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Hypernetted Chain Approximation, Convolution Approximation and Perfect Screening in Coulombic Many-Particle System

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Multi-particle correlations in dense plasmas are analyzed in terms of the density-functional formalism. It is proved that the higher-order correlation potentials and the bridge functions, which identically vanish in the convolution approximation (CA) and which are the neglected terms in the hypernetted chain (HNC) approximation, remain short-ranged despite the long-range nature of the Coulomb interaction.

§ 1. Introduction

It has been known empirically that the hypernetted chain (HNC) approximation[1),2)] provides an accurate description of correlations in the classical many-particle system interacting via the long-range Coulomb forces,[3),4)] that is, the classical charged liquid. This situation presents sharp contrast to the case of a short-range, hard-core system, for example, where the Percus-Yevick equation is known to be superior to the HNC equation.[5)] A question which naturally arises then is: Why the HNC equation works so well for the Coulomb system.

The HNC equation is obtained in the approximation where the contributions of the bridge diagrams (i.e., the elementary diagrams) are neglected in the cluster expansion of the potential of mean force.[5)] It is thus significant to explore the nature of those neglected terms or the bridge functions, which represent "errors" in the HNC scheme. By means of the nodal-expansion analysis, Deutsch, Furutani and Gombert[6)] investigated the long-range, asymptotic behavior of the bridge functions for the first few elementary diagrams in the classical charged liquid. They thereby concluded that those bridge functions are short-ranged in the sense that the long-range part exhibits an exponential decay reflecting a screening of the Debye-Hückel type.

Since the Coulomb potential itself is long-ranged, it is essential that the conservation of particles is secured at each stage of the sequential relations[7),8)] [cf., Eq. (27) below] between the correlation functions. Otherwise a spurious space-charge field arising from the resultant charge imbalance would produce an unscreened, long-range effect on the correlation functions. Overall charge neutrality and the associated screening properties must therefore be maintained carefully in the Coulomb system.

It is natural to conjecture at this stage that those three features —— accuracy of the HNC equation, the short-rangedness of the bridge functions and the particle conservation through the sequential relations —— are interrelated in the Coulomb system. The purpose of the present paper is then to prove explicitly that the conjecture is in fact true. We shall show in terms of the density-functional formalism[9)] that the convolution approximation (CA) to the correlation functions, which guarantees the sequential relations, leads directly to the HNC equation. It will also be shown that the Fourier transforms of the

higher-order correlation potentials[10),11)] and the bridge functions remain convergent in the long-wavelength limit of the wave vectors as long as the sequential relations are maintained in the correlation functions; hence the bridge functions are short-ranged to all order even in the Coulomb system. Those findings give a solid foundation to the density-functional theory of the charged many-particle system and provide a useful guide-line to a theoretical scheme of improvement over the HNC approximation.[10),11)]

§ 2. Density-functional theory of correlations

We begin by formulating the many-particle correlation functions for the one-component plasma (OCP) in terms of the density-functional theory;[9),10),11)] the OCP is a classical system of identical point ions with electric charge Ze, embedded in rigid, uniform background of neutralizing charges. We consider the case in which an external, electrostatic potential $\phi_{\rm ext}(\boldsymbol{r})$ is applied to the OCP; the system is inhomogeneous due to the presence of the external potential.

The thermodynamic potential of the system consists of five contributions expressed as functionals of the density deviation from the average, $\delta n(\boldsymbol{r})=n(\boldsymbol{r})-n$:

$$\Omega[n(\boldsymbol{r})]=F_0[n(\boldsymbol{r})]+\frac{1}{2}\int v(|\boldsymbol{r}-\boldsymbol{r}'|)\delta n(\boldsymbol{r})\delta n(\boldsymbol{r}')d\boldsymbol{r}d\boldsymbol{r}'+F_c[n(\boldsymbol{r})]$$
$$+Ze\int\delta n(\boldsymbol{r})\phi_{\rm ext}(\boldsymbol{r})d\boldsymbol{r}-\mu\int n(\boldsymbol{r})d\boldsymbol{r}\,. \tag{1}$$

