Short-range screening potentials for classical Coulomb fluids: Reanalysis of Monte Carlo sampling and cluster model studies

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Results for the short-range screening potentials of classical Coulomb fluids, which were significantly different from existing theory and from earlier approaches, were obtained by Ichimaru *et al.* by their analyses of extra long simulations. In a recent paper [Phys. Rev E **50**, 2977 (1994)], Ichimaru, Ogata, and Tsuruta (IOT) summarize these results and attempt to support them with more simulations and with cluster model studies. In this paper I present an alternative analysis of the same data, which is in contradiction with the analyses of Ichimaru *et al.*, as portrayed by IOT. I present an analysis of general axially symmetric clusters that is different from that of IOT and provides insight into the short-range screening potentials of strongly coupled plasmas. In particular, I give an exact mathematical proof that questions the main conclusion of IOT from their culster model studies [their Eq. (49b)].

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I. INTRODUCTION

Classical plasmas, namely, positive ions in a uniform neutralizing background of electrons, make important basic models for dense stellar materials and provide a most useful reference system in condensed-matter physics [1]. The screening potential, the balance between the bare Coulomb repulsion and the potential of mean force [1,2], and in particular its behavior at short separation between the particles, plays an essential role in estimating the enhancement factors for the thermonuclear reaction rates, which are important for stellar evolution [1,2]. The screening potentials play a key role in the study of the short-range behavior of the bridge functions, notably their universal properties, which proved seminal for developing an accurate theory of liquid structure [3,4]. The zero separation theorem for the screening potentials [5–7] provides an important consistency test for approximate theories of the equation of state and of the structure of fluid mixtures [3,4].

In a continued large effort during recent years [2,8–11], Ichimaru *et al.* presented simulation data for the equation of state and pair correlation functions of dense plasma fluids, from which they derived different results [9,11] for the screening potentials that are significantly different from earlier results and from existing theory. The differences are numerically small but have important conceptual implications and lead to marked variations of the phase diagrams and of the enhancement factors. The data analysis methods employed by Ichimaru *et al.* were criticized, however, and it was argued [12,13] that the simulations of Ichimaru *et al.* actually do support the earlier results and the existing theory. In a recent paper, Ichimaru, Ogata, and Tsuruta (IOT) [14] summarized the results of Ichimaru *et al.* [2,8–11] on short-range screening potentials for fluid classical plasmas and tried to refute the criticism with new simulations and cluster model studies.

In this work, I summarize and update the alternative viewpoint, namely, the criticism [12,13] of the Ichimaru *et al.* data analysis [2,8–11]. Following the presentation by IOT [14], I point out the questionable points in their data analysis and explain the way by which the individually questionable equations, Eqs. (20), (25), (31), and (33) of IOT [14] appear to be mutually consistent. The final part of the paper is devoted to various charge-cluster calculations and leads to results that are different from those of IOT [14]. Together with the analysis of *general* axially symmetric clusters, as given in the Appendix, it provides insight into the short-range screening potentials of strongly coupled plasmas. In particular, I give an exact mathematical proof that does not agree with the main conclusions of IOT from their cluster model studies Eq. (49b) in [14], and thus questions the basis for their subsequent discussion.

II. PROBLEM, GENERAL METHODOLOGY, AND EARLIER RESULTS

The system under consideration is a binary ionic mixture (BIM) consisting of N_i particles of species i with charges $Z_i e$ $(i=1,2)$, in a uniform background of neutralizing electrons of volume V at temperature T. The total number of particles is $N=N_1+N_2$, the molar fractions are $x_1=N_1/N$, $x_2=1-x_1\equiv x$, and the charge ratio is $R_Z=Z_2/Z_1>1$ where it is assumed that $Z_2>Z_1$. The thermodynamic state of the BIM is specified by the Coulomb coupling parameter, $\Gamma_e=e^2/a_e k_B T$, where $a_e=(3/4\pi n_e)^{1/3}$, and $n_e=(N_1Z_1+N_2Z_2)/V$ is the number density of the uniform electrons. It is useful to define the ion-sphere radii, $a_i=a_e Z_i^{1/3}$, and the coupling parameters, $\Gamma_i=\Gamma_e Z_i^{5/3}$ $(i=1,2)$. It is convenient to measure all distances in units of the total Wigner-Seitz radius, $a=(3/4\pi n)^{1/3}$, where $n=N/V$ is the total number density of the ions. For the one component plasma (OCP), with $Z_1=Z$ denote $\Gamma_1=\Gamma$.

The screening potential $H(r)$ of the OCP is defined in terms of the bare Coulomb interaction between the two ions and the pair correlation function $g(r)$:

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$$H(r)=\frac{\Gamma}{r}+\ln[g(r)]\ . \tag{1}$$

The pair correlation function can be expressed through the free energy change upon fixing the positions of the pair of fluid particles in the appropriate configuration to form an interaction-site molecule, so that

$$H(r)=-\frac{\{F_1^{ex}(r)-F_0^{ex}\}}{k_BT}+\frac{\Gamma}{r}\ . \tag{2}$$

Here F_0^{ex} is the configurational (excess over ideal gas) free energy of the N-particle system (in a uniform neutralizing background) and $F_1^{ex}(r)$ is that of the same system but with the pair of particles kept at fixed separation r, forming a two-site charge cluster. $F_1^{ex}(r)$ does contain the intramolecular interaction Γ/r, so that $H(r)$ is finite as $r\to 0$.

