Length-scale analysis of the coefficient of the square-gradient term in the density-functional expansion for nonuniform classical plasmas

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(Received 2 June 1988)

The coefficient of the square-gradient term, given by the second moment of the direct correlation function, is determined by *three* different length-scale parameters, each dominating a different range of the plasma coupling parameter Γ. It is the interplay between the relative contributions of these scales that provides the full form of the square-gradient term as a function of Γ.

The one-component plasma (OCP) consisting of point ions in a rigid, neutralizing, charge background, provides a highly idealized, yet useful reference point of description for some realistic systems.[1] Bulk properties of the OCP have been intensively studied,[1] and increasing attention has been given recently to its surface properties.[2] Several theoretical investigations of the OCP surface have been based on the density-functional formalism in the square-gradient approximation.[3–8] Since accurate computer-simulation data for the free-energy density of the bulk OCP are available,[1] the accuracy of these calculations of the surface density profiles and surface energy strongly depends on the employed coefficient of the square-gradient term, given by[9] the second moment of the bulk direct correlation function, $c(r)$:

$$G_2(\rho)=(k_BT/12)\int d^3r\, r^2[c(r)+(Ze)^2/rk_BT] \ . \qquad (1)$$

Using the ion-sphere radius $a=(3/4\pi\rho)^{1/3}$ as the unit of length, define the plasma parameter $\Gamma=(Ze)^2/ak_BT$ and the reduced length $x=r/a$, the coefficient takes the form[8]

$$G_2(\rho)=[(Ze)^2/528]a\rho^{-1}Y(\Gamma) \ , \qquad (2)$$

where

$$Y(\Gamma)=(132/\Gamma)\int_0^\infty x^4[c(x;\Gamma)+\Gamma/x]dx \ . \qquad (3)$$

The bulk OCP direct correlation function $c(x)$ is *not* directly accessible to computer simulations. The proper way to obtain it from the simulation data for the pair correlation function, $g(r)=h(r)+1$, is via a solution of the *inverse scattering problem* aimed at obtaining the bridge function.[10–12]

The sensitivity of $Y(\Gamma)$, and of the resulting density-functional calculations of the surface, to different model direct correlation functions was critically examined recently by Hasegawa and Watabe[8] (hereafter referred to as HW). The main finding in HW was that $Y(\Gamma)$ as obtained from the modified-hypernetted chain (MHNC) approximation[10] for $c(r)$ is quite different from that previously obtained from the mean-spherical approximation (MSA),[13] and the scaling model[14,15] for $c(r)$. When the MHNC results for the square-gradient term are used in the variational calculations for the surface density profile and surface energy, better agreement with the Monte Carlo results is obtained. Figure 1, following HW, com-