Here $v(r)$ is the Coulomb potential $(Ze)^2/r$, $F_0[n(\boldsymbol{r})]$ denotes the free-energy functional of the corresponding non-interacting system, the contribution $F_c[n(\boldsymbol{r})]$ stems from inter-ionic correlations, and μ denotes the chemical potential of the system. The stationary condition of $\Omega[n(\boldsymbol{r})]$ with respect to $n(\boldsymbol{r})$,

$$\frac{\delta\Omega[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}=\frac{\delta F_0[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}+\int v(|\boldsymbol{r}-\boldsymbol{r}'|)\delta n(\boldsymbol{r}')d\boldsymbol{r}'+\frac{\delta F_c[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}+Ze\phi_{\rm ext}(\boldsymbol{r})-\mu$$
$$=0\,, \tag{2}$$

determines the equilibrium ion-density distribution $n(\boldsymbol{r})$ in the presence of $\phi_{\rm ext}(\boldsymbol{r})$.[9)] If, in particular, we introduce a test particle of the same kind as the plasma particles at the origin, that is, if we set $\phi_{\rm ext}(\boldsymbol{r})=Ze/r$, the relative density $n(\boldsymbol{r})/n$ would amount to the radial distribution function $g(r)$ of the homogeneous OCP. Equation (2) then leads to the exact equation for $g(r)$, that is,

$$g(r)=\exp[-\beta v(r)+h(r)-c(r)+B(r)], \tag{3}$$

where $c(r)$ and $h(r)[\equiv g(r)-1]$ refer to the direct correlation function and the pair correlation function.

The remaining term $B(r)$ in the potential of mean force of Eq. (3) corresponds to the sum of all the bridge functions in the Mayer-Ursell cluster expansion theory. In the density-functional theory the bridge functions are arranged in the order of the particle correlations as

$$B(r)=-\sum_{\nu\geq 3}^{\infty}\frac{n^{\nu-1}}{(\nu-1)!}\int d\boldsymbol{r}_1\cdots\int d\boldsymbol{r}_{\nu-1}\beta K_c^{(\nu)}(\boldsymbol{r},\,\boldsymbol{r}_1,\cdots,\,\boldsymbol{r}_{\nu-1})\times h(\boldsymbol{r}_1)\cdots h(\boldsymbol{r}_{\nu-1}), \tag{4}$$

where β is the inverse temperature in energy units. The ν-body correlation potential $K_c^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)$ is defined as the νth derivative of the correlation contribution $F_c[n(\boldsymbol{r})]$ with respect to density $n(\boldsymbol{r})$:

$$K_c^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)=\frac{\delta^\nu F_c[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r}_1)\cdots\delta n(\boldsymbol{r}_\nu)}\bigg|_{n(\boldsymbol{r})\to n}; \tag{5}$$

it is related with the ν-body direct correlation function $c^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)$ through $\beta K_c^{(\nu)} = -c^{(\nu)}$ for $\nu \geq 3$. The HNC scheme amounts to an approximation where the bridge-function contribution is neglected in the potential of mean force. An improvement over the HNC scheme thus calls for an appropriate treatment of the higher-order correlation potentials $K_c^{(\nu)}$ with $\nu \geq 3$.

§ 3. Correlation potentials

Successive differentiation of Eq. (2) with respect to $n(\boldsymbol{r})$ yields the amenable expression for $K_c^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)$,

$$\beta K_c^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)=-\beta K_0^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)+K^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)-\beta v(|\boldsymbol{r}_1-\boldsymbol{r}_2|)\delta_{\nu,2}\,, \tag{6}$$

where

$$\beta K_0^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)=\frac{\delta^\nu \beta F_0[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r}_1)\cdots\delta n(\boldsymbol{r}_\nu)}$$

$$=(-1)^\nu(\nu-2)!\frac{\delta(\boldsymbol{r}_1-\boldsymbol{r}_2)\cdots\delta(\boldsymbol{r}_1-\boldsymbol{r}_\nu)}{[n(\boldsymbol{r}_1)]^{\nu-1}}, \tag{7}$$

$$K^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)=\frac{\delta^{\nu-1}\Phi(\boldsymbol{r}_1)}{\delta n(\boldsymbol{r}_2)\cdots\delta n(\boldsymbol{r}_\nu)}, \tag{8}$$

and $\Phi(\boldsymbol{r})=-Ze\beta\phi_{\text{ext}}(\boldsymbol{r})$.