The problem is to obtain the short-range screening potential $H(r<\sim 1)$. According to Widom [6] it can be expanded in even powers around $r=0$:

$$\begin{aligned}H(r)&=h_0-h_1r^2+\mathcal{H}_2(r)r^4\\&=h_0-h_1r^2+h_2r^4+h_3r^6\cdots\ .\end{aligned} \tag{3}$$

It is useful to define the relatively small and slowly varying (see below) function $\mathcal{H}_2(r)$, i.e., the "effective" coefficient of the r^4 term. We shall see below that Eq. (2) yields an expression for $h_0=H(r=0)$. The coefficient h_1 is known exactly [7], $h_1=\frac{1}{4}\Gamma$. Following the derivation [7] of h_1, expressions for the higher order coefficients can be easily derived. Their evaluation requires, however, dedicated simulations, which become increasingly costly as the order increases. In particular, h_2 has recently been calculated [9,14], with relatively large error bars, from extra long Monte Carlo (MC) samplings. The simulation data for $g(r)$ is limited to $r<R_{\min}$ where, e.g., $R_{\min}\sim 1$ for $\Gamma\sim 160$ and $R_{\min}\sim 0.8$ for $\Gamma\sim 10$. It is impossible to get $H(r\sim 0)$ by simulations directly from Eq. (1) because of the essentially zero probability for very close encounters, but it is possible to try to extrapolate these results down to $r=0$. On the basis of Eq. (2), however, the calculation of $H(0)$ can be carried out via the equation of state of the binary ionic mixture (BIM) plasma, if it is available. The equation of state of the BIM can be represented by the difference, $\Delta f_{ex}^{\mathrm{BIM}}(R_Z,x,\Gamma_1)=f_{ex}^{\mathrm{BIM}}=f_{LM}$, in order to obtain the (relatively small) deviation of the excess free energy (normalized by Nk_BT), f_{ex}^{BIM}, from its linear-mixing (LM) value, where $f_{LM}=(1-x)f_{ex}^{\mathrm{OCP}}(\Gamma_1)+xf_{ex}^{\mathrm{OCP}}(\Gamma_2)$. Thus [11]

$$h_0=h_0^{\mathrm{LM}}-\left[\frac{\partial}{\partial x}\Delta f_{ex}^{\mathrm{BIM}}(R_Z=2,x,\Gamma_1=\Gamma)\right]_{x\to 0}\ , \tag{4}$$

where the derivative of $\Delta f_{ex}^{\mathrm{BIM}}$ gives the deviation of h_0 from the liner-mixing (LM) approximation [15], $h_0^{\mathrm{LM}}=2f_{ex}^{\mathrm{OCP}}(\Gamma)-f_{ex}^{\mathrm{OCP}}(2^{5/3}\Gamma)$.

This first principles analysis defines *exactly* the required calculations, which nevertheless can be achieved only *approximately,* with an accuracy that depends on that of the required computer simulations and on the validity of the corresponding data analyses. The "Onsager molecule" concept [16–18], on the other hand, provides in a simple physically intuitive way the asymptotic strong coupling properties of the *exact* integral equations for classical plasmas. It provides better understanding of the numerical simulation results and has proven useful for their interpretation [12,19]. The asymptotic $\Gamma\to\infty$ solution of the exact diagramatic equations for $g(r)$ features the ion-sphere and the Onsager molecules: (i) The Onsager exact lower bound [20,21] for the potential energy is the sum of the self-energy of "Onsager atoms" (OA) (ion-spheres), $U/Nk_BT=u_{\mathrm{OA}}/k_BT=-0.9\Gamma$, where u_{OA} is the self-energy of an Onsager atom (ion-sphere [22]), consisting of a point charge at the center of a neutralizing unit sphere having the background charge density. (ii) Correlation functions and screening potentials feature the "Onsager molecules" (OM) naturally and by *recursive* definition [18]: $F_0^{ex}\geq Nu_{\mathrm{OA}}$, and $F_1^{ex}(r)\geq(N-2)u_{\mathrm{OA}}+u_{\mathrm{OM}}(r)$, where $u_{\mathrm{OM}}(r)$ is the self-energy of an Onsager molecule, consisting of a pair of ions separated by a distance r in a uniform neutralizing charge cloud of the background charge density. The *shape* of this molecule is determined by the surface on which the electrostatic field vanishes. It is a sphere of radius $2^{1/3}$ for $r=0$; it is then similar in shape to smoothed fused spheres [23] and eventually becomes two touching ion spheres (of radius 1 each) for $r=2$. Thus, from Eq. (2)

$$H_{\mathrm{OM}}(r)=\frac{\Gamma}{r}-\frac{u_{\mathrm{OM}}(r)}{k_BT}+2\frac{u_{\mathrm{OA}}}{k_BT}\ , \tag{5}$$

the OM approximation for the screening potential is the difference between exact lower bounds for F_0^{ex} and $F_1^{ex}(r)$. Onsager molecules have, by definition, the ability to *dissociate* when $r\geq 2$, $u_{\mathrm{OM}}(r\geq 2)=2u_{\mathrm{OA}}$, i.e., $H_{\mathrm{OM}}(r\geq 2)=\Gamma/r$. The OM limit for the short-range screening potential (before "dissociation"), $r\leq 2$, is of the form

$$\frac{H_{\mathrm{OM}}(r,\Gamma)}{\Gamma}=\tfrac{9}{10}(2^{5/3}-2)-\tfrac{1}{4}r^2+\frac{\mathcal{H}_{2,\mathrm{OM}}(r)}{\Gamma}r^4\ , \tag{6}$$

where numerical calculation [23] of the OM gives the following estimate [16]:

$$\frac{h_{2,\mathrm{OM}}(r)}{\Gamma}\cong 0.038-0.0026r^2;\quad \frac{\mathcal{H}_{2,\mathrm{OM}}(r=2)}{\Gamma}\cong 0.0277\ . \tag{7}$$

$\mathcal{H}_{2,\mathrm{OM}}(r)$ was obtained by fitting the Onsager-molecule numerical data [23], whereas its value at $r=2$ is determined by $H_{\mathrm{OM}}(r=2,\Gamma)/\Gamma=0.5$. Equations (6) and (7) represent the *asymptotic* form of $H(r)$ for the OCP fluid and are thus expected to give a good estimate of the result in strong coupling, as is indeed found by the simulations (see below).

