Improvement on the hypernetted-chain equations for dense plasmas

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We present a systematic scheme of improvement on the hypernetted-chain (HNC) equations, based on the density-functional formalism of correlations in high-density, classical plasmas. We show by a numerical comparison that the proposed scheme significantly improves the HNC results and leads to predictions almost identical to the exact Monte Carlo results.

The classical one-component plasma (OCP) makes an idealized model for description of salient properties in high-density plasmas, such as those found in the interior of degenerate stars and heavy planets. In thermodynamic equilibrium at temperature T, such an OCP with number density n is characterized by a single dimensionless parameter, $\Gamma=(Ze)^2/ak_BT$, where Ze is the electric charge of a particle and $a=(4/3\pi n)^{1/3}$ is the ion-sphere radius.

The hypernetted chain (HNC) approximation,[1,2] though superior to all the analytic schemes proposed thus far for a treatment of OCP,[3] still exhibits a systematic departure from the exact Monte Carlo (MC) results[4] in the strong-coupling regime, $\Gamma \gg 1$: Amplitudes of the oscillations in the radial-distribution function $g(r)$ are usually underestimated in HNC (see Fig. 2 below). The HNC form of "thermal energy" in the internal energy formula[5] differs substantially from the MC form, $\Gamma^{1/2}$ vs $\Gamma^{1/4}$; the HNC thermal-energy function is larger numerically than the MC thermal-energy function, with a difference amounting to 45% at $\Gamma=150$.[6] Such a thermal-energy contribution, for example, plays the central role in the theoretical calculation of miscibilities in dense, multi-ionic plasmas; accurate representation of thermal energy is crucial here. It is therefore a meaningful project to construct a workable theoretical scheme by which a systematic and significant improvement on HNC may be achieved for high-density plasmas.

Recently, Rosenfeld and Ashcroft[7] advanced a semiempirical scheme of modification to HNC, on the basis of universality ansatz for the bridge functions; the numerical results obtained for OCP are nearly indistinguishable from the exact MC data. Their scheme, however, relies heavily on the parametrized hard-sphere bridge functions, containing a free parameter to be determined from a self-consistency condition. Application of this scheme appears increasingly difficult for a multi-ionic plasma, where the number of free parameters correspondingly increases.

In this Communication, we wish to present a systematic scheme of improvement on the HNC results within a self-contained framework of the plasma theory. Technical difficulties involved in the numerical computations are no greater than those in the solution to the original HNC equations; the scheme does not contain free parameters and is applicable equally well to OCP and multi-ionic plasmas. Only for notational simplicity, we shall here describe the theory in terms of OCP, however. By a numerical example we shall demonstrate that the proposed scheme can lead to predictions almost identical to the exact MC results.

We begin with placing a test charge Ze at the origin ($\vec{r}=0$), and regard its potential $\phi_{\rm ext}(r)$ as an external disturbance to an otherwise uniform OCP. In the density-functional formalism,[8] the Helmholtz free energy of the system is expressed as a functional of density $n(r)=n+\delta n(r)$:

$$F[n(r)]=\int d\vec{r}\,\phi_{\rm ext}(r)\delta n(r)+\tfrac{1}{2}\int d\vec{r}\int d\vec{r}\,' v(|\vec{r}-\vec{r}\,'|)\delta n(r)\delta n(r')+F_0[n(r)]+F_c[n(r)]\ . \quad (1)$$

Here $v(r)=(Ze)^2/r$ is the Coulomb interaction, $F_0[n(r)]$ refers to the free-energy functional for the corresponding noninteracting system, and $F_c[n(r)]$ refers to the free-energy functional for the remaining correlation contribution.

We expand $F_c[n(r)]$ around the uniform density n as

$$F_c[n(r)]=F_c[n]+\frac{1}{2!}\int d\vec{r}\int d\vec{r}\,' K_c^{(2)}(|\vec{r}-\vec{r}\,'|)\delta n(r)\delta n(r')+\frac{1}{3!}\int d\vec{r}\int d\vec{r}\,'\int d\vec{r}\,'' K_c^{(3)}(\vec{r}-\vec{r}\,',\vec{r}-\vec{r}\,'')\delta n(r)\delta n(r')\delta n(r'')+\cdots\ , \quad (2)$$

where the term proportional to $\delta n(r)$ vanishes identically by virtue of particle-number conservation. The ν-body correlation potential $K_c^{(\nu)}(\vec{r}_1, \ldots, \vec{r}_\nu)$ can be calculated by means of the functional derivative method[9]; the results for the Fourier transforms of $K_c^{(2)}$ and $K_c^{(3)}$ are

$$4\pi(Ze)^2\beta/q^2 + \beta\tilde{K}_c^{(2)}(q) = -n\tilde{c}(q) \quad , \tag{3}$$

