Free-energy model for charged Yukawa mixtures: Asymptotic strong-coupling limit and a nonlinear mixing rule

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A free-energy model for mixtures of charged particles interacting through the Yukawa repulsive potential is derived analytically from the Onsager-type exact lower bound for the free energy of the system. It takes the form of a "nonlinear mixing rule," which relates the configurational free energy of the mixture to that of the one-component Yukawa system. This scaling law holds, under broad assumptions, for the exact Madelung (i.e., asymptotic strong-coupling) energy term for the fluid; within the hypernetted-chain approximation, it is very accurate also for conditions of intermediate and weak coupling. The physics relating this mixing rule with the well-known volume-additivity rule for the Thomas-Fermi mixing of elements is revealed.

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I. INTRODUCTION

Many quite disparate systems with screened Coulomb interactions can be described by Yukawa interparticle potentials which thus make important reference systems in condensed-matter physics [1]. Systems with *repulsive* Yukawa potentials [2–4] provide models for, e.g., dense stellar materials [5], inertially confined plasmas [5], and "mesoscopic plasmas" of charge-stabilized colloidal suspensions such as latex spheres in water [6–8]. They are useful to test general ideas about phase transitions [9] because the shape of the potential varies continuously with the screening length. Screened binary ionic mixtures [2–5] have an immediate application to astrophysical problems involving phase separation of elements [10,11] and to inertial-confinement experiments in plasma physics, which require [12–14] very accurate equations of state. The accurate free energy of the mixture is also required, through the zero-separation theorem, for calculating enhancement factors for nuclear reaction rates [15,16], and in liquid-state theory [17].

An accurate scaling law, which relates the configurational free energy of the mixture to that of the one-component system, is important because of its physics content and because it facilitates the representation of a large body of data for mixtures of, e.g., different charges and compositions, in a concise form. A widely used approximation of plasma mixtures is the empirical "linear mixing rule" [12,13]. It states that, e.g., the energy of the plasma mixture at constant temperature T and charge density ρ' can be expressed, to a high degree of accuracy, as a linear interpolation between the energies of the respective pure phases. The linear rule for unscreened [14] and moderately screened [2] binary ionic mixtures, is based on the "ion-sphere" model, which provides an Onsager-type [18] exact lower bound for the potential energy of the mixture, as first proven by Lieb and Narnhofer [19]. The linear mixing rule was first verified by extensive hypernetted-chain calculations, which provide a very useful tool for developing such theories [5,12,13], and only later was it validated by the heavy simulations [5] which were required. The main purpose of the present paper is to apply this methodology (as first taken for the Coulomb potential) to the Yukawa potential: The first step requires the generalization to the Yukawa potential, of the Lieb-Narnhofer procedure for obtaining the Onsager-type bound. The second step is the verification of the implied "rule" by the hypernetted-chain approximation. It is hoped that the results of these two analytical and semianalytical treatments, respectively, will motivate the heavy simulations required to test these approximations.

The observation of a special *renormalization* property of the Yukawa potential (Sec. II) makes it possible to evaluate analytically the Onsager-type *exact lower bound* for the energy of the general mixture with Yukawa *repulsive* interactions (Sec. III). The exact energy lower bound induces a *"nonlinear mixing rule"* for strongly coupled systems. The present nonlinear mixing rule reduces to the linear rule for weak screening, yet it is valid even for very strong screening conditions (Sec. IV). Pending the very heavy simulations needed for testing the new *"nonlinear mixing rule,"* a numerical solution of the hypernetted-chain equations for a large variety of binary Yukawa mixtures supports its validity even for intermediate and weak coupling (Sec. IV). The physics relating this nonlinear rule with the Thomas-Fermi equation of state for mixtures of elements is revealed (Sec. V). The relevance of these results for calculations of thermodynamic properties and phase behavior of the fluid mixture is pointed out (Sec. VI).

