Reply to "Comment on 'Equation of state and phase diagrams for dense multi-ionic mixture plasmas'"

Shuji Ogata and Setsuo Ichimaru
Department of Physics, University of Tokyo, Bunkyo, Tokyo 113, Japan
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Excess internal energies of binary-ionic mixture (BIM) plasmas containing small concentrations of larger-charge ions are reexamined critically. Through examination of the fitting formulas advanced for the energies of the one-component plasmas (OCP's), we show that the sign of the deviations for the BIM energies from the "linear mixing" values cannot be determined from Monte Carlo simulation data for the energies alone. Instead, the sum rule with respect to the OCP screening potential at the origin is shown to be useful in judging the sign of the deviations. By using the best values currently available for the screening potential, we find that the deviations take on negative values in accordance with the prediction by Ogata, Iyetomi, Ichimaru, and Van Horn [Phys. Rev. E **48**, 1344 (1993)].

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I. INTRODUCTION

A mixture of multiple species of ions immersed in a uniform background of charges is a fundamental model for alloys and well realized in the interiors of dense stars such as white dwarfs. A mixture plasma may exhibit a chemical separation associated with the solidification transition. Ogata, Iyetomi, Ichimaru, and Van Horn [1] (hereafter referred to as OIIVH) calculated the equation of state for binary-ionic mixture (BIM) plasmas for both fluid and solid phases by combining Monte Carlo (MC) simulation results and analytic calculations, and thereby constructed phase diagrams for the mixtures. Their analysis has been extended successfully to ternary mixtures.

Rosenfeld [2] criticized the analysis of OIIVH with regard to the deviations of the normalized excess internal energies for BIM fluids from the "linear mixing" (LM) values. In OIIVH, BIM energies were obtained by a MC simulation method and LM values were calculated using the Ogata-Ichimaru [3] (OI) formula for the energies of the one-component plasmas (OCP's). Negative deviations were thereby found for BIM's with small concentrations of larger-charge ions. They confirmed this finding from the point of view of thermodynamic consistency by using a sum rule for the OCP screening potential at the origin. In Ref. [2], Rosenfeld elected to use the DeWitt-Slattery-Stringfellow [4] (DWSS) formula for the OCP energies and found through comparison of the energies positive deviations for the cases of BIM's tabulated in Table I in OIIVH.

In this paper, we first show that neither the OI nor the DWSS formula has an accuracy sufficient to be able to judge the sign of the deviations. We then stress that a sum rule with respect to the OCP screening potential at the origin is useful for the analysis of the deviations. By using the best values [5] currently available in the light of a recent examination [6] for the screening potential at the origin, we show that the sum rule predicts *negative* deviations, irrespective of the OCP formulas adopted, in accordance with the OIIVH prediction.

II. ACCURACY OF EQUATION OF STATE FOR THE OCP FLUID

Let a BIM be composed of N_i ions with charge $Z_i e$ in a volume V ($i=1,2$); total number of ions is $N=N_1+N_2$. We find it useful to define the charge ratio $R_Z=Z_2/Z_1$ ($Z_2>Z_1$ is assumed) and the molar fraction of "2" ions, $x=N_2/N$. Coulomb coupling parameters which characterize the BIM are defined by

$$\Gamma_i=\frac{\beta(Z_i e)^2}{a_i} \ . \tag{1}$$

Here

$$a_i=\{4\pi N[(1-x)Z_1+xZ_2]/3VZ_i\}^{-1/3}$$

is the ion-sphere radius for an i ion, and β denotes the inverse temperature in energy units. Parameters Γ_i in Eq. (1) are related to each other as $\Gamma_2=R_Z^{5/3}\Gamma_1$. A BIM reduces to a OCP in the limit of $x\to 0$ or 1.

Excess internal energy normalized by N/β for a BIM fluid, denoted as $u_{\rm ex}^{\rm BIM}$, is sometimes represented as a sum of the linear-mixing (LM) value and the deviation therefrom; that is,

$$\Delta u_{\rm ex}^{\rm BIM}(R_Z,x,\Gamma_1)\equiv u_{\rm ex}^{\rm BIM}(R_Z,x,\Gamma_1)-u_{\rm LM} \ , \tag{2}$$

where

$$u_{\rm LM}\equiv(1-x)u_{\rm ex}^{\rm OCP}(\Gamma_1)+xu_{\rm ex}^{\rm OCP}(\Gamma_2) \tag{3}$$

and $u_{\rm ex}^{\rm OCP}(\Gamma)$ is the normalized excess internal energy for the OCP with the coupling parameter defined by $\Gamma=\beta(Ze)^2(4\pi N/3V)^{1/3}$.