In addition to these functions, we find it useful to introduce the particle distribution functions,

$$I^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)=\langle n(\boldsymbol{r}_1)\cdots n(\boldsymbol{r}_\nu)\rangle, \tag{9}$$

and the Ursell functions, the inverse of the K functions, defined as

$$U^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)=\frac{\delta^{\nu-1}n(\boldsymbol{r}_1)}{\delta\Phi(\boldsymbol{r}_2)\cdots\delta\Phi(\boldsymbol{r}_\nu)}. \tag{10}$$

The distribution functions I are then expanded[12),13)] in terms of the Ursell functions U. A first few terms are

$$I^{(1)}(\boldsymbol{r}_1)=U^{(1)}(\boldsymbol{r}_1), \tag{11}$$

$$I^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)=U^{(1)}(\boldsymbol{r}_1)U^{(1)}(\boldsymbol{r}_2)+U^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2), \tag{12}$$

$$I^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)=U^{(1)}(\boldsymbol{r}_1)U^{(1)}(\boldsymbol{r}_2)U^{(1)}(\boldsymbol{r}_3)+U^{(1)}(\boldsymbol{r}_1)U^{(2)}(\boldsymbol{r}_2, \boldsymbol{r}_3)$$
$$+U^{(1)}(\boldsymbol{r}_2)U^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_3)+U^{(1)}(\boldsymbol{r}_3)U^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)+U^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3). \tag{13}$$

As can be noticed immediately from the definition, the functions K_c, K_0, K and U have the following recursive relations:

$$\frac{\delta K_c^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)}{\delta n(\boldsymbol{r}_{\nu+1})} = K_c^{(\nu+1)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_{\nu+1}), \tag{14}$$

$$\frac{\delta K_0^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)}{\delta n(\boldsymbol{r}_{\nu+1})} = K_0^{(\nu+1)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_{\nu+1}), \tag{15}$$

$$\frac{\delta K^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)}{\delta n(\boldsymbol{r}_{\nu+1})} = K^{(\nu+1)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_{\nu+1}) \tag{16}$$

and

$$\frac{\delta U^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)}{\delta \Phi(\boldsymbol{r}_{\nu+1})} = U^{(\nu+1)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_{\nu+1}). \tag{17}$$

The two-body function $K^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is related with the two-body Ursell function $U^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ via

$$\int K^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) U^{(2)}(\boldsymbol{r}_2, \boldsymbol{r}_3) d\boldsymbol{r}_2 = \delta(\boldsymbol{r}_1 - \boldsymbol{r}_3). \tag{18}$$

If we assume homogeneity of the system, we obtain an explicit form for $K^{(2)}$ in the wave number (k) space as

$$K^{(2)}(k) = \frac{1}{U^{(2)}(k)} = \frac{1}{nS(k)}, \tag{19}$$

where $S(k)$ is the static structure factor. The three-body function $K^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$ can be calculated by differentiating Eq. (18) with respect to $n(\boldsymbol{r})$: The differentiation of Eq. (18) yields

$$K^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = -\iint d\boldsymbol{r}_4 d\boldsymbol{r}_5 K^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_4) K^{(2)}(\boldsymbol{r}_2, \boldsymbol{r}_5) \frac{\delta U^{(2)}(\boldsymbol{r}_4, \boldsymbol{r}_5)}{\delta n(\boldsymbol{r}_3)}, \tag{20}$$

where we used the recursion relation (16) and Eq. (18). The term $\delta U^{(2)}(\boldsymbol{r}_4, \boldsymbol{r}_5)/\delta n(\boldsymbol{r}_3)$ on the right-hand side of Eq. (20) is calculated as

$$\begin{aligned} \frac{\delta U^{(2)}(\boldsymbol{r}_4, \boldsymbol{r}_5)}{\delta n(\boldsymbol{r}_3)} &= \int d\boldsymbol{r}_6 \frac{\delta U^{(2)}(\boldsymbol{r}_4, \boldsymbol{r}_5)}{\delta \Phi(\boldsymbol{r}_6)} \cdot \frac{\delta \Phi(\boldsymbol{r}_6)}{\delta n(\boldsymbol{r}_3)} \\ &= \int d\boldsymbol{r}_6 U^{(3)}(\boldsymbol{r}_4, \boldsymbol{r}_5, \boldsymbol{r}_6) K^{(2)}(\boldsymbol{r}_6, \boldsymbol{r}_3) \end{aligned} \tag{21}$$

with the chain rule in the functional differentiation[13] and the recursion relation (17). Substituting Eq. (21) in Eq. (20), we finally obtain the explicit expression for $K^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$ depicted in Fig. 1, where the white circles refer to the particle coordinates under consideration; the solid circles, those to be integrated; the wavy line joining two particles represents the two-body function $K^{(2)}$; and the ν-polygon, minus the ν-body Ursell function $U^{(\nu)}$. Using the recursion formula (16) as a generator, we can successively express[12] the ν-body function $K^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)$, $\nu \geq 4$ in terms of the two-body functions $K^{(2)}$ and the Ursell functions U. The explicit expressions for $K^{(4)}$ and $K^{(5)}$ are also included in Fig. 1.