II. CHARGE RENORMALIZATION FOR THE YUKAWA POTENTIAL

The Yukawa intermolecular potential, $\phi_Y(r)=e^{-\alpha r}/r$, has the special property that it gives rise to the same functional form for the potential outside a spherically symmetric distribution of matter.

Consider the bipolar-coordinate result for the convolution of two spherically symmetric functions:

$$F(r)=\int \rho(u)\phi(|\mathbf{r}-\mathbf{u}|)d\mathbf{u}$$
$$=(2\pi/r)\int_0^\infty \rho(x)x\,dx\int_{|x-r|}^{x+r}\phi(y)y\,dy\ . \quad (1)$$

For a confined charge distribution, $\rho(x\geq R)=0$, and potential function $\phi(y)$, obtain the following expression for the potential *outside* the charge distribution:

$$\Phi(r\geq R)=(2\pi/r)\int_0^R \rho(x)x\,dx\int_{r-x}^{r+x}\phi(y)y\,dy \quad (2)$$

which for the Yukawa potential, $\phi(y)=\phi_Y(y)=\exp(-\alpha y)/y$, takes the form

$$\Phi(r\geq R)=[\exp(-\alpha r)/r]\left[(2\pi/\alpha)\int_0^R \rho(x)x[\exp(\alpha x)-\exp(-\alpha x)]dx\right], \quad (3)$$

i.e.,

$$\Phi(r\geq R)=[1/q(\alpha,R)][\exp(-\alpha r)/r]\ , \quad (4)$$

where

$$[1/q(\alpha,R)]=\left[(4\pi/\alpha)\int_0^R \rho(x)x\sinh(\alpha x)dx\right]\ . \quad (5)$$

Thus, if a point Yukawa charge Z is smeared out radially up to a finite radius R, and if at the same time the charge is appropriately renormalized, $Z_{\text{renorm}}=q(\alpha,R)Z$, then the potential outside the smearing radius R remains the same as for the original point charge.

For a uniform distribution inside a sphere of radius R, $\rho(r\leq R)=3/4\pi R^3$, I obtain

$$q(\alpha,R)_{\text{uniform}}=Q(\alpha R)\leq 1\ , \quad (6a)$$

$$Q(t)=(2t^3/3)/[e^t(t-1)+e^{-t}(t+1)]$$
$$=1-t^2/10+9t^4/1400+\cdots\ . \quad (6b)$$

The Gauss-Newton theorem for the Coulomb potential ($\alpha=0$) is manifestly satisfied by $Q(0)=1$. Consider two "renormalized" charges $Z_iQ(\alpha R_i)$ and $Z_jQ(\alpha R_j)$ uniformly smeared inside spheres of radii R_i and R_j, respectively, separated by a distance, r, and interacting via the Yukawa potential. The interaction between these two distributions, $\psi_{ij}(r)$, has the familiar convolution-type Fourier transform,

$$\psi_{ij}(k)=Z_iQ(\alpha,R_i)Z_jQ(\alpha R_j)\rho(kR_i)\rho(kR_j)\phi_Y(k)\ , \quad (7)$$

where $\phi_Y(k)=4\pi/(k^2+\alpha^2)$ and $\rho(k)=3[\sin(k)-k\cos(k)]/k^3$. Because of the renormalization property, however, it obeys

$$\psi_{ij}(r)=Z_iZ_j\phi_Y(r)=Z_iZ_je^{-\alpha r}/r,\quad \text{for } r\geq R_i+R_j\ , \quad (8a)$$

and it can be separately checked that

$$\psi_{ij}(r)<Z_iZ_j\phi_Y(r),\quad \text{for } r<R_i+R_j\ . \quad (8b)$$

The renormalization property now enables us to follow the Onsager "smearing" procedure as developed for obtaining a lower bound for the potential energy of Coulomb systems [18–20], and apply it to general Yukawa systems. Here I apply it to systems of point particles interacting through Yukawa repulsive potentials.

