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Lower Bounds for Correlation Energy of Mixtures of Charged Hard Spheres

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Synopsis

A method to obtain exact lower bounds for the correlation energy of one-component plasmas is extended to neutral mixtures of charged hard spheres. Upper bounds for the correlation functions of charge densities are derived. These upper bounds, the semi-positivity of correlation functions, and that of the charge-density-fluctuation spectrum are used to improve upon the known bound due to Onsager.

1. Introduction

It was shown [1,2] recently that exact lower bounds for the correlation energy of a one-component plasma (OCP) (a system of charged point particles in a uniform background) can be derived based on various semi-positivity conditions for the pair distribution function and the structure factor or, when Newton's theorem holds, based also on Mermin's inequality [3]. Exact lower bounds were given for systems in D-dimensional space with d-dimensional Coulomb interaction (the solution of Poisson's equation for a point source in d dimensions) where D=d=1, 2, and 3, and D=2 with d=3; this provided for the first time an exact lower bound in the last case [1] (where Newton's theorem does not hold), and gave improved lower bounds [4,5] in the domain of

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intermediate coupling in the other cases [1,2] (where Newton's theorem holds). The purpose of this paper is to extend these lower bounds to neutral mixtures of charged hard spheres with the same dimensionalities as in the case of OCP's. We also show that another (but weaker) exact lower bound can be derived for the correlation energy of OCP with D=2 and d=3 by modifying the method [4] used for D=d. Our results are based on the bounds for the charge-density correlation function and the semi-positivity of the charge-density-fluctuation spectrum, and therefore apply to all permissible configurations.

The method is described generally in Section 2, and the results for three-dimensional hard spheres are shown in Section 3. Upper bounds for the correlation function of charge densities of hard spheres are given in Appendix A. The lower bound for OCP with D=2 and d=3 is revisited in Appendix B.

2. Method

We consider a classical system of charged hard spheres in a volume V in D dimensions [6] consisting of species $\alpha=1,2,\ldots,s$. These interact via the d-dimensional Coulomb potential [2] $e_\alpha e_\beta \phi_d(r)$

$$\phi_d(r) = \begin{cases} r^{2-d}/(d-2) & d\neq 2 \\ -\ell n(r/\ell) & d=2 \end{cases} \tag{2.1}$$

where e_α denotes the charge of a sphere of species α and the zero of the potential is taken at $r=\ell$ for d=2. We denote the number, the number density, and the diameter of species α by N_α, $n_\alpha=N_\alpha/V$, and σ_α, and assume that the charge e_α is distributed according to a spherically symmetric D-dimensional density function $\Delta^\alpha(r)$ satisfying

$$\begin{aligned} &\Delta^\alpha(r) \geq 0, && r \leq \sigma_\alpha/2, \\ &\Delta^\alpha(r) = 0, && r > \sigma_\alpha/2, \\ &\int d^D r \Delta^\alpha(r) = 1, \end{aligned} \tag{2.2}$$

where $d^D r$ is the D-dimensional volume element.

In the case where $\sigma_\alpha > 0$ for some α, we assume no uniform background. The potential energy of our system in a given configuration does not therefore depend on the function $\Delta^\alpha(r)$ (due to Newton's theorem), and we can use these functions as a part of variational parameters in deriving bounds for the potential energy.

We also assume that our system is electrically neutral

$$\sum_\alpha n_\alpha e_\alpha + \rho_b = 0, \tag{2.3}$$

where ρ_b is the charge density of the uniform background.

We define the microscopic correlation function of the number densities of centers of species α and β, $h_{cc}^{\alpha\beta}(\underset{\sim}{r})$, by

$$\begin{aligned} n_\alpha n_\beta [h_{cc}^{\alpha\beta}(\underset{\sim}{r})+1] = \frac{1}{V}\int_V d^D r' \{ & \sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta} \delta[\underset{\sim}{r}+\underset{\sim}{r}'-\underset{\sim}{r}_{(i,\alpha)}]\delta[\underset{\sim}{r}'-\underset{\sim}{r}_{(j,\beta)}] \\ & -\delta_{\alpha\beta}\delta(\underset{\sim}{r})\sum_{i=1}^{N_\alpha}\delta[\underset{\sim}{r}'-\underset{\sim}{r}_{(i,\alpha)}]\} \end{aligned} \tag{2.4}$$