Salpeter and Van Horn [24] pioneered the calculation of h_0 from Eq. (2) and employed the ion-sphere model [22]. The first attempts [25] to extrapolate simulation $g(r)$ data using Eq. (1) were not very successful [as already explained in [31(b)], but there was improvement after Jancovici's proof [7] of $h_1=0.25\Gamma$. Alastuey and Jancovici [26] extrapolated $H(r)$ toward the origin by fitting the simulation data of Hansen [1(a)], keeping terms up to h_3 in Eq. (3). They found h_0 to be in agreement with h_0^{LM} as obtained by employing an early fit of DeWitt [27] to Hansen's OCP equation of state simulations data

[1(a)]. Linear mixing is predicted to hold in the asymptotic strong coupling (OM) limit for plasmas [19]. The first theoretical direct calculations of the short-range $H(r)$ were performed by the assumption of universality of the bridge functions in the modified hypernetted-chain theory [3]. The properties of strongly coupled plasmas as obtained analytically from the Onsager-molecule theory [16–19] are in complete agreement [12,13] with the simulations data in strong coupling, e.g., with the Alastuey-Jancovici fit $\mathcal{H}_2(r)\cong 0.039-0.0043r^2$ at $\Gamma=160$. The OM prediction of $H(r=2)/\Gamma=0.5$, which is the immediate result of the dissociation property of OM, holds well even down to $\Gamma=10$ (see Figs. 7 and 8 in IOT [14]). As an asymptotic theory, *without any free parameters,* the Onsager-molecule approach is remarkably successful in describing all the major features of the statics of strongly coupled plasmas as born out by the simulations, including the equation of state, direct correlation functions, and bridge functions [12,13,16–19].

III. METHOD AND RESULTS OF ICHIMARU *et al.*

Ichimaru *et al.* [2,8–11] presented MC simulation data for $g(r)$, h_2, and $\Delta f_{ex}^{\rm BIM}$, on the basis of which they arrived at significantly different results from Jancovici for the short-range $H(r)$ and were in contradiction with the asymptotic Onsager-molecule predictions. Ichimaru *et al.* [2,8–11] employ the following methodology.

(i) New and highly accurate simulations were performed [9,10] for the OCP $g(r)$. The simulation data for $H(r)/\Gamma$, from Eq. (1), were fitted by Ogata, Iyetomi, and Ichimaru (OII) [9] in the range $R_{\rm min}\le r\le 2$ to an accuracy of 0.1% by some function, denoted $f_{\rm OII}(r)$, for $5<\Gamma<180$.

(ii) An exact expression was derived [9] for the coefficient h_2 and calculated directly by the Monte Carlo method. On the basis of the MC sampling, OII concluded that [9]

$$\frac{h_2}{\Gamma}=0.00\pm 0.01\ . \tag{8}$$

(iii) Granting that $h_2/\Gamma=0$, they truncated the expansion at the second term with $h_1=0.25\Gamma$ and obtained the extrapolated screening potential in the following form [9]: $H(r)=h_0-h_1r^2$ for $r\le r_0$, and $H(r)=f_{\rm OII}(r)$ for $r\ge r_0$. The remaining two unknown parameters h_0, r_0 are determined from the requirement that the function and its first derivative are continuous at r_0, thus obtaining [9]

$$\frac{h_0^{\rm OII}}{\Gamma}=1.148-0.0094\ln(\Gamma)-0.00017[\ln(\Gamma)]^2\ . \tag{9}$$

At near freezing temperatures, for example at $\Gamma=160$ (corresponding to Fig. 7 in IOT [14]), OII obtain $r_0=0.780$, $h_0/\Gamma=1.095$. OII [9] estimate the error in their h_0 so extrapolated to stay on the order of 0.1%.

(iv) New extensive simulations for the BIM were performed by Ogata, Iyetomi, Ichimaru, and Van Horn (OIIVH) [11]. Their linear-mixing results were obtained from the Ogata-Ichimaru [8] representation for $f_{ex}^{\rm OCP}(\Gamma)$, denoted $f_0^{\rm OIIVH}(\Gamma)$, which they obtained from their fit to the simulations results for the potential energy $u_0^{\rm OIIVH}(\Gamma)$. On the basis of their BIM results and $f_{ex}^{\rm OCP}(\Gamma)=f_0^{\rm OIIVH}(\Gamma)$, they obtained a fit for $\Delta_{ex}^{\rm BIM}$. The results for h_0 thus obtained by OIIVH from Eq. (4) agree well with $h_0^{\rm OII}$ [Eq. (9)]. As stressed by OIIVH [11], this agreement for h_0, as well as important features of their phase diagrams, crucially depends on the *negative* sign and on the relatively large magnitude of their derivative of $\Delta f_{ex}^{\rm BIM}$ at $x\to 0$.

(v) Finally, IOT [14] present (a) additional BIM simulation data to further support the negative deviations from LM, (b) new and more accurate data for h_2 from very long MC runs to support their conclusion that $h_2=0$, and (c) cluster model studies that are meant to add weight to this conclusion.

IV. CRITIQUE OF DATA ANALYSIS OF ICHIMARU *ET AL.*

It should be emphasized at the outset that the main question [12,13] regarding these results by Ichimaru *et al.* [2,8–11] concerns the data analyses, and not the bare simulation data themselves. In this section I question the data analysis of Ichimaru *et al.* and offer an alternative analysis of the same data. I explain how the individually questionable Eqs. (20), (25), (31), and (33) of IOT [14] appear to be mutually consistent.

(i) On the basis of their Table 4, OII [9] conclude that h_2 virtually vanishes. They apparently give little weight to previous predictions [26] for $h_2/\Gamma\approx 0.04$ in *strong coupling* and to their own data point of 0.06 ± 0.13 at $\Gamma=160$, and they regard [9] their Table 4 as proof that $h_2\simeq 0$. IOT [14] already regard the assessment (8) as consistent only with all the data in their earlier series of simulations, as well as their new results. But even by this characterization, a large variety of choices can be considered "consistent" with all the data. For example, considering their Table 1 and Fig. 1 [14] (see also the present Fig. 1 and point (iv) below), there is no reason why a result like, e.g., $h_2/\Gamma=0.2\pm 0.01$, should be less "consistent" (in their sense) with the new IOT data [14] than their $h_2/\Gamma=0.00\pm 0.01$.

(ii) The analysis by OII [9] is based on questionable methodology: In strong coupling (e.g., $\Gamma=160$), the values of r_0 (e.g., $r_0=0.78$) is much smaller than $R_{\rm min}$ (e.g., $R_{\rm min}\sim 1.15$; see Fig. 7 in IOT). Thus, the connection point for the extrapolation is beyond the actual data points, making the procedure dependent on the choice of fitting function for the data. Ichimaro, Ogata, and Tsurta refer to Ref. [12], where this property of the OII method was first pointed out, but they do not address this issue.