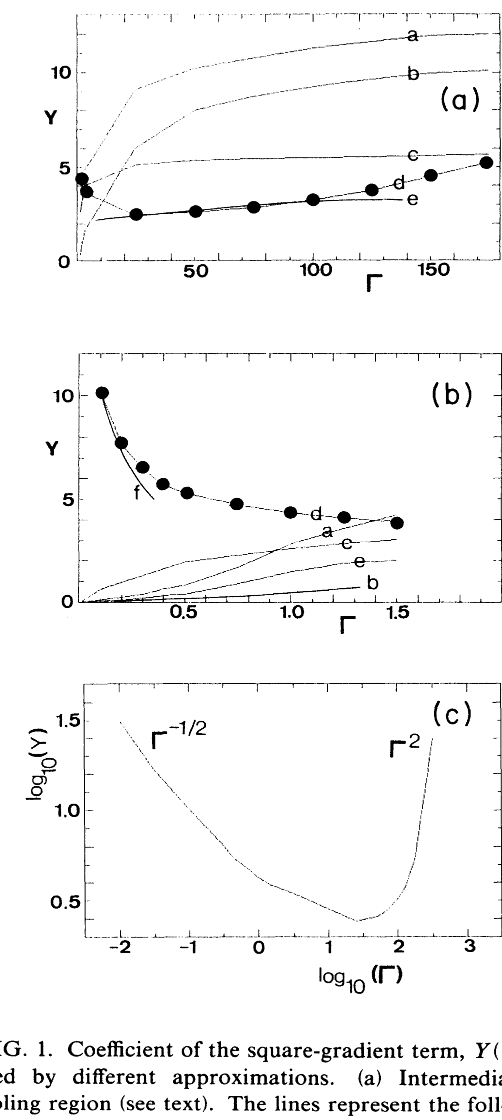

FIG. 1. Coefficient of the square-gradient term, $Y(\Gamma)$, as obtained by different approximations. (a) Intermediate-strong coupling region (see text). The lines represent the following: *a*, scaling model, Eq. (21), for the HNC approximation; *b*, mean-spherical model; *c*, the Baus-Hansen (BH) scaling model; *d*, modified-HNC results of Hasegawa and Watabe; *e*, scaling model, Eq. (25), for the modified-HNC approximation. (b) weak coupling region, see legend to (a). *f* represents Eq. (7). (c) schematic, semiquantitative, general behavior of the exact $Y(\Gamma)$, emphasizing the asymptotic behaviors (8) and (12).

pares $Y(\Gamma)$ as obtained from different approximation schemes.

In view of the central role played by the coefficient of the square-gradient term in the theory of nonuniform fluids, we seek a comprehensive understanding of the shape and values of $Y(\Gamma)$. In particular, we reconsider the analysis in HW in light of some recent developments in the theory of dense fluids and plasmas.[12,16,17]

The weak coupling limit of the small-k expansion of the structure factor[1] $S(k)=1-\rho c(K)$, $k^2/S(k)=3\Gamma+\chi k^2+a_1k^4+a_2k^6+\ldots$, was considered by Deutch *et al.*,[18] where

$$a_1=\frac{1}{2}\int_0^\infty x^4[c(x)+\Gamma/x]dx \tag{4}$$

and $\chi=(K_BT)^{-1}(\partial p/\partial\rho)_T$ is the inverse compressibility, given by

$$\chi=1+\chi^{\text{ex}}=1-3\int_0^\infty x^2[c(x)+\Gamma/x]dx\ . \tag{5}$$

This equation also defines χ^{ex}. Define[18] $\lambda=3^{1/2}\Gamma^{3/2}$ and $B(\lambda)=3\Gamma a_1/\lambda$, then comparing (4) with (3) obtain $Y(\Gamma)=264a_1/\Gamma=264B(\lambda)/(3\Gamma)^{1/2}$. As analyzed in Ref. 10, the results of Ref. 18 are equivalent to an analytic treatment to the second iteration in the solution of the HNC equation. Using[10,18] $B(\lambda)=\frac{1}{48}-\lambda/6\times54+\ldots$ we finally get

$$Y(\Gamma)=[264/(3\Gamma)^{1/2}](\tfrac{1}{48}-\lambda/6\times54+3\Gamma^3/6\times96+\ldots) \tag{6}$$

with the leading small-Γ term

$$Y(\Gamma)_{\Gamma\ll1}=\tfrac{264}{48}(3\Gamma)^{1/2}\sim3.1754\Gamma^{-1/2}\ . \tag{7}$$

This is the exact leading term in the small-Γ expansion of $Y(\Gamma)$. It is obviously a "tail" contribution resulting from $c(x)+\Gamma/x\sim h^2(x)/2\sim A(\Gamma e^{(x/\tau)}/x)^2$, where the "decay length" τ is equal to the Debye length, $\tau=\Gamma/\lambda=(3\Gamma)^{-1/2}$. This gives rise to a contribution of the type

$$Y(\Gamma)_{\text{tail weak coupling}}=Y_0\Gamma\tau^3\sim\Gamma^{-1/2}\ , \tag{8}$$

where Y_0 is a slowly varying function of Γ.

It should be noted[10] that the expansion (6) deviates by about 10% from the full solution of the HNC equation already at $\Gamma=0.2$, i.e., it gives $a_1=0.005\,27$ while the full HNC result is $a_1=0.005\,71$, yet the leading term (7) gives $a_1=0.005\,38$.

The Debye-Huckel result of HW for the weak coupling term is $Y(\Gamma)=2.3168\Gamma^{-1/2}$ which is about 30% smaller than (7). Their fit to the MHNC numerical results begins with the term $4.4405\Gamma^{-1/2}$, but this is due to their choice of fitting function in the coupling range $\Gamma>0.02$.

