Addendum to "Equation of state of classical Coulomb plasma mixtures"

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Recently developed analytic approximation for the equation of state of fully ionized nonideal electron-ion plasma mixtures [A. Y. Potekhin, G. Chabrier, and F. J. Rogers, Phys. Rev. E **79**, 016411 (2009)], which covers the transition between the weak and strong Coulomb coupling regimes and reproduces numerical results obtained in the hypernetted-chain (HNC) approximation, is modified in order to fit the small deviations from the linear mixing in the strong-coupling regime, revealed by recent Monte Carlo simulations. In addition, a mixing rule is proposed for the regime of weak coupling, which generalizes post-Debye density corrections to the case of mixtures and numerically agrees with the HNC approximation in that regime.

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I. INTRODUCTION

The high accuracy of the linear-mixing rule (LMR) for multicomponent strongly coupled Coulomb plasmas has been confirmed in a number of papers [1–7]. Nevertheless, the accuracy of modern Monte Carlo (MC) calculations allows one to reveal certain deviations from the LMR for the Coulomb energy U of binary ionic mixtures (BIM). On the other hand, for weakly coupled plasmas, the Debye-Hückel (hereafter DH) formula is applicable instead of the LMR. Several terms in the density expansion of U beyond the DH approximation were obtained by Abe [8] and by Cohen and Murphy [9] (hereafter ACM) in the one-component plasma (OCP) case.

In Ref. [3], deviations from the LMR for BIM were studied in the hypernetted-chain (HNC) approximation and fitted by Padé approximants. In Ref. [4], the LMR was confirmed by HNC method for *polarizable* background of partially degenerate electrons. In Ref. [5], deviations from the LMR for strongly coupled BIM were studied using both HNC and MC techniques. The corrections to the LMR for U were found to be on the same order of magnitude for HNC and MC but numerically different; in particular, it does not depend on the mean ion Coulomb coupling parameter Γ according to HNC results but decreases as a function of Γ in MC simulations. These results were confirmed in Ref. [7], where an analytic fit to the calculated corrections was suggested. The fitting formulas of Refs. [3,7] are applicable only at $\Gamma \geq 1$; in particular, they do not reproduce the DH limit at $\Gamma \to 0$ (besides, the fit parameters in [3] are given only for five fixed ionic charge ratios from 2 to 8).

In Ref. [10], HNC calculations of BIM and three-component ionic mixtures (TIMs) were performed in a wide range of values of Γ, charge ratios, and partial densities of the ion components, and a parametric formula was suggested to fit the *fractional* differences between the LMR and calculated plasma energies at any Γ in liquid multicomponent plasmas. It recovers the DH formula at $\Gamma \ll 1$ and gives a vanishing fractional difference from the LMR at $\Gamma > 1$.

However, in the regime of *strong* coupling, the accuracy of the HNC method (typically a few parts in 1000, for U) is not sufficient to reproduce the values of the energies of mixtures at the precision level needed to study deviations from the LMR (see, e.g., [5]). Indeed, according to Refs. [3,5,7] these deviations are typically on the order of a few $\times(10^{-3}-10^{-2})kT$ per ion (where k is the Boltzmann constant), while $U \sim -\Gamma kT$ per ion at $\Gamma \gg 1$.

In this Brief Report, we suggest two improvements for analytic treatment of ion mixtures. First, we introduce a mixing rule for weakly coupled plasmas, which provides an extension of the ACM formula to the case of ion mixtures and agrees with HNC results up to the values of the Coulomb coupling parameter $\Gamma \approx 0.1$ (whereas, the DH approximation becomes inaccurate at $\Gamma \gtrsim 0.01$). Second, using MC simulations of strongly coupled liquid BIM, supplementary to those already published in [5–7], we suggest a modified version of the formula [10], which maintains the accuracy of the previous fit at intermediate and weak coupling, but delivers consistency with the MC data for strongly coupled Coulomb liquids.

In Sec. II we introduce basic notations and formulas; in Sec. III we propose a mixing rule applicable at weak coupling; in Sec. IV we present a fitting formula for the internal energy of mixtures, applicable in the entire domain of Γ values for weakly and strongly coupled classical Coulomb gases and liquids; and in Sec. V we summarize the results.