(iii) An elementary consistency check, which can be performed [12] within the OII extrapolation method, is to see what happens with the addition of extra terms. By keeping the term h_2 free and repeating the fitting procedure of OII [9], it was found [12] that the connection point is now inside the data range, and the extrapolated results for h_0 are in 0.3% agreement with $h_0^{\rm LM}$ as obtained from the DeWitt, Slattery, and Stringfellow (DWSS) [28] fit to their most accurate MC equation of state for the OCP,

$$\frac{h_0^{\mathrm{LM}}}{\Gamma} = 1.056\,38 + 0.996\,43\Gamma^{-0.6747} - \frac{(0.268\ln\Gamma + 1.059\,69)}{\Gamma}. \quad (10)$$

The Ogata-Ichimaru [8] fit used by OII [9] gives very similar results for h_0^{LM}. This fit yields [12] $h_2/\Gamma \sim 0.3$, which is in accord with the Alasuey-Jancovici fit and the OM limit. A systematic study along this line (see iv below and Fig. 1) reveals that $h_2(\Gamma)/\Gamma$ decreases gradually with decreasing Γ, as does $h_2^{\mathrm{OM}}/\Gamma - O(\Gamma^{\theta})$ with $\theta \sim -2/3$ in agreement with the asymptotic analysis [19], and in better agreement with the new simulation results of IOT [14] than with their assertion by Eq. (8) in [14].

(iv) A further step to improve the analysis of the OII data is to employ the Alastuey-Jancovici "AJ(i)" type fit, i.e., by keeping terms up to h_i in Eq. (3), using the OII data as embodied by their fit $f_{\mathrm{OII}}(r)$, $R_m(\Gamma) \le r \le 2$. I found [12] that the function $f_{\mathrm{OII}}(r)$ in the actual data range for r, $R_m(\Gamma) \le r \le 2$, can be fitted to 0.05% by AJ (3) (i.e., up to the r^6 term) for all values of $\Gamma > \sim 70$, with results in about 0.3% agreement with the original Alastuey-Jancovici extrapolation result for h_0. This also shows that the functional form of $f_{\mathrm{OII}}(r)$ as chosen by OII, with four free coefficients, is not as effective as the Alastuey-Jancovici form, with three coefficients. Increasing the number of free coefficients to five almost does not affect the result of the extrapolation for relatively large values of $\Gamma > \sim 70$ (Figs. 1 and 2). The resulting function $h_0(\Gamma)/\Gamma$ decreases with Γ toward the asymptotic limit, $1.057\,32 + O(\Gamma^{\theta})$, $\theta \sim -\frac{2}{3}$, while the function $\mathcal{H}_2(r)/\Gamma$ gradually increases toward the predicted Onsager-molecule result of ~ 0.038. For $\Gamma = 10$, however, with only five coefficients, it is possible to fit the function $f_{\mathrm{OII}}(r)$ to better than 0.1%, and the result features a smaller coefficient h_2. As can be seen in Fig. 1, this last result, with its gradual change of h_2/Γ from its asymptotic value of about 0.038 to nearly zero, is in accord with the new simulation results of IOT [14] for the coefficient h_2. In particular, it is clearly seen in Fig. 1 that the AJ (5) result is more consistent with the actual MC data than the OII-OIT [9,14] conclusion of $h_2/\Gamma = 0.00 \pm 0.01$. The statement made by IOT [14] concerning the MC results with further increased sampling size is purely speculative, and it is not backed up by the actual data.

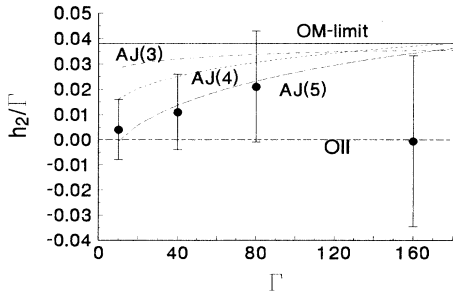

FIG. 1. The coefficient of the r^4 term in the Widom expansion of $H(r)$, h_2/Γ, from different approximation (lines), compared with the Monte Carlo data (full circles with error bars) of IOT [14].

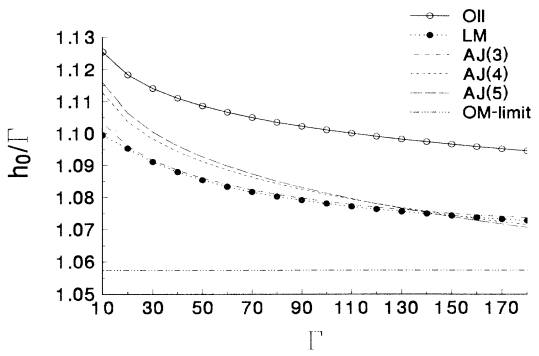

FIG. 2. The "zero-separation" sum-rule, $h_0/\Gamma = H(0)/k_B T/\Gamma$, as obtained from different approximations.

(v) Using the DWSS fit [28] to the OCP energies and repeating the OIIVH [11] procedure, I obtained [13] significantly different results: In particular, *positive* and relatively *small* (about an order of magnitude smaller than the positive deviation of OIIVH) deviations from the linear-mixing approximation for small x are obtained by using $f_{ex}^{\mathrm{OCP}} = f_0^{\mathrm{DWSS}}$. This is in agreement with the Jancovici-Alastuey extrapolation [26] and the LM result, h_0^{LM} (h_0^{LM} is almost the same with either f_0^{DWSS} or f_0^{OIIVH}), and is in agreement with the previous criticism [12] of the OII extrapolation method (see Fig. 2). First, this result demonstrated directly that the special features of $\Delta f_{ex}^{\mathrm{BIM}}$, as emphasized by OIIVH, are the result of their choice of $f_0^{\mathrm{OIIVH}}(\Gamma)$ and are not the reflection of their bare MC data for the BIM. Moreover, an analytic variational model [29], which provides the paradigm for the form of $f_0^{\mathrm{OIIVH}}(\Gamma)$ itself, also features small *positive* deviations from linear mixing. It is in good agreement [13] with the fluid binary ionic mixture data of OIIVH [11] if the DWSS [28] equation of state for the OCP, f_0^{DWSS}, is used (instead of f_0^{OIIVH}) to evaluate $\Delta f_{ex}^{\mathrm{BIM}}$.