where $\underset{\sim}{r}_{(i,\alpha)}$ is the position of the center of the sphere i of species α, and note that

$$h_{cc}^{\alpha\beta}(\underset{\sim}{r}) + 1 \geq 0. \tag{2.5}$$

When $\rho_b \neq 0$, we define $h_{cc}^{\alpha\beta}(\underset{\sim}{r})$ as the infinite volume limit, $V \to \infty$, $N_\alpha \to \infty$, $n_\alpha = N_\alpha/V$=constant, of Eq.(2.4). We assume in this case [7] that

$$\lim_{V\to\infty} \frac{1}{V}\int_V d^D r' \sum_{i=1}^{N_\alpha} \delta[\underset{\sim}{r} + \underset{\sim}{r}' - \underset{\sim}{r}_{(i,\alpha)}]\chi(\underset{\sim}{r}') = n_\alpha, \tag{2.6}$$

where $\chi(\underset{\sim}{r})$ is the characteristic function of the volume V. We have therefore

$$\begin{aligned} n_\alpha n_\beta h_{cc}^{\alpha\beta}(\underset{\sim}{r}) = \lim_{V\to\infty} \frac{1}{V}\int_V d^D r' \{ & \{ \sum_{i=1}^{N_\alpha} \delta[\underset{\sim}{r} + \underset{\sim}{r}' - \underset{\sim}{r}_{(i,\alpha)}] - n_\alpha \chi(\underset{\sim}{r} + \underset{\sim}{r}')\} \\ & \times \{ \sum_{j=1}^{N_\beta} \delta[\underset{\sim}{r}'-\underset{\sim}{r}_{(j,\beta)}] - n_\beta \chi(\underset{\sim}{r}')\} - \delta_{\alpha\beta}\delta(\underset{\sim}{r}) \sum_{i=1}^{N_\alpha}\delta[\underset{\sim}{r}'-\underset{\sim}{r}_{(i,\alpha)}]\}. \end{aligned} \tag{2.7}$$

The correlation function of the number density of centers of spheres α and the charge density of spheres β, $e_\beta n_\alpha n_\beta h_{cd}^{\alpha\beta}(\underset{\sim}{r})$, and that of charge densities of spheres α and β, $e_\alpha e_\beta n_\alpha n_\beta h_{dd}^{\alpha\beta}(\underset{\sim}{r})$, are related to $h_{cc}^{\alpha\beta}(\underset{\sim}{r})$ as

$$h_{cd}^{\alpha\beta}(\underset{\sim}{r}) = \int d^D r' h_{cc}^{\alpha\beta}(\underset{\sim}{r}-\underset{\sim}{r}')\Delta^\beta(r'), \tag{2.8}$$

$$h_{dd}^{\alpha\beta}(\underset{\sim}{r}) = \int d^D r' \Delta^\alpha(r') h_{cd}^{\alpha\beta}(\underset{\sim}{r}-\underset{\sim}{r}'). \tag{2.9}$$

We express the center-center distribution function $h_{cc}^{\alpha\beta}(\underset{\sim}{r})$ using the microscopic fluctuation spectrum $S^{\alpha\beta}(\underset{\sim}{k})$ of the distribution of centers defined by

$$S^{\alpha\beta}(\underset{\sim}{k}) = \rho_{\underset{\sim}{k}}^\alpha \rho_{-\underset{\sim}{k}}^\beta / \sqrt{N_\alpha N_\beta}, \tag{2.10}$$

$$\rho_{\underset{\sim}{k}}^\alpha = \sum_{i=1}^{N_\alpha} \exp[-i\underset{\sim}{k}\cdot\underset{\sim}{r}_{(i,\alpha)}] - \theta(|\rho_b|) n_\alpha \int d^D r\, e^{-\underset{\sim}{k}\cdot\underset{\sim}{r}} \chi(\underset{\sim}{r}) \tag{2.11}$$

as

$$\sqrt{n_\alpha n_\beta}[h_{cc}^{\alpha\beta}(\underset{\sim}{r})+1] = (2\pi)^{-D}\int d^D k\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}[S^{\alpha\beta}(\underset{\sim}{k})-\delta_{\alpha\beta}+\theta(|\rho_b|)(2\pi)^D\delta(\underset{\sim}{k})], \tag{2.12}$$