The general results are described in the diagrammatic language as

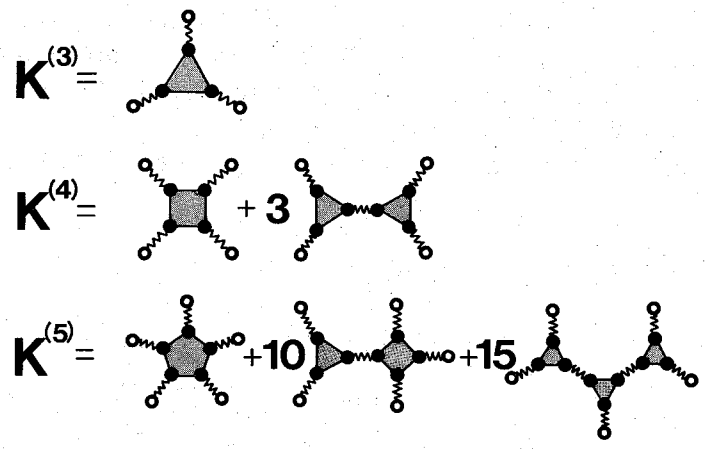

Fig. 1. Diagrammatic representation of $K^{(\nu)}$ for $\nu=3$, 4 and 5.

$$K^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)=\left[\begin{array}{l}\text{the collection of all topologically distinct normal } \nu\text{-rooted Cayley tree graphs, provided that the degree of each vertex is three or more. The vertex functions are minus the } U \text{ functions and the bonds are the two-body function } K^{(2)}.\end{array}\right] \tag{22}$$

For the diagrammatic notation used here, we refer the readers to Refs. 7) and 8). The functional natures of the correlation potentials K_c will be elucidated through Eq. (6), together with Eqs. (7) and (22) in the following sections.

§ 4. Long-range behavior of the correlation potentials

In this section we investigate the long-range asymptotic behavior of the ν-body correlation potential $K_c^{(\nu)}$ for $\nu \geq 3$ in the uniform system. Making the Fourier transformation to the expression (6) for $K_c^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)$ with Eqs. (7) and (22), one finds that products of the static structure factors appear in their denominators on account of Eq. (19); the explicit forms of $K_c^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{k}_\nu)$ with $\boldsymbol{k}_1+\cdots+\boldsymbol{k}_\nu=0$ have been given in Ref. 11) for $\nu=3$ and 4. There exists, therefore, a possibility that the higher-order correlation potentials K_c may remain long-ranged in the OCP due to the long-wavelength behavior, $S(k) \propto k^2$; divergence of $K_c^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{k}_\nu)$ in the long-wavelength limits may take place through accumulation of the structure factors in the denominators*) [see Eqs. (5) and (A1) in Ref. 11)].

Investigation into the long-wavelength behavior of $K_c^{(\nu)}$ requires a knowledge of the corresponding behavior of the U functions which appear in the numerators. The overall charge neutrality condition, in effect, offers the boundary condition for the asymptotic behavior of the U functions. In the charged system, including the inhomogeneous case, we may assume that if some of the plasma particles are fixed, then the fixed charges are perfectly screened by the others within the range independent of the system size. This

*) A similar divergence of $K_c^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{k}_\nu)$ may also take place when momentum conservation is partially maintained among the $\boldsymbol{k}$'s.

assumption is not only physically reasonable but also widely accepted;[14] recently, it has been proved[15] through analyses of the BBGKY hierarchy equations by placing certain limitation on the decaying behavior of the particle correlations. The peculiar behavior of $S(k)$ reflects the overall charge neutrality in the plasma.