III. EXACT "ONSAGER-TYPE" LOWER BOUND FOR THE POTENTIAL ENERGY

(a) Consider classical mixtures consisting of N_i positively charged, $Z_ie>0$, point particles of type i, interacting through the Yukawa pair potentials:

$$\phi_{ij}(r)/k_BT=Z_iZ_j\Gamma e^{-\alpha r}/r\ . \quad (9)$$

Hereafter distances are measured in units of the total Wigner-Seitz radius, $a=(3/4\pi n)^{1/3}$, $n=N/V=(\sum_i N_i/V)$ is the total number density, and Γ is the coupling constant (e.g., $\Gamma=e^2/ak_BT$ is the conventional plasma coupling parameter). The inverse screening length α can be density and temperature dependent. The interaction potential energy of the mixture (per particle, in temperature units) is given in general by the standard energy integral involving the pair (radial) distribution functions, $g_{ij}(r)$,

$$u=U/Nk_BT=(n/2)\sum_{i,j}x_ix_j\int g_{ij}(r)[\phi_{ij}(r)/k_BT]d^3r\ , \quad (10a)$$

where $x_i=N_i/N$ are the number concentrations. For the Yukawa potential this takes the special form

$$u=(3\Gamma/2)\sum_{i,j}x_ix_jZ_iZ_jG_{ij}(\alpha)\ , \quad (10b)$$

where $G_{ij}(\alpha)=\int rg_{ij}(r)e^{-\alpha r}dr$ is the Laplace transform of $[rg_{ij}(r)]$.

The Onsager smearing method [18–20] for the Yukawa potential now proceeds similarly to that for the Coulomb potential. Consider any physically allowed configuration of the point particles and denote its total potential energy by U_P. The energy is measured relative to the self-energy of the point charges. Consider a system, the "smeared system," with an identical configuration of the particles, but in which the point charges are smeared out within finite radii R_i, and the smeared charges are renormalized such that their potential outside the smearing radii remains identical to that of the original point charges. The total smeared charge inside a sphere of radius R_i is Z_iq_i where each renormalized charge q_i depends on R_i and on the smearing form. The total smeared charge density is $\rho_S=n\sum_i x_iZ_iq_i$, $n=N/V$ is the total number density. With the Wigner-Seitz radius, a, which is our unit of length, $n=3/4\pi$, and our energy unit is e^2/a. To neutralize the "smeared" system we immerse it in a uniform background Yukawa-charge of density $\rho_b=-\rho_S$. The neutralized "smeared" system thus consists of the smeared charges interacting via pair interaction $\Psi_{ik}(r)$, and the uniform background charge density. The total potential energy of the neutralized "smeared" system, U_S, is positive definite $U_S\geq 0$

since it is the total energy of a nonsingular Yukawa charge distribution of total charge density $\rho(\mathbf{r})$. Let $\Phi(\mathbf{r})$ be the corresponding potential at the point $\mathbf{r}$ in the "smeared" system, then

$$U_S=\tfrac{1}{2}\int \rho(\mathbf{r})\Phi(\mathbf{r})dV \ , \tag{11}$$

which in view of the differential relation

$$\nabla^2\Phi-\alpha^2\Phi=-4\pi\rho \tag{12}$$

and Green's identity

$$\int[\Phi\nabla^2\Phi+\nabla\Phi\cdot\nabla\Phi]dV=\int\Phi\nabla\Phi\cdot d\mathbf{S} \tag{13}$$

takes the form

$$U_S=\frac{1}{8\pi}\left[\int[|\nabla\Phi(\mathbf{r})|^2+\alpha^2\Phi^2(\mathbf{r})]dV-\int\Phi\nabla\Phi\cdot d\mathbf{S}\right] . \tag{14}$$

Since the surface integral is negligible in the thermodynamic limit, we find that U_S is a manifestly positive definite:

$$U_S=\frac{1}{8\pi}\left[\int[|\nabla\Phi(\mathbf{r})|^2+\alpha^2\Phi^2(\mathbf{r})]dV\right]\geq 0 . \tag{15}$$