where $\theta(x)$ is the unit step function. We denote the lower bound for the fluctuation spectrum of total charge density by $\underline{S}$

$$\sum_{\alpha,\beta} e_\alpha e_\beta \sqrt{n_\alpha n_\beta}\Delta^\alpha(k) S^{\alpha\beta}(\underset{\sim}{k})\Delta^\beta(k) \geq \underline{S}, \tag{2.13}$$

where $\Delta^\alpha(k)$ is the Fourier transform of the function $\Delta^\alpha(r)$. Since the left-hand side of Eq.(2.13) can be rewritten as $|\sum_\alpha e_\alpha \rho_{\underset{\sim}{k}}^\alpha|^2/V$, we have

$$\underline{S} \geq 0. \tag{2.14}$$

A positive bound $\underline{S} > 0$ can be derived for the case of D=d and $\sigma_\alpha=0$, $\alpha=1,2,\ldots,s$.

We note that $h_{cc}^{\alpha\beta}(\underset{\sim}{r})$ and $S^{\alpha\beta}(\underset{\sim}{k})$ are defined by Eqs.(2.4) and (2.10) for any permissible configuration without thermal averaging.

The potential energy per particle e_c is given by

$$e_c = \frac{1}{2n}\int d^D r \sum_{\alpha,\beta} e_\alpha e_\beta n_\alpha n_\beta h_{dd}^{\alpha\beta}(\underset{\sim}{r})\phi_d(r), \tag{2.15}$$

where

$$n = \sum_\alpha n_\alpha. \tag{2.16}$$

Since the interaction potential $\phi_d(r)$ is spherically symmetric, we use, in the calculation of the potential energy, spherically symmetric functions $h_{dd}^{\alpha\beta}(r)$, $h_{cd}^{\alpha\beta}(r)$, and $h_{cc}^{\alpha\beta}(r)$ which are defined as the average over angles of the corresponding expressions defined earlier. In Fourier space, the potential $\phi_d(r)$ is expressed as [2]

$$\phi_d(r) = (2\pi)^{-D}\int d^D k \phi_{Dd}(k)\left[\exp(i\underset{\sim}{k}\cdot\underset{\sim}{r}) - \begin{cases} \theta(2-d) & d\neq 2 \\ \exp(i\underset{\sim}{k}\cdot\underset{\sim}{\ell}) & d=2 \end{cases}\right] \tag{2.17}$$

where

$$\phi_{dd}(k) = 2\pi^{d/2}\Gamma(d/2)^{-1}k^{-2} \qquad d=1,\ 2,\ \text{and}\ 3 \tag{2.18}$$

or

$$\phi_{D3}(k) = (2\pi^{1/2})^{D-1}\Gamma\left(\frac{D-1}{2}\right)k^{1-D} \qquad D=2,\ \text{and}\ 3 \tag{2.19}$$

and $\underset{\sim}{\ell}$ is a vector of length ℓ. Using the relations (2.12), (2.15), and (2.17), we rewrite e_c as

$$e_c = \frac{1}{2}(2\pi)^{-D}\int d^D k \phi_{Dd}(k)\left[\sum_{\alpha,\beta} e_\alpha e_\beta (\sqrt{n_\alpha n_\beta}/n)\Delta^\alpha(k) S^{\alpha\beta}(\underset{\sim}{k})\Delta^\beta(k) - \overline{e^2|\Delta(k)|^2} + \overline{e^2}\begin{cases} \theta(2-d) & d\neq 2 \\ \exp(i\underset{\sim}{k}\cdot\underset{\sim}{\ell}) & d=2 \end{cases}\right], \tag{2.20}$$

where $\overline{Q}$ is defined by

$$\overline{Q} = \sum_\alpha n_\alpha Q_\alpha / n. \tag{2.21}$$

When Eq. (2.13) with $\underline{S}=0$ is substituted into Eq. (2.20), we have an exact lower bounds for e_c in the case of D=d as

$$e_c \geq B_0 = \frac{1}{2}(2\pi)^{-d}\int d^d k \phi_{Dd}(k)\left[-\overline{e^2|\Delta(k)|^2} + \overline{e^2}\begin{cases} \theta(2-d) & d\neq 2 \\ \exp(i\underset{\sim}{k}\cdot\underset{\sim}{\ell}) & d=2 \end{cases}\right]. \tag{2.22}$$