(vi) The source for discrepancy between the OIIVH and DWSS fits for the OCP was identified [13] as internal inconsistency in the OIIVH [11] data reduction and was demonstrated directly by new simulations [30]: With inherent uncertainties of about ± 0.001 for the MC energies, and in view of the deviations of u_0^{OIIVH} from u_{ex}^{MC}, possible errors for $u_{\mathrm{LM}}^{\mathrm{OIIVH}}$ are about ± 0.004. This relatively large uncertainty in the OCP fits is not taken into account by OIIVH. With errors of about ± 0.004 for u_0^{OIIVH}, OIIVH [11] still cite errors of about ± 0.001 for $\Delta u_{ex}^{\mathrm{BIM,OIIVH}}$ (in their Fig. 2) and for the accuracy of their fit for $\Delta f_{ex}^{\mathrm{BIM,OIIVH}}$. From this fit they subsequently obtain a large negative result for the derivative at $x = 0$, which makes the result from Eq. (4) compare well with h_0^{OII}. On the other hand, with correct error bars in their Fig. 2, which take into account the relatively large uncertainties in the OCP fits, the negative deviations from linear mixing, as found by OIIVH [11], now fade away.

It should be emphasized that similar possible errors apply also to $u_{\mathrm{LM}}^{\mathrm{DWSS}}$. However, DeWitt and Slattery [30] reported new and exceptionally long simulation runs [30] in which *both* the relevant OCP energies (at Γ_1 and Γ_2) and BIM energies were all obtained from MC sampling. These gave good agreement with OIIVH for the BIM and

good agreement with DWSS for the OCP, always finding *positive* deviations from linear mixing. This shows clearly that the function that OIIVH and IOT use for the OCP, $f_0^{\mathrm{OIIVH}}(\Gamma)$, does not represent correctly the OCP limit of their own results for the BIM. Thus, the new "extra long MC samplings in the specifically designed binary-ionic systems," as presented in Table 2 of IOT [14], cannot change the picture, since they also are processed via $f_0^{\mathrm{OIIVH}}(\Gamma)$ in the linear-mixing rule. This inconsistency can be verified by IOT if they will go one step further: Instead of simulating BIM systems with 999 charges Ze and one charge $2Ze$, they should do it also for the OCP with 1000 charges Ze. With their data points at $r=0$, which are derived on the basis of (4) but from data with inconsistent error bars (as explained above), the agreement with the OII extrapolation, as presented in Figs. 7 and 8 of IOT [14], seems to be accidental.

In summary, the case of Ichimaru *et al.* [2,8–11], as summarized by IOT [14], is based on analysis of their simulation data, by which the individually questionable Eqs. (20), (25), (31), and (33) of IOT [14] appear to be consistent. On the other hand, full consistency with the raw data of Ichimaru *et al.* [9–11] is obtained by using the Alastuey-Jancovic AJ(i) fits to the $H(r)$ data, in agreement with the Onsager-molecule asymptotic analysis, which represents well the new h_2 data of IOT. It is interesting to note that "AJ(5)" was already presented in Saint-Malo [1d], *before* the new h_2 data by IOT [14] were published. Deviations from linear law of the energy of mixture data, using the DWSS energies for the OCP, agree with the AJ(i) fits and are also in agreement with a variational hard-sphere model for the free energy. This alternative analysis achieves consistency of all the data and agrees with physically acceptable theoretical models.

V. "ONSAGER MOLECULES" AND CLUSTER MODEL CALCULATIONS

Following the introduction of charge-cluster plasmas [16–18], a detailed study of diatomic confined Onsager molecules was performed by Stein, Shalitin, and Rosenfeld (SSR) [23]. Of particular interest was the family of all neutral objects composed of the pair of point charges, with separation r, and a uniform neutralizing background charge density. These are the "clusters" as rediscovered by IOT [14], for which they find new results, namely, that [Eq. (49b) in [14]] $h_2=0$ for the clusters, which sustain their analyses of the simulation data. These main results of IOT [14] from their cluster model calculations are questioned below.

Stein *et al.* proved [23] that the cluster with minimal electrostatic energy (i.e., the Onsager molecule) must have an equipotential surface. It was found that the solution to the variational electrostatic problem of finding the optimal object (the OM) has a very shallow minimum with respect to variation of shape, as borne out also by the cluster calculations (see below). The general expressions needed for the calculation and discussion of the energy of axially symmetric clusters are provided in the appendix of [23], and particular cluster shapes, as approximations to the OM, were already considered [23]. The first two terms in (6) are the result for the spherical shape, and the contributions from the deviations from the spherical shape are represented by $\mathcal{H}_{2,c}(r)$, which is the analog for the general cluster of the optimal $\mathcal{H}_{2,\mathrm{OM}}(r)$. Because of its optimal shape, the OM yields the lowest energy for the cluster, and thus the largest value for its approximation of the screening potential:

$$\mathcal{H}_{2,\mathrm{OM}}(r)\geq\mathcal{H}_{2,c}(r)\ . \tag{11}$$

Ichimaru, Ogata, and Tsuruta [14] consider the spheroidal (SD) and spherocylindrical (SC) shapes and optimize the deformation parameter θ ($\theta=0$ for the sphere; see Ref. [14] and the Appendix) for every value of the interion separation r. In their notations,

$$\begin{aligned}\mathcal{H}_{2,c}(\theta,r)r^4/\Gamma&\equiv H_c(\theta,r)/\Gamma+\tfrac{8}{10}+\tfrac{1}{4}r^2\\&=B(\theta)-A(\theta,r)\ ,\end{aligned} \tag{12}$$

subject to the optimization

$$\begin{aligned}\partial[H_c(\theta,r)/\Gamma]/\partial\theta&=\partial[\mathcal{H}_{2,c}(\theta,r)r^4/\Gamma]/\partial\theta\\&=\partial[B(\theta)-A(\theta,r)]/\partial\theta=0\ ,\end{aligned} \tag{13}$$

which yields $\theta(r)$ and the optimized $H_{c,\mathrm{op}}(r)=H_c[\theta(r),r]$. The derivative of the final result $\mathcal{H}_{2,c,\mathrm{op}}(r)=\mathcal{H}_{2,c,\mathrm{op}}[\theta(r),r]$ with respect to r is given by

$$\begin{aligned}&d[\mathcal{H}_{2,c,\mathrm{op}}(r)r^4/\Gamma]/dr\\&\quad=\{(\partial[B(\theta)-A(\theta,r)]/\partial\theta)_r(\partial\theta/\partial r)\\&\qquad-[\partial A(\theta,r)/\partial r]_\theta\}_{\theta=\theta(r)}\ .\end{aligned} \tag{14}$$