II. BASIC EQUATIONS

Let n_e be the electron number density and n_j the number density of ion species with charge numbers Z_j $(j=1,2,\ldots)$. The total number density of ions is $n_{\rm ions}=\Sigma_j n_j$. The electric neutrality implies $n_e=\langle Z\rangle n_{\rm ions}$. Here and hereafter, the angular brackets denote averaging with statistical weights proportional to n_j

$$\langle Z\rangle \equiv \sum_j x_j Z_j, \quad \text{where } x_j \equiv \frac{n_j}{n_{\rm ions}}. \tag{1}$$

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The strength of the Coulomb interaction of ion species j is characterized by the Coulomb coupling parameter defined (in cgs units) as $\Gamma_j=(Z_je)^2/a_jkT=\Gamma_eZ_j^{5/3}$, where $a_j=a_eZ_j^{1/3}$ is the ion sphere radius, $\Gamma_e\equiv e^2/a_ekT$, and $a_e\equiv(4\pi n_e/3)^{-1/3}$. In other words, partial coupling parameters Γ_j and ion sphere radii a_j are defined to be those of the OCP of ions of the jth kind at the same electron density n_e, as in the considered multicomponent plasma. The Coulomb coupling in the mixture of different ions is conventionally characterized by the average coupling parameter $\Gamma=\Gamma_e\langle Z^{5/3}\rangle$.

A common approximation for the Coulomb contribution to the internal energy of a strongly coupled ion mixture is the LMR

$$u_{\mathrm{LM}}(\Gamma)=\sum_j x_ju(\Gamma_j,x_j=1), \tag{2}$$

where $u\equiv U/N_{\mathrm{ions}}kT$ is the reduced Coulomb energy, N_{ions} is the total number of all ions, and the subscript "LM" denotes the linear-mixing approximation. Obviously, the LMR has the same form for the Coulomb contribution to the reduced Coulomb free energy $f\equiv F/N_{\mathrm{ions}}kT$.

When the Coulomb interaction is sufficiently weak compared to the thermal energy, then the DH approximation can be applied $u_{\mathrm{DH}}=\langle q^2\rangle/kTr_D$, where $\langle q^2\rangle$ is the mean-squared charge of the considered mixture and $r_D=(kT/4\pi n_{\mathrm{ions}}\langle q^2\rangle)^{1/2}$ is the Debye radius. For the model of ions in the "rigid" electron background, applicable if the electrons are extremely strongly degenerate, $\langle q^2\rangle=e^2\langle Z^2\rangle$, whereas in the case of completely nondegenerate electrons, using our definition (1) of averaging over the *ion* species and taking into account the neutrality condition, we have $\langle q^2\rangle=e^2(\langle Z^2\rangle+\langle Z\rangle)$.

In this Brief Report, we consider the model of rigid electron background, but the extension to the case of compressible background is possible by adjusting the parameter δ in Eq. (9) below, according to the expression for $\langle q^2\rangle$. In Ref. [10], this extension was shown to be compatible with numerical HNC data [4] for ion mixtures with allowance for electron polarization.

III. WEAKLY COUPLED ION MIXTURES

For a OCP at $\Gamma\ll 1$, a cluster expansion yields [8,9]

$$u=-\frac{\sqrt{3}}{2}\Gamma^{3/2}-3\Gamma^3\left[\frac{3}{8}\ln(3\Gamma)+\frac{C_E}{2}-\frac{1}{3}\right]-\Gamma^{9/2}(1.687\,5\sqrt{3}\,\ln\Gamma-0.235\,11)+\cdots, \tag{3}$$

where $C_E=0.577\,21\ldots$ is the Euler constant. Here, the first term is the DH energy.