(In the case of D=2 with d=3, the right-hand side is $-\infty$.) This bound is equal to -(self energy of charged spheres), and for given values of e_α, n_α, and σ_α, its maximum is attained when charges are distributed on surfaces as

$$\begin{cases} \Delta^\alpha(r) = (2\pi^{d/2})^{-1}\Gamma(d/2)(\sigma_\alpha/2)^{1-d}\delta(r-\sigma_\alpha/2) \\ \\ \Delta^\alpha(k) = \Gamma(d/2)(k\sigma_\alpha/4)^{1-d/2}J_{d/2-1}(k\sigma_\alpha/2) \end{cases} \tag{2.23}$$

$$\text{Max } B_0 = \begin{cases} \frac{1}{4}\overline{e^2\sigma} & D=d=1 \\ \\ 0 & D=d=2 \\ \\ -\overline{(e^2/\sigma)} & D=d=3, \end{cases} \tag{2.24}$$

where $J_n(x)$ is the Bessel function of n-th order. The lower bound (2.24) was derived by Onsager [3] for the case of D=d=3.

In deriving Onsager's lower bound, we used only the semi-positivity of the charge density fluctuation spectrum (2.14). If other information on the correlation functions is used at the same time, it is possible to obtain improved lower bound for the correlation energy.

We note here that the correlation function of charge densities is semi-positive and, in the case of hard spheres, it is also bounded from above by some finite function due to inpenetrability of hard spheres;

$$h_{dd}^{\alpha\beta}(r) + 1 \geq 0, \tag{2.25}$$

$$h_{dd}^{\alpha\beta}(r) \leq H^{\alpha\beta}(r) < \infty. \tag{2.26}$$

The upper bound $H^{\alpha\beta}(r)$ is derived in Appendix A.

In order to use the above information in the calculation of lower bounds, we rewrite the interaction potential as [1,2]

$$\phi_d(r) = \int_0^\infty dtf(r,t) = (\int_0^G + \int_G^\infty) dtf(r,t), \qquad G \geq 0, \tag{2.27}$$

and obtain a hybrid-type expression for the potential energy

$$e_c = \frac{1}{2}(2\pi)^{-D}\int d^Dk\{\int_0^G dtf(k,t)[\sum_{\alpha,\beta} e_\alpha e_\beta(\sqrt{n_\alpha n_\beta}/n)\Delta^\alpha(k)S^{\alpha\beta}(\underset{\sim}{k})\Delta^\beta(k) - \overline{e^2|\Delta(k)|^2}]$$

$$+ \overline{e^2}\phi_{Dd}(k)\begin{Bmatrix}\theta(2-d)\\ \exp(i\underset{\sim}{k}\cdot\underset{\sim}{\ell})\end{Bmatrix}\} + \frac{1}{2n}\int d^Dr\int_G^\infty dtf(r,t)\sum_{\alpha,\beta} e_\alpha e_\beta n_\alpha n_\beta h_{dd}^{\alpha\beta}(r), \tag{2.23}$$

where $f(k,t)$ is the Fourier transform of the function $f(r,t)$. Choosing f so that

$$f(r,t) \geq 0 \qquad \text{and} \qquad f(k,t) \geq 0, \tag{2.29}$$

and using Eq.(2.14), Eq.(2.25) for the pair $e_\alpha e_\beta > 0$, and Eq.(2.26) for the pair $e_\alpha e_\beta < 0$, we have

$$e_c \geq B_1 = -\frac{1}{2}(2\pi)^{-D}\int d^Dk\{\int_0^G dtf(k,t)[\overline{e^2|\Delta(k)|^2} - \underline{S}/n] - \phi_{Dd}(k)\begin{Bmatrix}\theta(2-d)\\ e^{i\underset{\sim}{k}\cdot\underset{\sim}{\ell}}\end{Bmatrix}\}$$

$$-\frac{1}{2n}\int_G^\infty dtf(k=0,t)\sum_{\substack{\alpha,\beta\\ e_\alpha e_\beta>0}} e_\alpha e_\beta n_\alpha n_\beta + \frac{1}{2n}\int d^Dr\int_G^\infty dtf(r,t)\sum_{\substack{\alpha,\beta\\ e_\alpha e_\beta<0}} e_\alpha e_\beta n_\alpha n_\beta H^{\alpha\beta}(r). \tag{2.30}$$

We optimize the value of B_1 with respect to the variational parameters $f(r,t)$, $\Delta^\alpha(r)$, and G. Onsager's bound [8] is reproduced by taking $\Delta^\alpha(r)$=(surface distribution on the hard sphere α) and $G=\infty$.