Having defined the system composed of smeared charges and their neutralizing uniform background, consider now the "Ewald identity,"

$$U_P=(U_P-U_S)+U_S \ . \tag{16a}$$

Using $U_S\geq 0$ in this identity obtain the lower bound,

$$U_P\geq(U_P-U_S) \ , \tag{16b}$$

which is given by the following contributions:

$$(U_P-U_S)=\delta_{P,S}+B \ , \tag{16c}$$

where

$$\delta_{P,S}=[(\text{interaction between the point charges in } U)-(\text{interaction between the smeared charges in } U_S)] \tag{16d}$$

and

$$B=-[(\text{interaction between the smeared charges and the background in } U_S)+(\text{self-energy of the smeared charges in } U_S)+(\text{self-energy of the background in } U_S)] . \tag{16e}$$

If we consider only smeared-charge distributions, $\rho_i(r)$, for which [e.g., (8b)] the pair interaction between the point charges is greater or equal to that between the smeared charges, $Z_iZ_j\phi_Y(r)\geq\Psi_{ij}(r)$, then $\delta_{P,S}\geq 0$. The self-energy of the smeared charges is given by $(N/2)\sum_i x_i\Psi_{ii}(r=0)$. The self-energy of the background is $(\frac{1}{2})V(\rho_S)(\rho_S)\phi_Y(k=0)$. The interaction between the smeared charges and the background is $-V(\rho_S)(\rho_S)\phi_Y(k=0)=-V(\rho_S)^2(4\pi/\alpha^2)$. Using these expressions, a lower bound to the potential energy U is given by B in the form

$$U\geq B=-\frac{N}{2}\sum_i x_i\Psi_{ii}(r=0)+\frac{Nn}{2}\left[\sum_i x_iZ_iq_i\right]^2\phi_Y(k=0) . \tag{17}$$

By virtue of the Lieb-Narnhofer [19] result, the best such bound is obtained for the uniform smearing inside a radius R_i, for which the total volume of the smeared particles is equal to the volume of the system, i.e., their total packing fraction is equal to unity, $\eta=\sum_i x_iR_i^3=1$. For a uniform smearing obtain $q_i=Q(\alpha R_i)$ as given by (6), and $\Psi_{ij}(r)=\psi_{ij}(r)$ as given by (7) and (8), for which

$$n\psi_{ij}(k=0)=3Z_iQ(\alpha R_i)Z_jQ(\alpha R_j)/\alpha^2 \tag{18}$$

and

$$\psi_{ii}(r=0)=(Z_i^2/R_i)[Q(\alpha R_i)-(1+\alpha R_i)e^{-\alpha R_i}]\times 3Q(\alpha R_i)/(\alpha R_i)^2 . \tag{19}$$

Inserting (19) result into (17) and maximizing the bound B with respect to the radii R_i, subject to the constraint $\sum_i x_iR_i^3=1$, obtain the following optimized Onsager-Yukawa-type lower bound (denote $u_{OY}=B/Nk_BT$):

$$u_{OY}/\Gamma=\sum_i x_iu_i \ , \tag{20}$$

expressed as the sum of "self" (dependent only on each type i) terms:

$$u_i=(Z_i^2/R_i)u_0(\alpha R_i) \tag{21}$$

with the function $u_0(t)$ related to $Q(t)$ of (6b),

$$u_0(t)=(\tfrac{3}{2})Q(t)(t+1)e^{-t}/t^2 \tag{22}$$

and where the smearing radii, R_i [in Eq. (21)], are obtained from the solution of the following set of *nonlinear* coupled algebraic equations:

$$R_i^3=Z_iQ(\alpha R_i)/\sum_i x_iZ_iQ(\alpha R_i), \quad i=1,2,\ldots . \tag{23}$$

These results for the Yukawa mixture provide the first part in our program for generalizing the linear mixing rule to the Yukawa potential. They also provide concrete examples for general predictions [21] about the relation of the Onsager bound and the asymptotic strong-coupling limit of liquid-state theories [22].