$$n^2\beta\tilde{K}_c^{(3)}(\vec{p}, \vec{q}) = 1 - \frac{S^{(3)}(\vec{p}, \vec{q})}{S(p)S(q)S(k)} \quad , \tag{4}$$

where $\beta = (k_B T)^{-1}$ and $\vec{k} = \vec{p} + \vec{q}$. The functions, $S(q)$ and $\tilde{c}(q)$, refer to the static structure factor and the Fourier transform of the direct correlation function. The function $S^{(3)}(\vec{p}, \vec{q})$ is a three-body analog of $S(q)$, expressed in terms of the Fourier transform of the ternary correlation function $h^{(3)}(\vec{r}, \vec{r}')$ as

$$S^{(3)}(\vec{p}, \vec{q}) = -2 + S(p) + S(q) + S(k) + \tilde{h}^{(3)}(\vec{p}, \vec{q}) \quad . \tag{5}$$

The equilibrium distribution is determined from the usual condition[8] that the first functional derivative of $F[n(r)]$ with respect to $\delta n(r)$ vanish. Since the pair-correlation function, $h(r) = g(r) - 1$, is given by $\delta n(r)/n$, the equilibrium solution yields

$$g(r) = \exp[-\beta v(r) + h(r) - c(r) + B(r)] \quad , \tag{6}$$

where we use the Ornstein-Zernike relation[3] between $h(r)$ and $c(r)$, and set

$$B(r) = -\frac{n^2\beta}{2}\int d\vec{r}_1 \int d\vec{r}_2 K_c^{(3)}(\vec{r} - \vec{r}_1, \vec{r} - \vec{r}_2)h(r_1)h(r_2) - \frac{n^3\beta}{6}\int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3 K_c^{(4)}(\vec{r} - \vec{r}_1, \vec{r} - \vec{r}_2, \vec{r} - \vec{r}_3)h(r_1)h(r_2)h(r_3) + \cdots \quad . \tag{7}$$

This function corresponds to the sum of all bridge functions in the Mayer cluster expansion; Eq. (7) thereby connects the diagrammatic expansion theory with the density-functional formalism.[10] The HNC equation results if one sets $B(r) = 0$ in (6).

Since $S(q)$ for the Coulomb system behaves as asymptotically equal to q^2 in the long-wavelength limit, due care must be exercised in the evaluation of the three-body function $S^{(3)}(\vec{p}, \vec{q})$, so that a spurious divergence may be avoided in (4). One can in fact show[11] that such a divergence is avoided as long as the ternary correlation function satisfies the sum rule,

$$\int d\vec{r}_3 h^{(3)}(\vec{r}_1, \vec{r}_3, \vec{r}_3) = -\frac{2}{n}h(r_{12}) \quad , \tag{8}$$

where $r_{12} = |\vec{r}_1 - \vec{r}_2|$; $\tilde{K}_c^{(3)}(\vec{p}, \vec{q})$ actually represents a short-range potential. In particular, use of the convolution approximation,

$$h_{CA}^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = h(r_{12})h(r_{23}) + h(r_{23})h(r_{31}) + h(r_{31})h(r_{12}) + n\int d\vec{r}_4 h(r_{14})h(r_{24})h(r_{34}) \quad , \tag{9}$$

which satisfies (8) exactly, leads to $\tilde{K}_c^{(3)}(\vec{p}, \vec{q}) = 0$. Similarly we have confirmed that the four-body correlation potential $K_c^{(4)}$ vanishes identically when the quaternary correlation function is also expressed in the convolution approximation.

Since the convolution approximation, on which the HNC equation is based, takes accurate account of long-range correlation in the Coulomb system, we seek to improve the HNC approximation for the short-range correlation, writing

$$h^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = h_{CA}^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) + \delta h^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \quad . \tag{10}$$

The Kirkwood superposition-approximation term, given by the first, triangular diagram in Fig. 1, offers a simplest typical term describing such a short-range contribution. The sum rule (8) is violated; the use of this term alone in (10) would lead to a spurious divergence in $\tilde{K}_c^{(3)}(\vec{p}, \vec{q})$. To rectify this apparent flaw, we convolute each vertex and collect all the diagrams as depicted in Fig. 1; the result then is

$$\beta K_{CK}^{(3)}(\vec{r} - \vec{r}', \vec{r} - \vec{r}'') = -h(|\vec{r} - \vec{r}'|)h(|\vec{r}' - \vec{r}''|)h(|\vec{r}'' - \vec{r}|) \quad . \tag{11}$$

Substitution of (11) in (7) finally yields

$$B_{CK}(r) = \frac{n^2}{2}\int d\vec{r}' \int d\vec{r}'' h(|\vec{r} - \vec{r}'|)h(|\vec{r}' - \vec{r}''|)h(|\vec{r}'' - \vec{r}|)h(r')h(r'') \quad , \tag{12}$$

which turns out to be the simplest bridge-diagram contribution.