3. Charged Hard Spheres

Here we consider some examples of the lower bound (2.30) for the system of charged hard spheres with D=d=3 and compare the results with Onsager's bound [8] and with analytical results of the mean spherical approximation (MSA) [9,10,11].

3.1 Symmetrical Binary Mixture ($s=2$, $\sigma_1=\sigma_2=\sigma$, $e_1=-e_2=e$, $\rho_b=0$)

When we take as $\Delta^\alpha(r)$ the distribution on the surface of a sphere which is concentric with and included within the hard sphere α,

$$\Delta^\alpha(r) = \frac{1}{\pi\sigma_\alpha'}\delta(r-\sigma_\alpha'/2), \qquad \sigma_\alpha' \leq \sigma_\alpha \tag{3.1}$$

we find that, within some simple functions satisfying (2.29) [12],

$$f(r,t) = 2\pi^{-1/2}\exp(-r^2t^2) \tag{3.2}$$

gives the best bound

$$e_c \geq -0.960e^2/\sigma \tag{3.3}$$

which improves Onsager's bound [8] $-e^2/\sigma$ by 4.0%. We also tried the uniform (solid) distribution as $\Delta^\alpha(r)$ but the result is weaker than Onsager's bound [8] within the same trial functions for $f(r,t)$.

We note that since the lowest correlation energy of crystalline structure given by the NaCl structure is

$$[e_c]_{NaCl} = -0.87378e^2/\sigma, \tag{3.4}$$

our result on the ground state energy improves by 32% of the possible room for improvements.

In the mean spherical approximation [9,10], the correlation energy is given by

$$e_c = -\frac{e^2}{\sigma} + \frac{xT}{4\pi n\sigma^3}[(1+2x)^{1/2}-1] \tag{3.5}$$

$$x = (4\pi ne^2/T)^{1/2}\sigma, \tag{3.6}$$

where T denotes the temperature ($k_B=1$). The MSA values satisfy our bound (3.3) except when $x \geq 1.20\cdot 10^3$ which corresponds to a very low temperature or very high density.

3.2 Asymmetric Binary Mixture in Three Dimensions ($s=2$, $\sigma_1 > \sigma_2$, $e_1=-e_2=e$, $n_1=n_2=n/2$, $\rho_b=0$)

When there is a component with a large value of the self energy e^2_α/σ_α, Onsager's bound (2.24) is deteriorated by the contribution of that component.

We here consider the case of asymmetry in diameters, $\sigma_1 >> \sigma_2$. Since the minimum distance between opposite charges is $(\sigma_1 + \sigma_2)/2$, the ground state energy may be roughly proportional to $-e^2/(\sigma_1+\sigma_2) \sim -e^2/\sigma_1$, instead of $-e^2(1/\sigma_1+1/\sigma_2) \sim -e^2/\sigma_2$ as in Onsager's bound [8].

Our lower bound (2.30) gives the values proportional to $-(e^2/\sigma_1)[\ell n(\sigma_1/\sigma_2)]^{1/2}$ when $\sigma_1 >> \sigma_2$. Though our bound also diverges to $-\infty$ when σ_2 goes to zero, it gives improved values upon Onsager's bound which diverges more strongly. Some numerical examples are shown in Table together with the symmetric case. Surface distributions and (3.2) are used for $\Delta^\alpha(r)$ and $f(r,t)$ after some trials within the same possibilities as the case of symmetric mixture. As is also shown in Table, the MSA values satisfy our bounds except for the domain of low temperature or high density where the Debye length $(T/4\pi ne^2)^{1/2}$ is much smaller than the hard sphere radius.