Because of the optimization [Eq. (13)], however, it takes the form

$$d[\mathcal{H}_{2,c,\mathrm{op}}(r)r^4/\Gamma]/dr=-[(\partial A(\theta,r)/\partial r)_\theta]_{\theta=\theta(r)}\ .$$

Ichimaru, Ogata, and Tsuruta [14] find linear behavior, $\theta(r)=t_1r+\ldots$, in the small r limit for both the SD and SC shapes, as can be seen in their Eq. (A5) and in the equation following it. From Figs. 5 and 6 of IOT, estimate $t_1\approx0.85$ for the SD and $t_1\approx0.92$ for the SC shapes. The leading term for the small-r and small-θ expansions of $A(\theta,r)$ is of the form $A(\theta,r)=-a_2\theta^2r^2+\ldots$, where $a_2=\frac{1}{10}$ for the SD [there is a misprint in Eq. (41) of IOT: 2θ should be replaced by $(2\theta-4\theta^3/3)$] and $a_2=\frac{3}{32}(11-8\times2^{1/3})\approx1/11.6$ [from Eq. (44) of IOT] for the SC. Thus, in the limit of small r, we find that $d[\mathcal{H}_{2,c,\mathrm{op}}(r)r^4/\Gamma]/dr=2a_2t_1^2r^3+\ldots$, or

$$\mathcal{H}_{2,c}(r=0)/\Gamma=a_2t_1^2/2\ ; \tag{15}$$

i.e., $\mathcal{H}_{2,c}(r=0)/\Gamma=\approx0.0361$, 0.0365, for the SD and SC, respectively, in agreement with the earlier analysis [23] and the OM result [Eq. (7)]. With the help of Figs. 5 and 6 and Eqs. (47) in IOT [14], it is possible to reconstruct the full $\mathcal{H}_{2,c,\mathrm{op}}(r)$. As can be seen in Fig. 3, the cluster models behave as expected by SSR [23], sustaining the Onsager-molecule analysis and supporting my criticism [12,13] of Ichimaru *et al.*, instead of sustaining Eq. (8), i.e., Eq. (20) of IOT [14].

Actually there is no need to use any specific result from IOT [14] in order to question their Eq. (49b). It was found numerically [23] that the OM energies and those for the cluster of the shape denoted $R^{(2)}$ in [23] (see Eq. (19) in [23]) are almost the same, especially near $r=0$. In Table II of [23], we find $B=2/r$, $\lambda_0=1/\theta^{1/2}$, from which we estimate $t_1\approx0.877$ and $\mathcal{H}_{2,c}(r=0)/\Gamma\approx0.0384$,

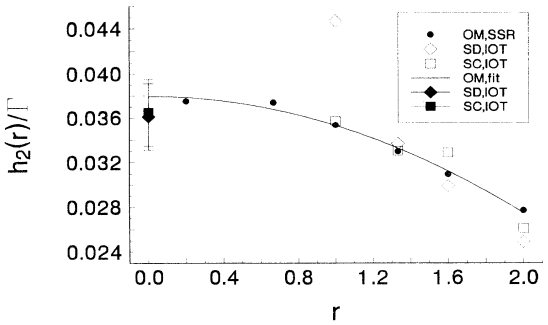

FIG. 3. Effective coefficient for the r^4 term of the OCP screening potential $h_2(r)$ [denoted $\mathcal{H}_2(r)$ in the text] as approximated by charge clusters of the spheroidal (SD) and spherocylindrical (SC) shapes, and by the optimally shaped Onsager molecule (OM). The exact relation $h_{2,\mathrm{OM}}(r) \geq h_{2,c}(r)$ does not always hold because of the limited accuracy of the numerical calculations and of the representations by Eq. (17) in IOT [14]. The error bars for the point at $r=0$ reflect the uncertainty in determining the coefficient t_1 from Figs. 5 and 6 in Ref. [14].

which compares well with the extrapolated value in Eq. (7) above. This estimate also compares well with those obtained from the IOT data. It is proven in the Appendix that the $R^{(2)}$ cluster shape and the SD should give the same results in the small-r expansion. Note, however, that the $R^{(2)}$ cluster does have the dissociation property (i.e., interpolates between one sphere and two adjacent spheres), while the spheroidal (SD) and spherocylindrical (SC) shapes are more like a mathematical exercise.

Moreover, it should be noted that the SC and SD shapes are just two specific examples of cluster shapes obtained by continuous axially symmetric deformation of the sphere, for which we obtain (see the Appendix) the following general *exact* bound,

$$\mathcal{H}_{2,c}(r=0)/\Gamma > 3\times 2^{1/3}/160 \approx 0.024 , \tag{16}$$

which is *independent of the shape of the cluster.* Together with the OM result we thus have the following exact inequalities *for all clusters:*

$$0.038 \approx \mathcal{H}_{2,\mathrm{OM}}(r=0)/\Gamma \geq \mathcal{H}_{2,c}(r=0)/\Gamma > 3\times 2^{1/3}/160 \approx 0.024 . \tag{17}$$

The source of the different IOT [14] result is probably the last term in their Eq. (A7), which implies (unlike our result) that $a_2=0$. Obviously, the IOT mathematical proof of their Eq. (49b) is questionable. Instead of supporting (8), my exact cluster model calculations give a physical picture that is different from the IOT results {Eqs. (20) and (49b) in [14]}.