In order to generalize this expression to the case of multicomponent Coulomb plasmas, let us write the OCP energy in the form

$$u(\Gamma)=\Gamma\tilde{u}(a/r_D), \tag{4}$$

where a is the ion sphere radius for the OCP, and $\tilde{u}$ is the Coulomb energy per ion in units of $(eZ)^2/a$ ($\tilde{u}=-0.9$ in the ion sphere model [11]). Then the following relation holds in the DH approximation for multicomponent plasmas:

$$u=\sum_j x_j\Gamma_j\tilde{u}(\kappa_j),\quad \kappa_j\equiv\frac{a_j}{r_D}=\sqrt{3\Gamma_e\frac{\langle Z^2\rangle}{\langle Z\rangle}}Z_j^{1/3}. \tag{5}$$

Let us assume that relation (5) can be applied also to the higher-order corrections beyond DH. In this case, according to Eqs. (3) and (4), in the ACM approximation

$$\tilde{u}(\kappa)=-\frac{\kappa}{2}-\kappa^4\left[\frac{1}{4}\ln\kappa-0.014\,908\,5\right]-\kappa^7\left[\frac{1}{8}\ln(\kappa)-0.073\,69\right]. \tag{6}$$

Since $\kappa\propto\sqrt{\Gamma}$ for a fixed composition, f can be obtained from u by integration, which yields

$$f=\sum_j x_j\Gamma_j\tilde{f}(\kappa_j), \tag{7}$$

where

$$\tilde{f}(\kappa)=-\frac{\kappa}{3}-\frac{\kappa^4}{12}(\ln\kappa-0.226\,3)-\kappa^7(0.027\,78\ln\kappa-0.019\,46). \tag{8}$$

In Figs. 1–4, deviations from the LMR $\Delta u\equiv u-u_{\mathrm{LM}}$, calculated according to Eqs. (5) and (6), are plotted by long-dashed lines and compared to the DH formula (short-dashed lines) and the HNC data (crosses). We see that the suggested approximation (5) agrees with the data to much higher Γ values than the DH approximation.

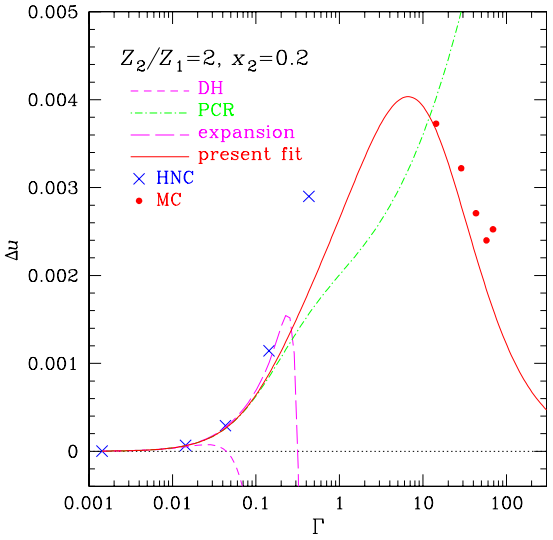

FIG. 1. (Color online) Correction to the LMR $\Delta u=u-u_{\mathrm{LM}}$ as a function of Γ for BIM with $Z_2/Z_1=2$, $x_2=0.2$. HNC (crosses) and MC (dots) data are compared to the DH approximation (short-dashed lines), the modified ACM approximation (5) (long-dashed lines), the fit from [10] (dot-dashed lines), and the present fit (9) (solid lines).