The generalized overall charge-neutrality condition for the U functions is obtained in the Appendix as

$$\int U^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)d\boldsymbol{r}_i=0\,. \qquad (i=1\sim\nu) \tag{23}$$

In the wave-number space, the condition (23) reads

$$U^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{k}_i=0, \cdots, \boldsymbol{k}_\nu)=0. \qquad (i=1\sim\nu) \tag{24}$$

Subject to the constraint of the translational invariance ($\boldsymbol{k}_1+\cdots+\boldsymbol{k}_\nu=0$), the first derivative of $U^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{k}_\nu)$ in $\boldsymbol{k}_i$ also vanishes at $\boldsymbol{k}_i=0$ owing to Eq. (24): The derivative is calculated with the aid of Eq. (24) as

$$\left.\frac{\partial U^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{k}_\nu)}{\partial \boldsymbol{k}_i}\right|_{\boldsymbol{k}_i=0}=i\int d\boldsymbol{r}_i \boldsymbol{r}_i U^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{r}_i, \cdots, \boldsymbol{k}_\nu). \tag{25}$$

Momentum conservation holds among the wave vectors on the right-hand side of Eq. (25), that is, $\boldsymbol{k}_1+\cdots+\boldsymbol{k}_{i-1}+\boldsymbol{k}_{i+1}+\cdots+\boldsymbol{k}_\nu=0$. Hence, the function $U^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{r}_i, \cdots, \boldsymbol{k}_\nu)$ in the integral of Eq. (25) is independent of $\boldsymbol{r}_i$ and vanishes by virtue of Eq. (24), so that

$$\left.\frac{\partial U^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{k}_\nu)}{\partial \boldsymbol{k}_i}\right|_{\boldsymbol{k}_i=0}=0\,. \tag{26}$$

Equations (24) and (26) attributed to the overall charge neutrality determine the asymptotic behavior of the correlation functions in the OCP. The condition (23) is equivalent to the sequential relations between the many-particle correlation functions $h^{(\nu)}$,

$$\int h^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)n(\boldsymbol{r}_\nu)d\boldsymbol{r}_\nu=-(\nu-1)h^{(\nu-1)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_{\nu-1}), \tag{27}$$

as was shown by Wu[8] in the homogeneous case. The correlation functions $h^{(\nu)}$ correspond to those parts of $U^{(\nu)}$ that are devoid of the self-correlations. The relation between the two-body correlation functions, $h^{(2)}$ and $U^{(2)}$, is shown in Fig. 2.

If we expand $U^{(\nu)}(\boldsymbol{k}_1, \cdots, \boldsymbol{k}_\nu)$ around $\boldsymbol{k}_i=0$, the zeroth- and first-order terms with respect to $\boldsymbol{k}_i$ do not appear on account of the relations (24) and (26); in the long-wavelength limit the U functions behave in the same way as the static structure factor $S(k)$ does. Therefore, the divergence of $K_c^{(\nu)}$ due to the structure factors in the denominators is completely canceled out by this asymptotic behavior of the U functions in the numerators, so that the correlation potentials K_c are proved to be short-ranged even in the OCP. The bridge functions given by Eq. (4) are likewise short-ranged at each order of the correlation potential.

We see that the overall charge neutrality has played an essential role in the present analysis. This fact suggests the importance of the charge-neutrality condition in constructing approximate theories for the charged system; an inappropriate approximation adopted for the higher-order correlation functions would lead to spurious divergences of the correlation potentials in the long-wavelength limit. This point was carefully taken

into account in the improved HNC scheme,[10),11)] and has been remarked by other authors[15)] in the context of the perfect screening for charged systems.

In connection with the aforementioned charge-neutrality condition, it is instructive to compare the STLS scheme[16)] and the convolution scheme[17),18)] proposed for the OCP, both of which are based upon decoupling procedures in the BBGKY hierarchy of the kinetic equations. The STLS scheme, which was originally developed in the study of the degenerate electron liquid, is obtained by adopting the following ansatz for the inhomogeneous two-particle distribution function:

$$n^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)=n(\boldsymbol{r}_1)n(\boldsymbol{r}_2)g(|\boldsymbol{r}_1-\boldsymbol{r}_2|), \tag{28}$$

where $g(r)$ is taken to be the pair distribution function in the corresponding uniform system. The ansatz (28) does not satisfy the overall charge-neutrality condition (23) at $\nu=2$. In contrast, Ichimaru closed the second-order BBGKY equation by adopting the convolution approximation for the homogeneous ternary correlation function,

$$\begin{aligned} h^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)=&h(|\boldsymbol{r}_1-\boldsymbol{r}_2|)h(|\boldsymbol{r}_1-\boldsymbol{r}_3|)+h(|\boldsymbol{r}_1-\boldsymbol{r}_2|)h(|\boldsymbol{r}_2-\boldsymbol{r}_3|) \\ &+h(|\boldsymbol{r}_1-\boldsymbol{r}_3|)h(|\boldsymbol{r}_2-\boldsymbol{r}_3|)+n\int d\boldsymbol{r}_4 h(|\boldsymbol{r}_1-\boldsymbol{r}_4|)h(|\boldsymbol{r}_2-\boldsymbol{r}_4|)h(|\boldsymbol{r}_3-\boldsymbol{r}_4|), \end{aligned} \tag{29}$$