My analysis here, in particular Eq. (17), demonstrates the insensitivity of the cluster screening potentials to the shape. This gives an idea why the AJ(i) type fits for $\mathcal{H}_2(r)$, obtained from the MC $H(r)$ data for strongly coupled plasmas, feature a slow change with Γ from the asymptotic prediction by the Onsager molecules. Considering the thermodynamics and structure of the strongly coupled OCP, it can be understood in terms of slowly varying boundary conditions (e.g., the shape) of the Onsager atoms and molecules. Thus $h_0(\Gamma)/\Gamma$ slowly increases with decreasing Γ from its asymptotic "ion-sphere" value of ≈ 1.057 (Fig. 2). The ion-sphere result $h_1/\Gamma = \frac{1}{4}$ turns out to be exact by virtue of the uniform neutralizing background. $\mathcal{H}_2(r)$ is slowly varying from its asymptotic limit because of the dissociation property of the molecules, which sets $\mathcal{H}_2(r=2)/\Gamma \approx 0.028$, and the insensitivity of $h_2/\Gamma = \mathcal{H}_2(r=0)/\Gamma \approx 0.038$ to the shape of the cluster (Fig. 3). The AJ (i) fits (Fig. 1) to the new simulations [9] show that $\mathcal{H}_2(r \leq 2)/\Gamma$ monotonically decreases from $\mathcal{H}_{2,\mathrm{OM}}(r \leq 2)/\Gamma$ as Γ decreases from the asymptotic $\Gamma \to \infty$ limit, in accord with the inequality (11).

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APPENDIX: ANALYSIS OF GENERAL AXIALLY SYMMETRIC CHARGE CLUSTERS

Consider the general axially symmetric cluster, composed of the pair of identical point ions of charge Ze at $\pm(r/2)$ on the symmetry axis, and a uniform distribution of electrons. Recall that we measure distances in units of a, so that the uniform electron charge density is $-(3/4\pi)Ze$. Let the shape of the cluster be described by the radius vector from the origin to the boundary $R(\Theta)$, where Θ is the azimuthal angle in spherical coordinates, and let $\mu = \cos\Theta$. In particular, consider the rather general shape

$$R(\cos\Theta) = R_0(\theta) s(\theta^2\mu^2) , \tag{A1}$$

where θ is the deformation parameter, and the shape function $s(y)$ can be expanded in the form $s(y) = 1 + s_1 y + s_2 y^2 + \cdots$. The normalization factor $R_0(\theta)$ is determined from the condition that the volume remain the same throughout the deformation (Eq. (17) in [23]),

$$R_0(\theta) = \left[\frac{2}{{}_0\!\int^1 s^3(\theta^2\mu^2) d\mu} \right]^{1/3} . \tag{A2}$$

Using (19) above and Eqs. (A2)–(A5) in [23], we obtain the following leading terms in the expansion of the ion-electron interaction in the cluster, in powers of θ and r:

$$\frac{u_{ie}(\theta,r)}{k_B T \Gamma} = -\tfrac{3}{2}\times 2^{5/3} + \frac{r^2}{4} + b_4^{(ie)}\theta^4 - a_2\theta^2 r^2 + \cdots . \tag{A3}$$

The first two terms are the well known results for the ion-sphere, and the leading coefficients are given by

$$b_4^{(ie)} = (\tfrac{3}{2}\times 2^{5/3})\tfrac{4}{45} s_1^2 \tag{A4}$$

$$a_2 = \tfrac{1}{5} s_1 .$$

Note that $b_4^{(ie)}$ is always *positive,* while a_2 is *positive* for the physically correct deformation $s_1 > 0$, i.e., with elongation along the line joining the two point charges. The leading order in the expansion of the electron-electron interaction $u_{ee}(\theta)$, in powers of θ, beyond the spherical contribution $u_{ee}(\theta=0)/\Gamma = \frac{3}{5}\times 2^{5/3}$, can be represented as an infinite series using Eqs. (A6)–(A9) in [23]. Consider the total cluster energy (excluding the

ion-ion interaction) when the two charges are at the center ($r=0$), and consider its change upon any infinitesimal deformation of its initial spherical shape. If ϵ is the infinitesimal charge outside the maximal sphere that can be inscribed inside the deformed sphere, then it can be easily established from elementary electrostatics that the change in the total energy of the cluster is of order ϵ^2. Since the sphere is the optimal cluster (Onsager molecule) for $r=0$, then this change must be *positive*. For the case at hand we thus have

$$\frac{u_c(\theta,r)}{k_BT\Gamma}-\frac{1}{r}=\frac{u_{ie}(\theta,r)+u_{ee}(\theta)}{k_BT\Gamma}$$
$$=-\tfrac{9}{10}\times 2^{5/3}+\frac{r^2}{4}+b_4\theta^4-a_2\theta^2r^2+\ldots, \quad \text{(A5)}$$

where b_4 is *positive*, $b_4>0$. In view of (A3) and (A5), we must have

$$\frac{u_{ee}(\theta)}{\Gamma}=\tfrac{3}{5}\times 2^{5/3}-b_4^{(ee)}\theta^4+\ldots, \quad \text{(A6)}$$

where $b_4^{(ee)}$ is *positive*, $b_4^{(ee)}>0$, since for a uniform charge density the sphere has the maximal self-energy. Because $b_4=b_4^{(ee)}+b_4^{(ie)}$ is *positive*, we thus have $b_4<b_4^{(ie)}$. Optimizing $u_c(\theta,r)$ with respect to θ,

$$\frac{\partial}{\partial\theta}u_c(\theta,r)=0\ , \quad \text{(A7)}$$

we obtain $\theta(r)=t_1r+\ldots$, where $t_1=(a_2/2b_4)^{1/2}$, so that the coefficient of the r^4 term for the cluster screening potential takes the form

$$\mathcal{H}_{2,c}(r=0)/\Gamma=a_2^2/(2b_4)=a_2t_1^2/2\ . \quad \text{(A8)}$$

Since $b_4<b_4^{(ie)}$ we obtain the following exact bound,

$$\mathcal{H}_{2,c}(r=0)/\Gamma>a_2^2/(2b_4^{(ie)})=3\times 2^{1/3}/160\approx 0.024\ , \quad \text{(A9)}$$

which is *independent of the shape of the cluster* since the s_1 dependence cancels out. Together with the OM results we thus have the following exact inequalities *for all nonspherical clusters:*

$$0.038\approx\mathcal{H}_{2,\mathrm{OM}}(r=0)/\Gamma\geq\mathcal{H}_{2,c}(r=0)/\Gamma>3\times 2^{1/3}/160$$
$$\approx 0.024\ . \quad \text{(A10)}$$

Finally, note that the $R^{(2)}$ cluster shape of (A6) with $s(y)=(1+y)^{1/2}$ and the spheroidal shape of [14] with $s=(1-y)^{-1/2}$ have the same coefficient $s_1=\frac{1}{2}$, and thus should give the same results in the small-r expansion. Note, however, that unlike the spheroidal clusters used by IOT [14], the $R^{(2)}$ cluster does have the dissociation property (i.e., it interpolates between one sphere and two adjacent spheres).