From the analysis of the asymptotic strong coupling properties of the HNC integral equation[16] we find that the leading contribution to $Y(\Gamma)$ comes from the long-range oscillatory behavior of $c(x)+\Gamma/x\sim h^2(x)/2$. It was found[16] that $h(x)$ can be expressed in the form

$$h(x)=\sum_{j=1}^{\infty}A_je^{-\alpha_jx}\sin(\beta_j+\theta_j)/x\ , \tag{9}$$

where the inverse decay-length parameters have the property

$$\alpha_j\sim1/\Gamma\ \text{for}\ \Gamma\gg1\ . \tag{10}$$

Following the analysis of Ref. 16 we obtain

$$\begin{aligned}Y(\Gamma\gg1)&\sim(132/\Gamma)\int^\infty dx\,h^2(x)/2\\&\sim(64/3\Gamma)(3/16)\sum_{j=1}^{\infty}A_j^2/\alpha_j^3\\&\sim[(8A)_1/(\alpha_1\Gamma)^3]\Gamma^2\sim10^{-6}\Gamma^2\ .\end{aligned} \tag{11}$$

In analogy with (8) we now have

$$Y(\Gamma)_{\text{tail strong coupling}}=Y_1\tau^3/\Gamma\sim\Gamma^2\ , \tag{12}$$

where $\tau\sim\alpha^{-1}\sim\Gamma$ is the decay length of the oscillations, and Y_1 is a relatively slowly varying function of Γ.

Examining the numerical values of A_1 and α_1 in Ref. 16 we find that A_1 varies relatively slowly with Γ while $\alpha_1\Gamma$ decreases from about 440 at $\Gamma\to\infty$ to about 80 for Γ around 200. In the region of $\Gamma\sim200$ we estimate the long-range contribution to $Y(\Gamma)$ by $10^{-4}\Gamma^2/5$ (i.e., 0.8 for $\Gamma=200$). This contribution decreases as Γ is further decreased.

A major feature of both the HNC and MSA approximations for the OCP, is the saturation property of $c(x;\Gamma)/\Gamma$. This ratio changes relatively slowly in the range $\Gamma>1$ and saturates in the limit $\Gamma\to\infty$: $[c(x;\Gamma)/\Gamma]_{\Gamma\to\infty}\to\Psi(x)$. The function $\Psi(x)$ has the property $\Psi(x\geq x_\infty)=-1/x$, where $x_\infty=2$ is the asymptotic pair exclusion diameter, corresponding to two impenetrable hard spheres of radius equal to the ion-sphere radius, a. For both the MSA and HNC, $\Psi(x)$ is the electrostatic interaction between two uniformly charged spheres of the unit radius and unit total charge. The saturation property combined with the correlation-hole effect of pair exclusion prompted scaling models for the OCP direct correlation function, which are based on the MSA-type form:

$$c(x)=(\Gamma/x_0)\psi(x/x_0)\ , \tag{13a}$$

$$\psi(y)=-1/y\quad\text{for}\ y>1\ , \tag{13b}$$

with x_0 playing the role of an effective hard-core diameter.

Defining the Ewald function $f(x)$ (see Ref. 16)

$$f(y)=[\psi(y)+y\psi'(y)]/\psi(0) \tag{14}$$

with the property $f(0)=1$ and $f(y\geq1)=0$, we insert (13) into (3) and (5) to obtain

$$Y_{\text{scaling}}=-\tfrac{132}{4}\psi(0)c_4x_0^4\sim\text{const}\times x_0^4\ , \tag{15}$$

$$\chi^{\text{ex}}_{\text{scaling}}/\Gamma=\tfrac{3}{2}\psi(0)c_2x_0^2\ , \tag{16}$$

where the constants c_k are given by

$$c_k=\int_0^1z^kf(z)dz\ . \tag{17}$$

Combining (15) and (16), and denoting by ξ and δ the $\Gamma\to\infty$ limit of x_0 and χ^{ex}/Γ, respectively, we obtain

$$Y(\Gamma)_{\text{scaling}} = Y^{\infty}_{\text{scaling}}(\chi^{\text{ex}}/\delta\Gamma)^2 \sim \text{const}[x_0(\Gamma)/\xi]^4 , \quad (18)$$

where the saturation value of Y_{scaling} is

$$Y^{\infty}_{\text{scaling}} = 132 \int_0^{\infty} y^4[\psi(y)+1/y]dy . \quad (19)$$

The length scale characterizing the scaling region of $Y(\Gamma)$ is the effective hard-core diameter, x_0, of the charges in the plasma. The value of $x_0(\Gamma)$ decreases with decreasing Γ, and $x_0(\Gamma=0)=0$, giving full account of the qualitative behavior of both the MSA and Baus and Hansen (BH) curves in Fig. 1.