which satisfies the condition (27) at $\nu=3$ exactly. The convolution scheme reproduces the known weak coupling result beyond the Debye-Hückel term, while the STLS scheme does not; furthermore, superiority of the convolution scheme to the STLS scheme was demonstrated through the numerical investigations of the static properties of the OCP in the intermediate coupling domain ($\Gamma\sim 1$).[18),19)]

§ 5. Convolution approximation for the correlation potentials

In this section we verify the proposition that the correlation potentials of the three-body and higher-order vanish identically, including the inhomogeneous cases, on using the convolution approximation[7),8)] (CA) for the evaluation of the Ursell functions U. The convolution scheme is one of those approximations which express the many-body correlation functions in terms of the two-body correlation function. The general convolution forms for the U functions were obtained by Wu in the uniform system;[8)] however, we need to extend his results to the non-uniform cases in the present proof. Since the extension can be carried out straightforwardly, we refer the readers to Ref. 8) for its derivation and present here only the final results:

$$U^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)_{\mathrm{CA}}=\left[\begin{array}{l}\text{the collection of all topologically distinct normal } \nu\text{-rooted Cayley tree graphs, provided that each double black point (◉) is a node. All terminal lines are double (solid and dotted) and all internal lines are, in contrast, single (solid).}\end{array}\right] \tag{30}$$

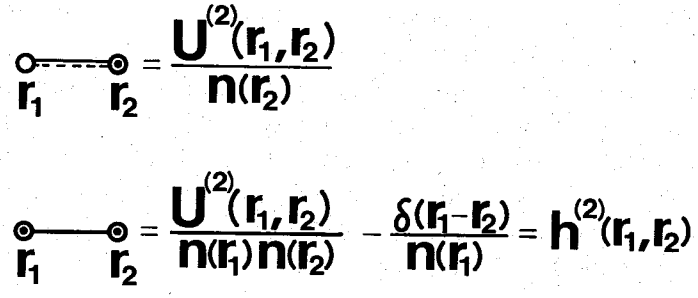

Fig. 2. Definition of the single and double lines.

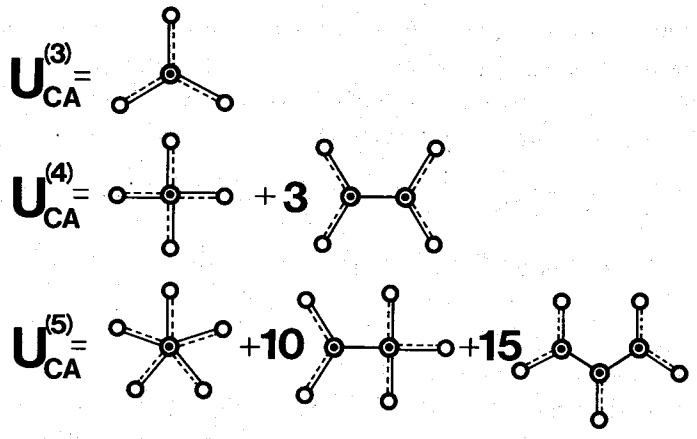

Fig. 3. Diagrammatic representation of $U_{CA}^{(\nu)}$ for $\nu=3$, 4 and 5.

Here the double black point refers to the particle coordinate to be integrated with density $n(\boldsymbol{r})$; the double and single lines have the meaning as shown in Fig. 2. For $\nu=2$, one has

$$U^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)_{CA}=U^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2). \tag{31}$$

The convoluted forms of $U^{(\nu)}$ for $\nu=3\sim5$ in the diagrammatic representation are shown in Fig. 3. Since all the terminal lines of $U_{CA}^{(\nu)}$ are double, the convolution form $U_{CA}^{(\nu)}$ satisfies the overall charge neutrality condition (23) exactly, as long as the two-body Ursell function $U^{(2)}$ satisfies the corresponding condition at $\nu=2$.