(b) The excess (over ideal-gas) energy of the plasma as evaluated in the standard linear-response approximation of the electrons screening effects is related [3,17] to our energy expression, u, by using $[g_{ij}(r)-1]$ instead of $g_{ij}(r)$

in (10), and by subtracting the value of $(1/2k_BT)\langle Z^2\rangle e^2 \lim r\to 0[1/r-\phi(r)]$. Averages are defined hereafter by

$$\langle Z^m\rangle=\sum_i x_i Z_i^m \ . \tag{24}$$

The linear-response excess energy of the plasma is thus defined as

$$u_{\text{mix,lin.resp.}}=\frac{n}{2}\sum_{i,j}x_i x_j\int[g_{ij}(r)-1][\phi_{ij}(r)/k_BT]d^3r -(1/2k_BT)\langle Z^2\rangle e^2\lim_{r\to 0}[1/r-\phi(r)] \ . \tag{25a}$$

For Thomas-Fermi screening the effective potential is the Yukawa function, $\phi(r)=\phi_Y(r)$, and the linear-response excess energy of the plasma is

$$u_{\text{mix,lin,resp.}}=\frac{3\Gamma}{2}\sum_{i,j}x_i x_j Z_i Z_j G_{ij}(\alpha) -3\Gamma\langle Z\rangle^2/2\alpha^2-(\Gamma/2)\langle Z^2\rangle\alpha \tag{25b}$$

for which the Onsager bound (7) and (8) corresponds to replacing $u_0(t)$ in (22) by

$$u_{0,\text{lin.resp.}}(t)=u_0(t)-3/(2t^2)-t/2 =-\tfrac{9}{10}-(\tfrac{18}{175})t^2+\cdots \tag{25c}$$

[see also Eq. (34) below]. It should be noted that the functions $Q(t)$ and $u_{0,\text{lin.resp.}}(t)$ are *even functions* of their argument so that the Onsager bound for (25b) is an *even function* of α. Thus, for small values of α the Onsager bound predicts the following expansion for the linear-response excess free energy:

$$F(\Gamma,\alpha)/\Gamma=-\tfrac{9}{10}-(\tfrac{18}{175})\alpha^2+O(\alpha^4) \ . \tag{26a}$$

It is interesting to note here that the best fits [23,24] to simulation data yield

$$F(\Gamma,\alpha)/\Gamma=-0.8992-(0.3261/\pi)\alpha^2+\cdots \tag{26b}$$

for large values of Γ, in excellent agreement with the bound (26a). The weak screening expansion for the Onsager bound for the mixture [Eqs. (20)–(23)] is given by

$$u_{\text{mix,lin.resp.}}=-0.9\langle Z^{5/3}\rangle\langle Z^{1/3}\rangle+A_{\text{nonlin}}\alpha^2+O(\alpha^4) \ , \tag{27a}$$

where the first term is the standard linear-mixing (ion-sphere) result [12,13] for unscreened plasmas, and

$$A_{\text{nonlin}}=-(\langle Z^{7/3}\rangle/\langle Z\rangle^{1/3})\{(\tfrac{18}{175})+(\tfrac{3}{100})[1-\langle Z^{5/3}\rangle^2/\langle Z^{7/3}\rangle/\langle Z\rangle] +(\tfrac{1}{100})[(\langle Z^{5/3}\rangle^2/\langle Z^{7/3}\rangle/\langle Z\rangle)-(\langle Z^{5/3}\rangle\langle Z\rangle^{2/3}/\langle Z^{7/3}\rangle)]\} \ . \tag{27b}$$