The scaling model was introduced by Baus and Hansen[14] who modeled $c(x)$ by a polynomial in x^2 for $x < x_0$. It was subsequently analyzed in detail.[15,17] In particular it was found[16] that in order to mimic the HNC and MSA general behavior, the scaling function should be $\psi(y)=1\Psi(y)$, with $\xi = x_\infty = 2$, i.e.,

$$\begin{aligned} &f(z)=1-5z^2+5z^3-z^5, \quad z \le 1 , \\ &\psi(0)=2\times(-1.2)=-2.4 , \end{aligned} \quad (20)$$

giving $c_4=0.010714\ldots$ and $c_2=0.041666\ldots$. Combining (15) and (16) in view of (13) we get

$$Y(\Gamma)_{\text{scaling}} = 13.5777\ldots(\chi^{\text{ex}}/0.6\Gamma)^2 \quad (21)$$

which represents accurately the MSA results provided χ^{ex} is taken from the MSA compressibility equation of state. For large Γ, we have $(\chi^{\text{ex}})_{\text{MSA,HNC}} \to -0.6\Gamma$, i.e., $y_{\text{scaling}} \to 13.577\ldots$. Equation (21) also accounts correctly for the MSA behavior of $Y(\Gamma\to 0)=0$. This last feature contradicts the correct HNC behavior in the limit $\Gamma \to 0$, yet the MSA Y_{scaling} represents accurately the dominant contribution to $Y_{\text{HNC}}(\Gamma)$ in the intermediate-strong coupling region. The scaling function was chosen by Baus and Hansen[14] (BH) to fit better the computer-simulation results and as a consequence their values for Y_{scaling} are lower than the MSA Y_{scaling}. The BH results roughly correspond to (21) with χ^{ex} taken from simulations, thus lowering $Y(\Gamma \to \infty)$.

To summarize the results write the direct correlation functions in the form

$$c(x)=c(x)_{\text{scaling}}+c(x)_{\text{tail}} . \quad (22)$$

From the point of view of the second moment, the dominant tail contributions are given by (8) and (12) in the limits of weak and strong coupling, respectively, while the HNC scaling contribution is given by (21). Correspondingly we obtain

$$Y(\Gamma)=Y_{\text{scaling}}+Y_{\text{tail}} \quad (23)$$

with different tail contributions, (8) and (12), in the weak and strong coupling limits, respectively. Both weak and strong coupling limits are dominated by Y_{tail}, characterized by the decay-length parameter ($\tau \sim \Gamma^{-1/2}$ and $\tau \sim \Gamma$, respectively) while the intermediate region is dominated by Y_{scaling}, which is characterized by the hard-core length scale, x_0. This picture holds for both the HNC approximation, and the modified HNC with nonsingular bridge functions.

As pointed out by HW, the MSA and BY models feature only the scaling part, and as a result they provide only an estimate of the true behavior in the intermediate coupling region. Without taking into account the tail contributions, these models incorrectly predict a concave curve of $Y(\Gamma)$. Using (18) we can essentially reproduce the full MSA and BH calculations. Using (23) however, we obtain a good estimate of the full HNC calculation. The difference between the HNC and MHNC curves is only quantitative mainly due to the difference in the functions ψ of the scaling part, i.e., differences on the asymptotic direct correlation functions.

Very recently[12] it was found that the exact solution of the self-consistent MHNC with nonsingular bridge functions must feature the following asymptotic $\Gamma \to \infty$ direct correlation function:

$$\Psi_{\text{MHNC}}(x)=\Psi_{\text{HNC}}(x)-0.2\omega(x)/\omega(x=0) , \quad (24)$$

where $\omega(x)$ is the overlap volume of two unit spheres at distance x. Using (19) and (24) we obtain

$$Y(\Gamma)_{\text{MHNC, scaling}}=3.017\ldots(\chi^{\text{ex}}/0.4\Gamma)^2 \quad (25)$$

in agreement (see Fig. 1) with the numerical results of HW using the hard-sphere bridge functions.

This research was supported by The Fund for Basic Research administered by the Israel Academy of Science and Humanities.

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