One can readily check $K_c^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)=0$ in the convolution approximation by substituting $U_{CA}^{(3)}$ for $U^{(3)}$ involved in $K^{(3)}$ of Eq. (6) [see also Refs. 11) and 13)]. If we show that the recursion relation (14) for the K_c functions remains valid in the convolution approximation, then the proposition will be verified generally by mathematical induction. By virtue of Eq. (6), we turn our attention to the recursion relation (16) for the K functions, because the recursion relation (15) for the K_0 functions holds, irrespective of the approximations. Recalling the derivation of Eq. (22), we see that the relation (16) holds, provided that the U functions satisfy the recursion relation (17). Thus, the proof of the proposition reduces to that of Eq. (17) in the convolution approximation.

In the calculation of the functional derivative of $U^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)_{CA}$ with respect to $\Phi(\boldsymbol{r}_{\nu+1})$, the differentiation operates on three different parts of the diagrams, that is, the node, the terminal line, and the internal line, as shown in Fig. 4. Here we have substituted

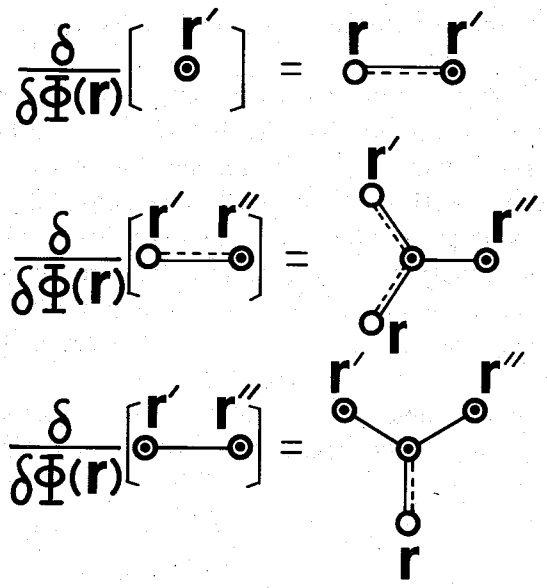

Fig. 4. Fundamental operations appearing in the calculation of $\delta U^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)_{CA}/\delta\Phi(\boldsymbol{r}_{\nu+1})$.

the convolution form $U_{CA}^{(3)}$ in place of $U^{(3)}$ appearing on these calculations. In the light of these fundamental operations, we find that the differentiation of $U^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)_{CA}$ with respect to $\Phi(\boldsymbol{r}_{\nu+1})$ yields only the $(\nu+1)$-rooted normal Cayley tree graphs, all of which are elements of the diagram set of $U_{CA}^{(\nu+1)}$. Conversely, each graph belonging to the diagram set of $U_{CA}^{(\nu+1)}$ is derived uniquely from the operation on $U_{CA}^{(\nu)}$. Hence, there exists one-to-one correspondence between the graphs of $\delta U^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)_{CA}/\delta\Phi(\boldsymbol{r}_{\nu+1})$ and $U^{(\nu+1)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_{\nu+1})_{CA}$, and it turns out that the recursion relations (17) remain valid in the convolution approximation. This concludes the proof.

It is also possible to prove that the convolution approximation scheme for the U functions is a unique one resulting in $K_c^{(\nu)}=0$ for $\nu\geq 3$. Let us begin with assuming that there exists another approximation scheme (X) for the U functions which is a solution to the set of the equations, $K_c^{(\nu)}=0$ $(\nu\geq 3)$. From this assumption we can choose an integer $\eta(\geq 3)$: The Ursell functions $U^{(\nu)}$ are identical in the two schemes for $\nu<\eta$, but this identity breaks at $\nu=\eta$, namely, $U_{CA}^{(\eta)}\neq U_X^{(\eta)}$. Structural analysis of Eq. (22) decomposes the ηth order equation, $\beta K_c^{(\eta)}=-\beta K_0^{(\eta)}+K^{(\eta)}=0$, satisfied by the U functions in both schemes as

$$\beta K_0^{(\eta)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\eta)+\int U^{(\eta)}(\boldsymbol{r}_1', \cdots, \boldsymbol{r}_\eta')K^{(2)}(\boldsymbol{r}_1', \boldsymbol{r}_1)\cdots \times K^{(2)}(\boldsymbol{r}_\eta', \boldsymbol{r}_\eta)d\boldsymbol{r}_1'\cdots d\boldsymbol{r}_\eta'+(\text{remainder})=0\,, \tag{32}$$

where the remainder involves only the U functions of order less than η and the two-body functions $K^{(2)}$. The function $K_0^{(\eta)}$ is independent of the approximations and the remainder in Eq. (32) is identical in the two schemes by virtue of the assumption. Therefore, the second term of Eq. (32) evaluated in the X scheme must amount to the one in the convolution scheme,