Table. Lower Bounds for Correlation Energy of Charged Hard Spheres

	$n_1=n_2=n/2$, $e_1=-e_2=e$			
	$\sigma_1/\sigma_2=1.0$	5.0	10.0	100.0
Present Result $e_c/(e^2/\sigma_1) \geq$	-0.960	-2.16	-2.68	-3.65
Onsager [8] $e_c/(e^2/\sigma_1) \geq$	-1.0	-3.0	-5.5	-50.5
MSA satisfies our bound when $(4\pi ne^2/T)^{1/2}\sigma_1 \geq$	$1.20\cdot10^3$	$9.2\cdot10^*$	$4.1\cdot10^*$	$2.1\cdot10^*$

* In these cases, the value depends slightly on the packing fraction $(\pi/6)n\sigma_1^3$.

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Appendix A. Upper Bounds for the Correlation Function of Charge Densities of Hard Spheres

We describe here a derivation of upper bounds for the correlation function of charge densities in the three-dimensional system of charged hard spheres. We assume that the charges are distributed isotropically on the surface of a sphere with diameter σ_α' which is concentric with and included inside the hard sphere S_α; $\sigma_\alpha' \leq \sigma_\alpha$. We denote the charged sphere of radius $\sigma_\alpha'/2$ by S_α'.

When the center of S_α is fixed at the origin, $h_{cd}^{\alpha\beta}(r)+1$ is given by the average of the surface charge on the imaginary sphere $S(r)$ of radius r (centered at the origin) contributed by S_β' included in S_β surrounding S_α.

We here note that the contribution of S_β' with the center at r' to the surface charge on $S(r)$ is (when there is an intersection) given by

$$e_\beta r/\sigma_\beta' r'. \tag{A.1}$$

Obviously,

$$h_{cd}^{\alpha\beta}(r) = -1 \qquad \text{for} \qquad r \leq (\sigma_\alpha + \sigma_\beta - \sigma_\beta')/2 \tag{A.2}$$

For $r \geq (\sigma_\alpha+\sigma_\beta-\sigma_\beta')/2$, we use the smaller of the following two upper bounds for $h_{cd}^{\alpha\beta}(r)$, (A.3) or (A.8).

Since the total volume of spheres S_β whose charged spheres S_β' really intersect $S(r)$ is smaller than the volume of the domain such that a sphere S_β which is included within the domain can contribute

to the surface charge on S(r), we have

$$0 \leq n_\beta[h_{cd}^{\alpha\beta}(r)+1] \leq \begin{cases} \dfrac{1}{4\pi r^2\sigma_\beta'}\dfrac{2r}{\sigma_\alpha+\sigma_\beta}\dfrac{(2r+\sigma_\beta+\sigma_\beta')^3-\sigma_\alpha^3}{\sigma_\beta^3}, \\ \qquad (\sigma_\alpha+\sigma_\beta-\sigma_\beta')/2 \leq r \leq (\sigma_\alpha+\sigma_\beta+\sigma_\beta')/2, \\ \dfrac{1}{4\pi r^2\sigma_\beta'}\dfrac{2r}{2r-\sigma_\beta'}\dfrac{(2r+\sigma_\beta+\sigma_\beta')^3-(2r-\sigma_\beta-\sigma_\beta')^3}{\sigma_\beta^3}, \\ \qquad (\sigma_\alpha+\sigma_\beta+\sigma_\beta')/2 \leq r. \end{cases} \tag{A.3}$$

Here we used (A.1).

For any configuration of spheres around a spheres S_α, there is no overlap of the traces of S_β, on the surface of S(r). We can thus divide the surface of S(r) so that each domain includes one intersection. Denoting the surface area of the domain attached to the i-th intersection by A_i, we have

$$0 \leq n_\beta[h_{cd}^{\alpha\beta}(r)+1] = \sum_i \frac{r}{\sigma_\beta' r_i} \Big/ \sum A_i \leq \max_i \left(\frac{r}{\sigma_\beta' r_i A_i}\right). \tag{A.4}$$

