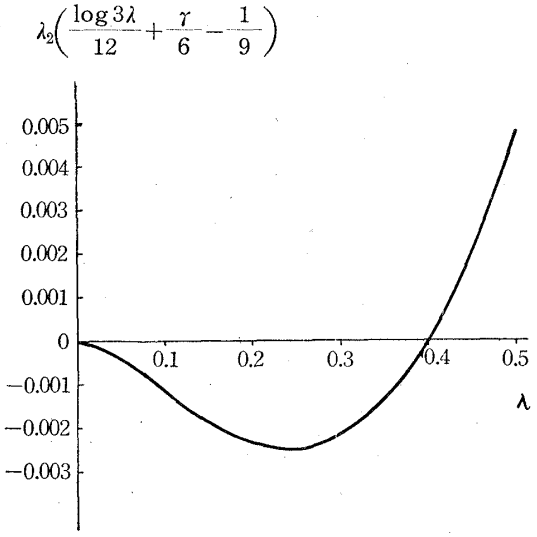

Fig. 11. Graphical representation of $\lambda^2(\log 3\lambda/12+\gamma/6-1/9)$ as a function of λ.

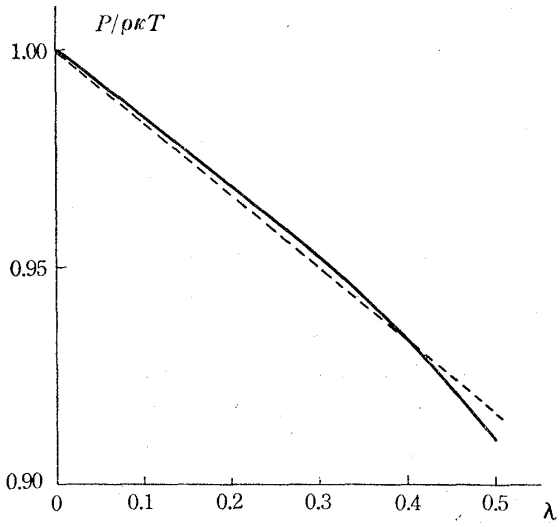

Fig. 12. Equation of state for high temperature plasma. The dotted line is the Debye-Hückel limiting law and the full line is based on our calculation.

temperature is, the smaller the correction becomes. Thus we may conclude that the Debye-Hückel law is accurate within the error of a few per cent for the plasma at sufficiently high temperature.

Here we wish to add some remarks about the functional dependence of S/ρ on λ, which is suggested by the present calculations. We have shown that S_2/ρ includes the terms λ^2 and $\lambda^2\log\lambda$, $S_3^{(a)}/\rho$ the terms λ^3, $\lambda^3\log\lambda$ and $\lambda^3(\log\lambda)^2$ for small λ. Furthermore, it is easily verified that S_2/ρ is a sum of terms λ^m and $\lambda^m\log\lambda$ $(m=2, 3,\cdots)$. In all these cases, the S/ρ is expressed as a sum of terms $\lambda^m(\log\lambda)^n$ $(m>n)$. If we assume these properties to be more general, S/ρ may be written as

$$S/\rho=\sum_{m>n=0}^{\infty} b_{mn}\lambda^m(\log\lambda)^n$$

where b_{mn} is independent of λ. This implies that the thermodynamic function of plasma is a double power series of λ and $\log\lambda$.

§ 6. Concluding remarks

A systematic expansion scheme quite suitable to dealing with the long-range interaction has been developed. We can safely conclude that the fundamental difficulties associated with the interaction of this sort are completely solved by this method, as far as the behaviour of the system at low densities and high temperatures is concerned. The method has been applied to the study of equilibrium properties of high temperature plasma, and the equation of state beyond the Debye-Hückel limiting law has been obtained exactly up to the order of λ^2. It in turn indicates that the Debye-Hückel law is exact up to the order of λ.

Now, with respect to this point, we must mention the calculation carried out by Ichikawa.[5] He has shown that the long-range correlation effects of the Coulomb interaction increase the free energy of the Debye-Hückel law by about 22%. Obviously, his conclusion is not consistent with ours. The origin of this discrepancy is due to the fact that he dealt with the high density behaviour of plasma, though his result is reduced to the Debye-Hückel law at low density limit.

The giant cluster expansion developed here may be generalized to the multi-component system, and more realistic description of plasma in which the positive ion is not smeared may be possible. Moreover, it seems that the similar technique combined with the recent theories[10] on the irreversible process will be usefully applied to the investigation of non-equilibrium quantities such as mobility, relaxation time, of plasma. We shall discuss these problems elsewhere.

Furthermore, it may also be possible to extend the present method to quantum statistics. In this case the expansion scheme corresponding to the classical cluster expansion is "linked cluster expansion" in terms of Feynman graphs[11]. These graphs have a strong resemblance to the bond diagrams in classical theory, except for the terms representing the exchange effects. In fact, the summation of Feynman graphs of ring type leads to the result derived by Montroll and Ward[12] in a quite simple way.[13] It is further possible to develop the expansion scheme in terms of prototype Feynman graphs, in parallel with classical theory. We hope that the quantum statistical treatment of electron gas along the line conjectured here may give a deeper insight into the electron correlation in metals and prove useful in connection with the problems on correlation energy, thermodynamic properties, electromagnetic properties, transport phenomena, superconductivity, etc. In a forthcoming paper we shall undertake a quantum statistical generalization of the present method.

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Note added in proof After I had written this paper I knew that Dr. Harold L. Friedman developed the similar expansion scheme for the multi-component system (Molecular Phys. **2** (1959), 23). I would like to express my sincere thanks to Prof. S. Ono at Tokyo University for informing me of this paper.