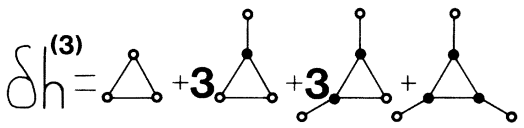

FIG. 1. Kirkwood superposition-approximation terms with vertex corrections. The open circles refer to the particle coordinates under consideration; the filled circles, those to be integrated; and a line joining two particles represents the pair-correlation function $h(r)$.

On the basis of those calculations, one now has a systematic scheme of improving the HNC equations in the framework of the plasma theory: One first solves the HNC equations and writes the resulting correlation functions as $h_{\mathrm{HNC}}(r)$ and $c_{\mathrm{HNC}}(r)$. The bridge function is then evaluated by stretching the short-range part to approximate ion-sphere values as

$$B(r)=\left\{(C-1)\exp\left[-\left(\frac{r}{\xi a}\right)^2\right]+1\right\}B_{\mathrm{CK}}(r)\ , \qquad (13)$$

where $B_{\mathrm{CK}}(r)$ is calculated[12] by substituting $h_{\mathrm{HNC}}(r)$ in (12). The stretching coefficient C is determined[13] as

$$C=[1.057\Gamma+c_{\mathrm{HNC}}(0)+1]/B_{\mathrm{CK}}(0)\ ; \qquad (14)$$

the other parameter takes on the value, $\xi=1.6$, reflecting the condition, $B_{\mathrm{CK}}(\xi a)\simeq 0$. Finally, one substitutes (13) in (6) and solves the resulting modified HNC equation, regarding $v(r)-B(r)/\beta$ as the effective potential. In Fig. 2 a numerical computed result is compared with the HNC and MC results at $\Gamma=160$; a significant improvement over the original HNC result is clearly observed. The final result as illustrated in Fig. 2 turns out to be almost identical to the MC result; the excess internal energy obtained in the improved scheme now agrees with the Monte Carlo data[4] with digression less than 0.15%.

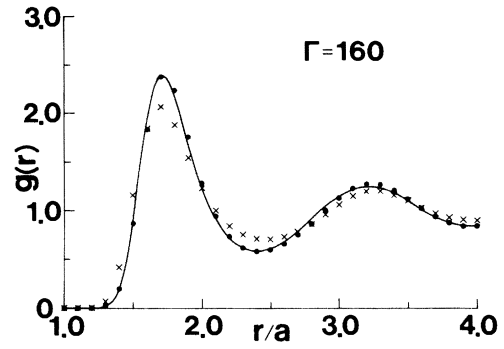

FIG. 2. The radial-distribution function $g(r)$ for OCP at $\Gamma=160$. The filled circles represent the MC values; the crosses, the HNC values. The solid curve depicts the result on the basis of Eqs. (13) and (14).

The detailed theory and numerical results are planned to be published elsewhere.

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[1]J. M. J. van Leeuwen, J. Groeneveld, and J. De Boer, Physica (Utrecht) 25, 792 (1959).
[2]J. F. Springer, M. A. Pokrant, and F. A. Stevens, J. Chem. Phys. 58, 4863 (1973); K. C. Ng, *ibid.* 61, 2680 (1974).
[3]For a review, see, e.g., M. Baus and J. P. Hansen, Phys. Rep. 59, 1 (1980).
[4]W. L. Slattery, G. D. Doolen, and H. E. DeWitt, Phys. Rev. A 21, 2087 (1980).
[5]The thermal energy here is defined as the balance between the excess internal energy and its static, Madelung-like part proportional to Γ; see, e.g., Refs. 4 and 6.
[6]H. E. DeWitt, Phys. Rev. A 14, 1290 (1976).
[7]Y. Rosenfeld and N. W. Ashcroft, Phys. Rev. A 20, 1208 (1979).
[8]P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, *ibid.* 140, A 1133 (1965).
[9]J. K. Percus, in *The Equilibrium Theory of Classical Fluids,* edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), p. II-33.
[10]J. Chihara, Prog. Theor. Phys. 59, 76 (1978).
[11]S. Chakravarty and N. W. Ashcroft, Phys. Rev. B 18, 4588 (1978).
[12]The numerical computations of the multiple integrals involved in (12) may be facilitated by expanding $h(|\vec{r}-\vec{r}'|)$, etc., in the Legendre polynomials. With the aid of the addition theorem, Eq. (12) reduces to a form involving double integrations with respect to r' and r'' only; those double integrations may be easily evaluated numerically.
[13]The first term on the right-hand side is evaluated on the basis of the ion-sphere model. See, e.g., E. E. Salpeter, Aust. J. Phys. 7, 373 (1954).