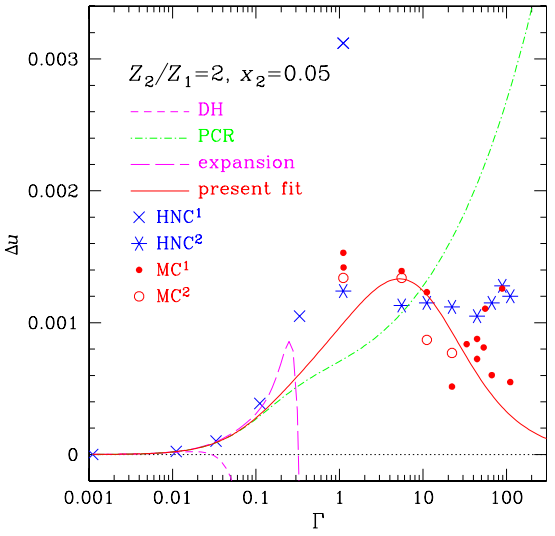

FIG. 2. (Color online) $\Delta u = u - u_{\rm LM}$ as a function of Γ for BIM with $Z_2/Z_1=2$, $x_2=0.05$. Here crosses (HNC[1]) correspond to Δu obtained from the HNC data using the OCP fit from [12] for calculation of $u_{\rm LM}$, and asterisks (HNC[2]) correspond to Δu from Ref. [5], where *both* u and $u_{\rm LM}$ are based on the HNC results. Dots (MC[1]) correspond to Δu calculated from the recent MC data for u, and $u_{\rm LM}$ calculated from the OCP fit [12], while circles (MC[2]) represent MC data [5] for Δu.

IV. COULOMB LIQUIDS AT ARBITRARY COUPLING

In order to find an analytic approximation for the correction to the LMR in the largest possible interval of Γ for ion gases and liquids, we have selected from the numerical HNC data [10] the subset related to $\Gamma \le 1$, which counts 161 different combinations of x_2, Z_2, and Γ in BIM and 54 combinations of x_2, Z_2, x_3, Z_3, and Γ in TIM (assuming $Z_1=1$), supplemented this HNC data by numerical MC data for BIM at $\Gamma > 1$ (94 combinations of x_2, Z_2, and Γ), and looked for an analytic formula, which provides a reasonable compromise between simplicity and accuracy for representing this data. The MC data have been partly taken from the previous work [5–7] and partly obtained by new MC simulations using the same computer code as before. Our fitting formula for the addition to the reduced free energy $f=F/N_{\rm ions}kT$, relative to the LMR prediction $f_{\rm LM}$, reads as

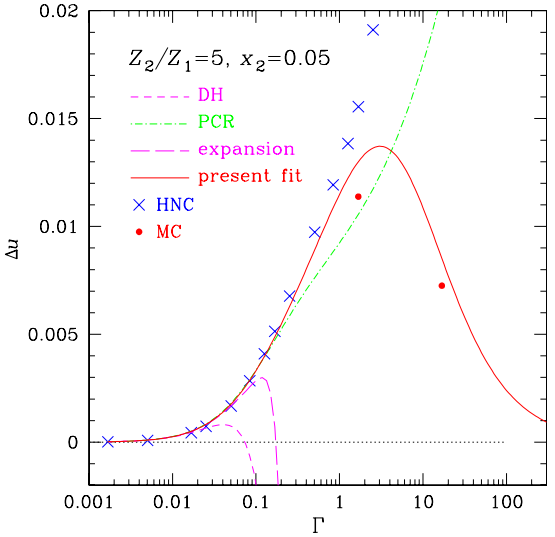

FIG. 3. (Color online) The same as in Fig. 1 but for $Z_2/Z_1=5$ and $x_2=0.05$.

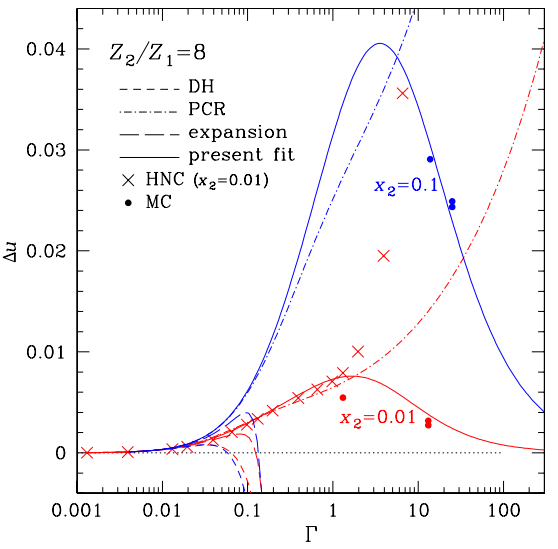

FIG. 4. (Color online) The same as in Fig. 1 but for $Z_2/Z_1=8$ and two values of x_2: 0.01 and 0.1 (marked near the dots).