[1] (a) J. P. Hansen and M. Baus, Phys. Rep. **59**, 1 (1980); (b) *Strongly Coupled Plasma Physics,* edited by F. J. Rogers and H. E. DeWitt (Plenum, New York, 1987); (c) *Strongly Coupled Plasma Physics,* edited by S. Ichimaru and H. M. Van Horn (Rochester University Press, Rochester, NY, 1993); (d) *The Equation of State in Astrophysics,* edited by G. Chabrier and E. Schatzman, IAU Colloquium 147 (Cambridge University Press, Cambridge, 1994); (e) D. G. Yakovlev and D. A. Shalybkov, Sov. Sci. Rev. **4**, part 7 (1989); (f) M. Sahrling, Astron. Astrophys. **283**, 1004 (1994); **284**, 484 (1994); M. Sahrling and G. Chabrier (unpublished).

[2] S. Ichimaru, Rev. Mod. Phys. **65**, 255 (1993); S. Ichimaru, *Statistical Plasma Physics, Volume II: Condensed Plasmas* (Addison-Wesley, Reading, MA, 1994).

[3] (a) Y. Rosenfeld and N. W. Ashcroft, Phys. Rev. A **20**, 1208 (1979); (b) Y. Rosenfeld, Phys. Rev. Lett. **44**, 146 (1980); (c) J. Phys. (Paris) Colloq. **41**, C77 (1980).

[4] Y. Rosenfeld, Phys. Rev. Lett. **63**, 980 (1989); **72**, 3831 (1994); J. Chem. Phys. **93**, 4305 (1990); **98**, 8126 (1993).

[5] W. G. Hoover and J. C. Poirer, J. Chem. Phys. **37**, 1041 (1962).

[6] B. Widom, J. Chem. Phys. **39**, 2808 (1963).

[7] B. Jancovici, J. Stat. Phys. **17**, 357 (1977).

[8] S. Ogata and S. Ichimaru, Phys. Rev. A **36**, 5451 (1987).

[9] S. Ogata, H. Iyetomi, and S. Ichimaru, Astrophys. J. **372**, 259 (1991).

[10] H. Iyetomi, S. Ogata, and S. Ichimaru, Phys. Rev. A **46**, 1051 (1992).

[11] S. Ogata, H. Iyetomi, S. Ichimaru, and H. M. Van Horn, Phys. Rev. E **48**, 1344 (1993); *Strongly Coupled Plasma Physics* [Ref. [1(c)]], pp. 53–62.

[12] Y. Rosenfeld, Phys. Rev. A **46**, 1059 (1992); *The Equation of State in Astrophysics* [Ref. [1(d)]], pp. 78–105.

[13] Y. Rosenfeld, Phys. Rev. E **52**, 3292 (1995).

[14] S. Ichimaru, S. Ogata, and K. Tsuruta, Phys. Rev. E **50**, 2977 (1994).

[15] J. P. Hansen, G. M. Torrie, and P. Viellefosse, Phys. Rev. A **16**, 2153 (1977).

[16] *Strongly Coupled Plasma Physics* [Ref. [1(b)]], pp. 573–585; *The Equation of State in Astrophysics* [Ref. [1(d)]], pp. 78–105.

[17] Y. Rosenfeld, in *High-Pressure Equations of State: Theory and Applications,* edited by S. Eliezer and R. Rici (North-Holland, Amsterdam, 1991).

[18] Y. Rosenfeld, Phys. Rev. A **35**, 938 (1987).

[19] Y. Rosenfeld, Phys. Rev. A **32**, 1834 (1985); **33**, 2025 (1986); **37**, 3403 (1988); Phys. Rev. E **47**, 2676 (1993); Y. Rosenfeld, D. Levesque, and J. J. Weis, Phys. Rev. A **39**, 3079 (1989).

[20] L. Onsager, J. Phys. Chem. **43**, 189 (1939).

[21] E. L. Lieb and H. Narnhofer, J. Stat. Phys. **12**, 291 (1975).

[22] E. E. Salpeter, Aust. J. Phys. **7**, 373 (1954).

[23] J. Stein, D. Shalitin, and Y. Rosenfeld, Phys. Rev. A **37**, 4854 (1988).

[24] E. E. Salpeter and H. M. Van Horn, Astrophys. J. **155**, 183 (1969).

[25] H. E. DeWitt, H. C. Graboske, and M. S. Cooper, Astrophys. J. **181**, 439 (1973); N. Itoh, H. Totsuji, S.Ichimaru, and H. E. DeWitt, *ibid.* **234**, 1079 (1979).

[26] A. Alastuey and B. Jancovici, Astrophys. J. **226**, 1034 (1978).

[27] H. E. DeWitt, Phys. Rev. A **14**, 1290 (1976).

[28] H. E. DeWitt, W. L. Slattery, and G. S. Stringfellow, in *Strongly Coupled Plasma Physics,* edited by S. Ichimaru (North-Holland, Amsterdam, 1990).

[29] H. D. Jones, J. Chem. Phys. **55**, 2640 (1971); D. Stroud and N. W. Ashcroft, Phys. Rev. A **13**, 1660 (1976); B.

Firey and N. W. Ashcroft, *ibid.* **15,** 2072 (1977); H. E. DeWitt and Y. Rosenfeld, Phys. Lett. A **75,** 79 (1979).

[30] (a) *Strongly Coupled Plasma Physics* [Ref. [1(c)]]; (b) H. E. DeWitt, W. L. Slattery, and G. Chabrier, in *Strongly Coupled Plasma Physics,* edited by W. Kraeff and M. Schlanges (World Scientific, Singapore, in press). (c) H. E. DeWitt, Contrib. Plasma Physics, **33,** 399 (1993). This paper contains a misprint in Table II: I was informed by Dr. DeWitt that the entry for the linear mixing value for $Z_2=5$ is incorrect (a copy mistake), but the stated result for the positive deviation from linear mixing is correct.