This expansion is in agreement only with general trends along the coefficients in a fit [25] to simulation data which, as they stand, cannot be compared in full detail with the present result. To obtain A_{nonlin} we solve Eqs. (23) to leading order:

$$R_i=(Z_i/\langle Z\rangle)^{1/3}\{1-(\alpha^2/30)[(Z_i/\langle Z\rangle)^{2/3}-(\langle Z^{5/3}\rangle/\langle Z\rangle^{2/3}/\langle Z\rangle)]+O(\alpha^4)\} \ . \tag{27c}$$

IV. NONLINEAR MIXING RULE: VERIFICATION WITHIN THE HYPERNETTED-CHAIN APPROXIMATION

The second part of our program is to identify the mixing rule as implied by the Onsager bound and to check it within the hypernetted-chain approximation.

Considering again Eqs. (20)–(23), define

$$\Gamma_i=(Z_i^2/R_i)\Gamma, \quad \alpha_i=\alpha R_i \ , \tag{28}$$

with R_i given by Eqs. (23), and obtain

$$u_{\text{OY}}=\sum_i x_i\Gamma_i u_{\text{O}}(\alpha_i)=\sum_i x_i u_{\text{OY},1}(\Gamma_i,\alpha_i) \ , \tag{29}$$

where $u_{\text{OY},1}(\Gamma,\alpha)$ is the Onsager bound for the one-component Yukawa system with unit charges, $Z_i=1$.

Under broad assumptions the Onsager bound is the exact leading term in the strong coupling expansion for the fluid potential energy [21]. To the extent that its scaling properties apply also for arbitrary values of the coupling parameter, this strong-coupling limit suggests the following general scaling approximation for repulsive-Yukawa fluids:

$$u_{\text{mix}}=\sum_i x_i u_i(\Gamma_i,\alpha_i) \ , \tag{30}$$

where u_{mix} and u_1 refer to the mixture and to the one-component energies, as given by (10) with the *exact* $g_{ij}(r)$, and where Eqs. (23) are used in (28). This *"nonlinear mixing rule,"* Eqs. (30), (28), and (23), is the main result of this work. In accordance with how α depends on the density and on the temperature, relation (30) can be integrated to yield the configurational free energy. The limit $\alpha=0$ of the nonlinear mixing rule corresponds to the "linear mixing rule" [2,12–14] for unscreened plasmas. The limit $\alpha=0$ of Eqs. (23), $R_i=(Z_i/\langle Z\rangle)^{1/3}$, when employed in (28) and (30) with $\alpha\neq 0$ is a generalization of the "linear mixing rule" to the Yukawa potential. In the expansion for $u_{\text{mix,lin.resp.}}$ it corresponds to a different coefficient of the α^2 term, namely

$$A_{\text{lin}}=-(\langle Z^{7/3}\rangle/\langle Z\rangle^{1/3})\{(\tfrac{18}{175})+(\tfrac{1}{100})[(\langle Z^{5/3}\rangle^2/\langle Z^{7/3}\rangle/\langle Z\rangle)-(\langle Z^{5/3}\rangle\langle Z\rangle^{2/3}/\langle Z^{7/3}\rangle)]\} \ , \tag{31}$$

which is the expression for A_{nonlin} but without the second term. The comparison of A_{nonlin} with A_{lin} gives some indication of the difference between the linear and nonlinear mixing rules as applied to electron-screened plasmas.