The principal issue under debate is the sign of $\Delta u_{\rm ex}^{\rm BIM}$ at $x\ll 1$. Rosenfeld [2] criticized the use of the OI formula for $u_{\rm ex}^{\rm OCP}$ in OIIVH on the premise of DWSS's improved accuracy over OI's. In the following, we investigate accuracy of OI and DWSS formulas through examination of the MC data for the $u_{\rm ex}^{\rm OCP}$ themselves as well as through comparison of those formulas with the MC data.

In 1982, Slattery, Doolen, and DeWitt [7] (SDD) per-

formed MC simulations for OCP fluids by using $N=128$, 250, 432, 686, and 1024 MC particles to calculate u_{ex}^{OCP} at various values of Γ in the range $1\leq\Gamma\leq200$. They applied a "center-of-mass correction" to u_{ex}^{OCP} as

$$u'_{ex}=u_0+(u_{ex}^{OCP}-u_0)\frac{N}{N-1}$$

where u_0 is the Madelung energy for a crystalline solid, and obtained a fitting formula [Eq. (15) in [2]] for u'_{ex}.

Ogata and Ichimaru [3] examined the validity of such a center-of-mass correction on the basis of MC data for u_{ex}^{OCP} from newly performed simulations at $\Gamma=80$, 120, and 160, with $N=128$, 250, 432, 686, and 1024 MC particles as well as those from SDD simulations. It was thereby concluded that the correction could not always be justified for the OCP fluid; the values of u_{ex}^{OCP} exhibited no systematic N dependence for the cases with $N\geq432$, discernible within the statistical errors inherent in the MC samplings [8]. OI thereby fitted u_{ex}^{OCP} from SDD and OI simulations with $N\geq432$ in the form

$$u_{ex}^{OI}(\Gamma)=-0.898\,004\Gamma+0.967\,86\Gamma^{1/4}-0.860\,97+0.220\,703\Gamma^{-1/4}\,, \quad (4)$$

without the use of the center-of-mass corrections. The normalized excess free energies were then derived as

$$f_{ex}^{OI}(\Gamma)=-0.898\,004\Gamma+3.871\,44\Gamma^{1/4}-0.860\,97\ln\Gamma-2.526\,92-0.882\,812\Gamma^{-1/4}\,. \quad (5)$$

Later on, DeWitt, Slattery, and Stringfellow [4] performed additional MC simulations for the OCP fluid at $\Gamma=150$ ($N=686$), 160 (500,686), 180 (500), and 200 (686). MC data for u_{ex}^{OCP} obtained by SDD and DWSS simulations with $N=686$, without the center-of-mass corrections, were then fitted in the form

$$u_{ex}^{DWSS}(\Gamma)=-0.8992\Gamma+0.596\Gamma^{0.3253}-0.268. \quad (6)$$

They thereby obtained the free energy as

$$f_{ex}^{DWSS}(\Gamma)=-0.8992\Gamma+1.8322\Gamma^{0.3253}-0.268\ln\Gamma-1.3693\,. \quad (7)$$

Table I compiles all the MC data for u_{ex}^{OCP} as well as comparisons with OI and DWSS representations in Eqs. (4) and (6). Here σ denotes the possible extent of the statistical errors inherent in the MC sampling. DWSS used 22 data, cases 1 to 22, to obtain u_{ex}^{DWSS} in Eq. (6), of which only case 21 represents a so called "long" simulation run.

We find from Table I the following. (i) For both DWSS and OI formulas, root-mean-square (rms) values of the

TABLE I. Comparison of the normalized excess internal energies for OCP fluids.