$$\int U^{(\eta)}(\boldsymbol{r}_1', \cdots, \boldsymbol{r}_\eta')_X K^{(2)}(\boldsymbol{r}_1', \boldsymbol{r}_1)\cdots K^{(2)}(\boldsymbol{r}_\eta', \boldsymbol{r}_\eta)\, d\boldsymbol{r}_1'\cdots d\boldsymbol{r}_\eta'$$

$$=\int U^{(\eta)}(\boldsymbol{r}_1', \cdots, \boldsymbol{r}_\eta')_{CA}K^{(2)}(\boldsymbol{r}_1', \boldsymbol{r}_1)\cdots K^{(2)}(\boldsymbol{r}_\eta', \boldsymbol{r}_\eta)d\boldsymbol{r}_1'\cdots d\boldsymbol{r}_\eta'\,. \tag{33}$$

Applying matrix multiplications of the $U^{(2)}$ functions to cancel the $K^{(2)}$ functions on both sides of Eq. (33), we finally obtain

$$U^{(\eta)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\eta)_X=U^{(\eta)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\eta)_{CA}\,. \tag{34}$$

Since this result contradicts the assumption postulated at the onset, we see that the

convolution forms U_{CA} constitute unique solutions for the set of the equations, $K_c^{(\nu)}=0$ $(\nu \geq 3)$.

It therefore follows from Eq. (4) that the HNC scheme obtained by setting $B(r)=0$ in Eq. (3) is equivalent to evaluating the correlation potentials K_c in the convolution approximation. This fact elucidates the reason why the HNC scheme has been so successful[3),4)] in describing the correlational properties for the OCP; the convolution approximation on which it is based satisfies exactly the overall charge neutrality condition (23) as noted earlier, so that the HNC approximation takes an accurate account of the long-range correlations crucial in the Coulomb systems. It is worth noting that the scheme[17),18)] proposed by Ichimaru is included in the HNC scheme as the lowest-order iterative solution.[18),20)]

We can readily extend the present results in the one-component system to the cases of a multicomponent plasma by transforming the particle coordinates and the integrations appearing in the previous equations as

$$\boldsymbol{r} \to q=(\boldsymbol{r}, \sigma), \tag{35}$$

$$\int d\boldsymbol{r} \to \sum_{\sigma} \int d\boldsymbol{r}\,, \tag{36}$$

where σ distinguishes different species of the ions; the HNC equation for a multicomponent system results if we adopt the generalized convolution approximation in the evaluation of the correlation potentials, which exactly satisfies the overall charge-neutrality condition (A·5).

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Appendix

—— Derivation of Eq. (23) ——

We can write the overall charge-neutrality condition for the pair distribution function $g(\boldsymbol{r}_1, \boldsymbol{r}_2)$ in the inhomogeneous OCP as

$$\int n(\boldsymbol{r}_2)\{g(\boldsymbol{r}_1, \boldsymbol{r}_2)-1\}d\boldsymbol{r}_2=-1\,. \tag{A·1}$$

With the aid of the relation

$$U^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)=n(\boldsymbol{r}_1)\delta(\boldsymbol{r}_1-\boldsymbol{r}_2)+n(\boldsymbol{r}_1)n(\boldsymbol{r}_2)\{g(\boldsymbol{r}_1, \boldsymbol{r}_2)-1\}, \tag{A·2}$$

the condition (A·1) is rewritten in terms of the function $U^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ as

$$\int U^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)d\boldsymbol{r}_2=0\,. \tag{A·3}$$

Then, the generalized overall charge-neutrality condition for the U functions,

$$\int U^{(\nu)}(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_\nu)\, d\boldsymbol{r}_i = 0\,, \qquad (i=1\sim\nu) \tag{A·4}$$

is generated from (A·3) with the aid of the recursion formula (17). The extension of the condition (A·4) to the multicomponent plasmas is readily performed:

$$\sum_{\sigma_i}\int U^{(\nu)}(q_1, \cdots, q_\nu) e_{\sigma_i} d\boldsymbol{r}_i = 0\,, \qquad (i=1\sim\nu) \tag{A·5}$$

where e_σ denotes charge of the particle of species σ and $q=(\boldsymbol{r}, \sigma)$. The condition (A·5) is one of the equivalent expressions for the overall charge neutrality,[21] and recently was used in the study of the charge fluctuations in Coulomb systems.[21),22)]

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