The *nonlinear* mixing rule, Eqs. (30), (28), and (23), should be verified eventually by simulations but, similarly to the past experience with the linear rule, it is expected that a good indication for its general validity can be obtained within the hypernetted-chain approximation. From such extensive calculations [26] for binary mixtures I find that the nonlinear rule holds to an accuracy of about 0.1% for a wide range of values for the physically relevant parameters, namely, values of $\alpha \leq 3$, charge ratios $Z_1/Z_2 \leq 30$, and effective coupling $1 \leq \Gamma_{\text{eff}} = (\sum_i x_i \Gamma_i) e^{-\alpha} \leq 200$. This high accuracy increases with increasing Γ_{eff}, and is expected to hold for even more extreme values of the charge ratio Z_1/Z_2 and screening parameter α. This parameter Γ_{eff} was chosen such that at constant Γ_{eff} and α the mixtures have roughly the same linear-response energy $u_{\text{mix,lin.resp.}}$. The generalized linear mixing rule for Yukawa mixtures, i.e., $R_i^3 = Z_i/\langle Z \rangle$, is overall much less accurate than the full solution of the nonlinear equations (23). The improvement of the nonlinear rule over the linear mixing rule becomes more significant as α or Γ increase. For example, taking $Z_1 = 32$, $Z_2 = 1$, $x_1 = x_2 = 0.5$, $\alpha = 2.5$, $\Gamma = 1.479$ then, within the hypernetted-chain approximation $u_{\text{mix,lin.resp.}} = -85.894$ vs -85.942 and -85.316 by the nonlinear and linear rules, i.e., of 0.06% and 0.7% accuracy, respectively. The corresponding numbers of $x_1 = 0.30$, $\Gamma = 2.872$ are, respectively, -67.212, -67.264, and -65.986.

If this comparison between the linear and nonlinear mixing rules is validated by simulations, such relatively small variations in favor of the nonlinear rule should still make [10,11] an important difference in phase-separation calculations for these strongly coupled and strongly screened Coulomb fluids. From the physics point of view, however, the nonlinear mixing rule for screened plasmas is a significant improvement (see below) over the linear rule.

V. PHYSICAL MEANING OF THE NONLINEAR MIXING RULE: THOMAS-FERMI CONFINED-ATOM MODEL FOR DENSE MATTER IN LINEAR RESPONSE

The Onsager exact energy bound for charged Yukawa mixtures and the corresponding nonlinear mixing rule have a simple physical meaning which is revealed by treating the "Yukawa" problem in "Coulomb" language. In the standard linear-response [2,3] treatment for point ions in, e.g., a nearly degenerate Fermi sea of electrons, it is assumed that the electron number density varies in space according to (let $e = 1$)

$$\rho_e(\mathbf{r}) = \langle \rho_e \rangle + \Delta\rho_e(\mathbf{r}) = n\langle Z \rangle + (\alpha^2/4\pi)\Phi(\mathbf{r}) , \quad (32)$$

where $\Phi(\mathbf{r})$ is the electrostatic Coulomb potential at the point $\mathbf{r}$ in space, and [27] α is related to the Fermi function $I_{1/2}$. Let U_P be the total electrostatic potential energy (relative to the infinite self-energy of the point charges) of this electroneutral system, and let U_K be the nonideal kinetic energy of the electrons in the linear-response leading order. Their sum,

$$U_P + U_K = \frac{1}{8\pi} \int [|\nabla\Phi(\mathbf{r})|^2 + \alpha^2\Phi^2(\mathbf{r})] dV , \quad (33a)$$

satisfies the following *electrostatic* inequality [28]:

$$U_P + U_K \geq \sum_i N_i u_{\text{OA},i} = U_{\text{OTF}} , \quad (33b)$$

where

$$u_{\text{OA},i} = \frac{1}{8\pi} \int [|\nabla\Phi(r)|^2 + \alpha^2\Phi^2(r)] dv_i . \quad (33c)$$

The integral $\int \cdots dv_i$ is over the volumes v_i of individual, confined, isolated, spherical, and neutral "Onsager-atoms" (OA) composed of a central point charge Z_i and an electron cloud of number density (32) and radius R_i. To evaluate the Onsager-atom energy, $u_{\text{OA},i}$, define

$$\Psi_i(r) = r\Phi_i(r) \quad (34a)$$

to obtain (recall $e = 1$),

$$\Psi_i''(r) - \alpha^2\Psi_i(r) = 4\pi n\langle Z \rangle r, \quad \text{for } r \leq R_i , \quad (34b)$$

with the boundary conditions

$$\text{(i)} \quad \Psi_i(r=0) = Z_i ,$$
$$\text{(ii)} \quad \frac{\partial\Phi}{\partial r}\Big|_{r=Ri} = 0, \quad \text{i.e.,} \Psi'(R_i) = \Psi(R_i)/R_i . \quad (34c)$$