Case	Γ	N	Configurations (millions)	Ref.	u_{ex}^{OCP}	σ	$u_{ex}^{OI}-u_{ex}^{OCP}$	$u_{ex}^{DWSS}-u_{ex}^{OCP}$
1	1.0	686	4.0	SDD	−0.572	<0.001	0.0016	0.0008
2	2.0	686	3.1	SDD	−1.321	<0.001	0.0006	0.0013
3	3.0	686	8.0	SDD	−2.114	<0.001	0.0005	0.0004
4	4.0	686	7.3	SDD	−2.929	<0.001	0.0008	−0.0002
5	5.0	686	5.2	SDD	−3.758	<0.001	0.0019	0.0001
6	6.0	686	9.5	SDD	−4.595	<0.001	0.0018	−0.0007
7	10.0	686	7.7	SDD	−7.999	0.001	0.0032	−0.0005
8	15.0	686	5.5	SDD	−12.320	0.001	0.0059	0.0022
9	20.0	686	19.9	SDD	−16.675	0.001	0.0051	0.0023
10	30.0	686	13.9	SDD	−25.443	0.001	0.0013	0.0010
11	40.0	686	18.0	SDD	−34.257	0.001	−0.0023	−0.0002
12	50.0	686	19.7	SDD	−43.104	0.001	−0.0005	0.0038
13	60.0	686	15.9	SDD	−51.964	0.001	−0.0042	0.0018
14	80.0	686	30.8	SDD	−69.728	0.001	−0.0049	0.0033
15	100.0	686	23.8	SDD	−87.527	0.002	−0.0039	0.0049
16	120.0	686	31.8	SDD	−105.346	0.002	−0.0054	0.0028
17	140.0	686	23.7	SDD	−123.182	0.002	−0.0061	0.0003
18	150.0	686	31.9	DWSS	−132.107	0.0016	−0.0043	0.0008
19	160.0	686	38.6	SDD	−141.039	0.002	0.0017	0.0053
20	170.0	686	10.1	SDD	−149.970	0.003	0.0043	0.0062
21	180.0	686	143.0	DWSS	−158.900	0.0008	0.0037	0.0036
22	200.0	686	83.0	DWSS	−176.774	0.0011	0.010	0.006
23	160.0	500	78.0	DWSS	−141.038	0.0012	0.0007	0.0043
24	180.0	500	90.0	DWSS	−158.894	0.0012	−0.0023	−0.0024
25	80.0	686	6.7	OI	−69.729	0.0025	−0.0039	0.0043
26	80.0	1024	6.7	OI	−69.732	0.0023	−0.0009	0.0073
27	120.0	686	6.7	OI	−105.351	0.0031	−0.0004	0.0078
28	120.0	1024	6.7	OI	−105.353	0.0029	0.0016	0.0098
29	160.0	686	7.7	OI	−141.031	0.0031	−0.0063	−0.0027
30	160.0	1024	7.7	OI	−141.035	0.0032	−0.0023	0.0013

deviations $u_{ex}^{OI\{DWSS\}} - u_{ex}^{OCP}$ over cases 1 to 21 are virtually the same and take on a magnitude ~ 0.003. Since these rms values are comparable to $\sigma = 0.001-0.003$ in each MC value, we may regard both DWSS and OI formulas as adequate representations of the MC data. (ii) MC values of u_{ex}^{OCP} have weak but significant N dependence as can be seen in a comparison between case 19 with $N=686$ and case 23 with $N=500$, and also between case 21 with $N=686$ and case 24 with $N=500$. Overall, including the remark made in Ref. [8], we assess that the current values of u_{ex}^{OCP} have inherent uncertainties, *at least,* of $\sim \pm 0.001$ for the data listed in Table I.

Combining (i) and (ii) above, we assess possible errors in $u_{ex}^{OI\{DWSS\}}$ to be ± 0.004 for either OI or DWSS. Differentials between OI and DWSS may thus contain errors $\sim \pm 0.008$. The comparisons exhibited in Fig. 2 in Ref. [2] are thus all immersed in these errors. The graph may simply show the differences in formulas between a linear function of $\Gamma^{0.3253}$ and a polynomial with $\Gamma^{1/4}$. With the errors inherent in $u_{ex}^{OI\{DWSS\}}$, errors in u_{LM} are again on the order of ± 0.004 for both DWSS and OI. Since the magnitude of Δu_{ex}^{BIM} at $x=0.01$ under the present examination (cf. Table I in Ref. [2]) is on the order of or smaller than 0.004, we may conclude that one cannot judge the sign and magnitude of Δu_{ex}^{BIM} through a combination of $u_{ex}^{OI\{DWSS\}}$ and MC data for u_{ex}^{BIM}.

It must be pointed out in this connection that the DWSS formulas [Eqs. (6) and (7)] contain certain inconsistencies in the numerical representations as follows. (i) Since their leading first terms are expressed as -0.8992Γ, one would assess uncertainty on the order of 10^{-4} for their coefficient, 0.8992. This, in turn, would mean uncertainty on the order of 10^{-2} in the evaluation of u_{ex}^{DWSS}, exceeding the limit of uncertainty for the issues under consideration, which should be on the order of 10^{-3} (see Table I). (ii) The coefficient of the second term of $0.596\Gamma^{0.3253}$ in Eq. (6) has been given a three-digit accuracy. The coefficient of the corresponding term $1.8322\Gamma^{0.3253}$ in Eq. (7) derived from Eq. (6), on the other hand, has been given a five-digit accuracy.