$$\Delta f \equiv f - f_{\rm LM} = \frac{\Gamma_e^{3/2}\langle Z^{5/2}\rangle}{\sqrt{3}} \frac{\delta}{(1+a\Gamma^\alpha)(1+b\Gamma^\alpha)^\beta}, \qquad (9)$$

where δ is determined by the difference between the LMR and DH formula at $\Gamma \to 0$ (exactly as in Ref. [10])

$$\delta = 1 - \frac{\langle Z^2\rangle^{3/2}}{\langle Z\rangle^{1/2}\langle Z^{5/2}\rangle}, \qquad (10a)$$

for rigid electron background model, and

$$\delta = \frac{\langle Z(Z+1)^{3/2}\rangle}{\langle Z^{5/2}\rangle} - \frac{(\langle Z^2\rangle + \langle Z\rangle)^{3/2}}{\langle Z\rangle^{1/2}\langle Z^{5/2}\rangle}, \qquad (10b)$$

for polarizable background. The expression (10b) for δ is exact in the limit of nondegenerate electrons, but its use in Eq. (9) provides a satisfactory agreement with numerical data [4] obtained with allowance for the polarizability of partially degenerate electron gas (see [10]).

The fit parameters a, b, and α are chosen so as to minimize the mean-square difference between the fit and the data for $\Delta u/u_{\rm LM}$ at $\Gamma \le 1$ and for Δu at $\Gamma > 1$, while the power index β is defined so as to quench the increase of Δf at $\Gamma \to \infty$. These parameters depend on the plasma composition as follows:

$$a = \frac{2.6\delta + 14\delta^3}{1-\alpha}, \quad \alpha = \frac{\langle Z\rangle^{2/5}}{\langle Z^2\rangle^{1/5}}, \qquad (11)$$

$$b = 0.0117\left(\frac{\langle Z^2\rangle}{\langle Z\rangle^2}\right)^2 a, \quad \beta = \frac{3}{2\alpha} - 1. \qquad (12)$$

The numerical difference of Eq. (9) from the formula in Ref. [10] is small at $\Gamma \lesssim 1$, but at $\Gamma \gg 1$ the correction to the LMR prediction for the reduced internal energy

$$\Delta u = \Gamma \frac{\partial(\Delta f)}{\partial \Gamma} = \left(\frac{3}{2} - \frac{a\alpha\Gamma^{\alpha}}{1 + a\Gamma^{\alpha}} - \frac{b\alpha\beta\Gamma^{\alpha}}{1 + b\Gamma^{\alpha}} \right) \Delta f \qquad (13)$$

now decreases at large Γ in agreement with the MC results. Moreover, Eq. (13) describes most of the data with much higher accuracy than the fit to Δu suggested in Ref. [7] for BIM at $\Gamma > 1$.

A comparison of the numerical HNC data for Δf and Δu and MC data for Δu to Eq. (9) and to the previous fit [10] shows that the present fit has nearly the same accuracy as the previous one for BIM at $\Gamma < 1$ (slightly worse for small $\Delta u/u$, slightly better for larger $\Delta u/u$), but it is generally better for TIM at $\Gamma \leq 1$ and substantially better for BIM at $\Gamma > 1$. Examples of Γ dependences of Δu are shown in Figs. 1–4, where the dot-dashed lines correspond to the older fit and the solid lines to the present fit. The modification of the fit at small Γ values proves to be negligible, which has been checked by comparison of fractional differences between the Coulomb part of the free energy and the LMR prediction, as in Ref. [10]; whereas the modification at large Γ can be significant, as confirmed by Figs. 1–4.

V. CONCLUSIONS

We have reconsidered free and internal energies of classical ionic mixtures in the liquid state, taking into account the results of HNC calculations in the regime of weak and moderate Coulomb coupling and MC simulations at strong coupling, and proposed two analytic approximations for such mixtures: the mixing rule (5), which works well at the Coulomb coupling parameter $\Gamma < 1$, and the analytic fitting formula (9), which is along with its derivative (13) applicable at any values of Γ.

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