This is precisely the confined-atom Thomas-Fermi model [29] (in its linear-response version) revealed as a best-bound problem in the Onsager sense. The solution is

$$\Psi(r) = Ae^{\alpha r} + Be^{-\alpha r} - 4\pi n\langle Z \rangle r/\alpha^2 , \quad (34d)$$

with A and B determined by the two boundary conditions (34c). The Onsager-atom self-energy is given by $2u_{\text{OA},i}/Z_i = \Psi'(0)$, to yield finally (in our units $n = 3/4\pi$)

$$u_{\text{OTF}} = U_{\text{OTF}}/Nk_BT/\Gamma = \sum_i x_i [(Z_i^2/R_i) u_0(\alpha R_i) - 3\langle Z \rangle Z_i/2\alpha^2 - \alpha Z_i^2/2] . \quad (35)$$

Compared to (25b) it features the expected [3] linear-response relation to the Yukawa potential energy. In the Coulomb limit, $\alpha = 0$, the divergent α^{-2} term in $u_0(\alpha R_i)$ cancels with the contributions of the uniform background charge to yield the Lieb-Narnhofer [19] "ion-sphere" bound with $u_i = u_{\text{OA},i} = -0.9(Z_i^2/R_i)$, and $R_i^3 = Z_i/\langle Z \rangle$. Using the definition of $Q(t)$ in Eqs. (6) the electron density at the surface can be written as

$$\rho_e(R_i) = Z_i Q(\alpha R_i)/(4\pi R_i^3/3) . \quad (36)$$

Optimization of the bound (35), subject to the total charge neutrality condition, $\sum_i x_i R_i^3 = 1$, yields Eqs. (10). Comparison of (23) with (36) reveals its true physical meaning: it is the condition of constant (independent of

i) electron surface density, i.e., constant surface electrostatic potential [30]. This is of course the expected result on physical grounds, and which is missing in the linear rule. In view of the dominance of the electron contribution to the total pressure of the plasma, which is determined for Thomas-Fermi theory by their density at the surface of the confined atom, the condition (23) also corresponds to the well-known "volume-additivity rule" for Thomas-Fermi mixing of elements [31], $v(P,T)=\sum_i x_i v_i(P,T)$, namely, combining specific volumes at same pressure and temperature.

VI. CONCLUSION

The present nonlinear mixing rule is a physically significant improvement over the widely used linear rule [2,12–14]. It provides a simple scaling relation between the thermodynamics of the mixtures and the pure phase, and thus simplifies appreciably the representation of thermodynamic properties. The accuracy of this approximation must be eventually checked by simulations, but the very favorable hypernetted-chain results provide at least some indication for the general validity of the mixing rule.

In addition, the present results can be utilized in other approximate theoretical methods, e.g., the recently discovered [26] instability of the diagrammatic iteration process, which correlates well with the freezing density for all classical monodisperse systems, and in particular for the Yukawa potential. Thermodynamic calculations based on the nonlinear mixing rule for the free energy, combined with the instability calculations for Yukawa mixtures, may eventually provide new tools for calculating the phase behavior of mixtures (freezing and phase separation in the fluid) as a function of the softness of the interaction. The renormalization property (as defined in Sec. II) of the Yukawa potential is much stronger than its semi-infinite slab [1] (i.e., $R\rightarrow\infty$) limit, and can be fruitfully applied for the analysis [32] of the analytical solutions of the mean-spherical approximation [4,33] with Yukawa closure, and in the general context of the Ewald method [34]. Finally, the present results already proved useful for analyzing electron-screening effects on the screening potentials in strongly coupled plasmas [16], and for developing mode free-energy functionals for inhomogeneous charged-particle fluids [35].

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