III. SUM RULE ANALYSIS

The screening potential for the OCP fluid is defined [1,5,6] in terms of the radial distributions $g(r)$ as

$$H(r)=\frac{(Ze)^2}{r}+\beta \ln[g(r)] \ . \tag{8}$$

It has been shown [1,5,6] that the screening potential at the origin is related to the difference in excess free energy before and after the nuclear fusion; that is,

$$H(0)=F_{ex}^{BIM}(N,0)-F_{ex}^{BIM}(N-2,1) \ ,$$

where $F_{ex}^{BIM}(N_1,N_2)$ denotes the excess free energy of a BIM composed of N_1 ions with $Z_1=Z$ and N_2 ions with $Z_2=2Z$. Hence

TABLE II. Values of each term in $(\partial/\partial x)\Delta f_{ex}^{BIM}|_{x=0}$ [Eq. (9)].

Γ	$2f_{ex}^{OCP}(\Gamma)-f_{ex}^{OCP}(2^{5/3}\Gamma)$ DWSS	OI	$\beta H^{OII}(0)$
10	10.994	10.993	11.254
20	21.905	21.912	22.356
40	43.515	43.528	44.437
80	86.421	86.425	88.275
160	171.795	171.743	175.325

$$\left.\frac{\partial}{\partial x}\Delta f_{ex}^{BIM}(R_Z=2,x,\Gamma_1)\right|_{x=0} = 2f_{ex}^{OCP}(\Gamma_1)-f_{ex}^{OCP}(2^{5/3}\Gamma_1)-\beta H(0) \ , \tag{9}$$

where

$$\Delta f_{ex}^{BIM}(2,x,\Gamma_1)=\int_0^{\Gamma_1}\frac{d\Gamma'}{\Gamma'}\Delta u_{ex}^{BIM}(2,x,\Gamma') \ .$$

Recently, Ichimaru, Ogata, and Tsuruta [6] examined the accuracy of $H(0)$ calculated in various schemes. They have clarified the approximate nature of the extrapolation scheme adopted by Rosenfeld [9] and confirmed the accuracy of a first-principles calculation by Ogata, Iyetomi, and Ichimaru [5] (OII),

$$\beta H^{OII}(0)=1.148\Gamma-0.009\,44\Gamma\ln\Gamma -0.0001\,168\Gamma(\ln\Gamma)^2 \ . \tag{10}$$

In this connection, we note that Alastuey-Jancovici values [10] for $H(0)$ referred to in Ref. [2] were obtained by *assuming*

$$\beta H^{AJ}(0)=2f_{ex}^{OCP}(\Gamma)-f_{ex}^{OCP}(2^{5/3}\Gamma) \ .$$

Table II compares calculated values of each term in the right hand side of Eq. (9) at various values of Γ. Here we have set $H(0)=H^{OII}(0)$ [Eq. (10)] and used either f_{ex}^{OI} [Eq. (5)] or f_{ex}^{DWSS} [Eq. (7)] for f_{ex}^{OCP}. In either case, $(\partial/\partial x)\Delta f_{ex}^{BIM}|_{x=0}$ takes on *negative* values, which imply $\Delta u_{ex}^{BIM}<0$ at $x \ll 1$.

IV. CONCLUDING REMARKS

In conclusion, the present analyses for the accuracy of the formulas Eqs. (4), (6), and (10) consolidated the OIIVH prediction of $\Delta u_{ex}^{BIM}<0$ for BIM's with $x \ll 1$.

Rosenfeld proposed a variational hard-sphere model to examine $\Delta u_{ex}^{BIM,var}$ in Sec. IV in Ref. [2]. As may be clear from the foregoing arguments, any meaningful examination for Δu_{ex}^{BIM}, however, must be based on a theory or a representation which can describe u_{ex}^{OCP} with an accuracy of 10^{-3} or better. Since no such proof of accuracy has been given on that model, the comparison between $\Delta u_{ex}^{BIM,var}$, $\Delta u_{ex}^{BIM,DWSS}$, and $\Delta u_{ex}^{BIM,OI}$ in Table I in Ref. [2] may be of no physical significance.

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