Here r_i is the radial distance of the center of the sphere S_β (S_β') giving i-th intersection. When

$$r_i \leq [(\sigma_\alpha+\sigma_\beta)^2-\sigma_\beta^2]^{1/2}/2+3^{1/2}\sigma_\beta/2, \tag{A.5}$$

we can attach, to the i-th intersection, an area of at least $A_0(r,r_i) = r^2\times$ (minimum solid angle of seeing directly from the origin the sphere S_β, giving i-th intersection without being blocked by other spheres S_β), or

$$A_0(r,r_i) = 2\pi r^2\left\{1-[2/(\sigma_\alpha+\sigma_\beta)^2 r_i]\left[[(\sigma_\alpha+\sigma_\beta)^2-\sigma_\beta^2]^{1/2}[(\sigma_\alpha+\sigma_\beta)^2/4+r_i^2-\sigma_\beta^2]/2\right.\right.$$

$$\left.\left.+\{(\sigma_\alpha+\sigma_\beta)^2\sigma_\beta^2 r_i^2/4 - \sigma_\beta^2[(\sigma_\alpha+\sigma_\beta)^2/4+r_i^2-\sigma_\beta^2]^2/4\}^{1/2}\right)\right\}. \tag{A.6}$$

Combining Eqs.(A.4) and (A.6) and noting

$$\underset{r'}{\mathrm{Max}}[r/\sigma_\beta' r' A_0(r,r')] = r/\sigma_\beta'(r+\sigma_\beta'/2)A_0(r,r+\sigma_\beta'/2), \tag{A.7}$$

we have

$$0 \leq n_\beta[h_{cd}^{\alpha\beta}(r)+1] \leq r/\sigma_\beta'(r+\sigma_\beta'/2)A_0(r,r+\sigma_\beta'/2). \tag{A.8}$$

From Eqs.(A.2), (A.3), and (A.8) and the relation

$$h_{dd}^{\alpha\beta}(r)+1 = \frac{1}{\sigma_\alpha' r}\int_{|r-\sigma_\alpha'/2|}^{r+\sigma_\alpha'/2} dr' r'[h_{cd}^{\alpha\beta}(r')+1], \tag{A.9}$$

we obtain upper bounds for the correlation function of charge densities.

Appendix B. A Lower Bound for the Correlation Energy of Two-Dimensional One-Component Plasmas with Three-Dimensional Coulomb Interaction

We consider a system composed of point charges e confined in the plane z=0 which is uniformly charged by opposite charges so as to satisfy the charge neutrality of the system. We use a two-dimensional version of the arguments on the correlation energy by Lieb and Narnhofer [4] for three-dimensional one-component plasmas, taking into account that Newton's theorem for our potential holds in three dimensions.

The total potential energy Ne_c of our system is given by

$$Ne_c = H_{pp}+H_{pb}+H_{bb}, \tag{B.1}$$

where H_{pp}, H_{pb}, and H_{bb} denote the potential energy between particles, that of particles and background, and the self energy of background, respectively.

We compare the potential energy of our system with that of a system where our point charges are replaced by uniformly charged

spheres (not discs) of radius r with their centers at the same positions. For the latter system, we have

$$Ne_c' = H_{pp}' + H_{pp}^{self} + H_{pb}' + H_{bb}' \geq 0, \tag{B.2}$$

where Ne_c', H_{pp}', H_{pb}', H_{pp}^{self}, and H_{bb}' $(=H_{bb})$ denote the total potential energy, the potential energy between different spheres, that of spheres and background, the self energy of spheres, and that of background, respectively.

Noting that

$$H_{pp} \geq H_{pp}' \tag{B.3}$$

and

$$H_{pb} = H_{pb}' + (3\pi/4)Ner\rho_b, \qquad H_{pp}^{self} = (3/5)Ne^2/r \tag{B.4}$$

we have

$$Ne_c \geq -H_{pp}^{self} + (3\pi/4)Ner\rho_b. \tag{B.5}$$

After optimizing with respect to the value of r, we obtain a lower bound for the correlation energy

$$e_c \geq -6(20)^{-1/2}e^2(\pi n)^{1/2} = -1.3416e^2(\pi n)^{1/2}. \tag{B.6}$$

This result is weaker than the previous result [1,13] which has been compared with numerical experiments [14,15].

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[6] The same results hold also in the case of periodic boundary condition. In this case, we include periodic images in the

density of centers of spheres or charges, change integrals over the wave number into summations over reciprocal lattice vectors and $-n_\alpha \int d^D r \exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r})\chi(\underset{\sim}{r})$ in Eq.(2.11) into $-N_\alpha \delta_{\underset{\sim}{k},0}$, and do not need $\lim_{V\to\infty}$ in Eqs.(2.4) and (2.7) nor the assumption (2.6); Eq.(2.7) holds automatically.

[7] In Refs.1 and 2, this assumption has been made implicitly.

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