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Equation of state and correlation functions of strongly coupled plasma mixtures: Density functional theory and analytic models

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A recent free-energy model for charged-Yukawa mixtures, based on an extension of the Coulomb ''linear-mixing rule'' to Yukawa charges, enables us to obtain a very accurate equation of state of bulk dense-plasma mixtures. A self-consistent density functional theory for pair correlations predicts the energy to better than a few parts in 10^4 when compared with the best available simulations for both Yukawa and Coulomb plasmas. The simulations results for the tiny deviations from ''linear mixing'' are accurately represented by the hypernetted-chain approximation, as well as by an analytic variational hard-sphere model (which, ironically, both provide only two figures of accuracy for the potential energy). The self-consistent density functional theory provides the most accurate presently available ''first principles'' description for the structure and equation of state of the bulk Coulomb and Yukawa mixtures, and can be applied also to inhomogeneous plasmas. [S1063-651X(96)00708-8]

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I. INTRODUCTION

Many quite disparate systems with screened Coulomb interactions, of importance in condensed matter physics, can be described with the Yukawa interparticle potentials $e^{-\alpha r}/r$ as a reference point [1]. Systems with repulsive Yukawa potentials [2–4] provide models for, e.g., dense stellar materials [5–6], inertially confined plasmas [5–6], and ''mesoscopic plasmas'' of charge stabilized colloidal suspensions such as latex spheres in water [7–12]. Because the shape of the potential varies continuously with the screening length, the Yukawa form for the interaction is useful for testing general ideas about phase transitions [10]. Screened binary ionic mixtures [2–5] are applicable to astrophysical problems involving phase separation of elements (e.g., in white dwarf star interiors) [13,14] and to inertial-confinement experiments in plasma physics. These problems require [15–17] very accurate equations of state for the mixture. Accurate free energy of the mixture is also required, through the zero separation theorem, for calculating enhancement factors for nuclear reaction rates in very dense stellar interiors [18], and in relation to fundamental liquid state theory [19]. There is a growing interest in this important reference system in condensed matter physics, and systems of particles interacting through the repulsive Yukawa pair potential have been the object of intensive investigations in recent years, using simulations [9–12,20–22] and additional theoretical methods [23–26].

In simulations for weak screening, near the Coulomb limit, it is important to use the ''Ewald'' potential [27–29] which takes into account the contributions from outside the simulation box. Indeed, the Ewald potential has already been used in earlier works on the Yukawa [30] and other [31] screened-Coulomb potentials. Earlier simulation studies of the Yukawa system [9–12] employed the standard minimal-image method with a cutoff radius for particle interactions, which is justified for short range potentials resulting from stronger screening. An additional treatment of the Ewald method for simulating Yukawa systems was presented recently [32] which highlights certain general properties of the method, and enables instant adaptation of well documented existing codes for Coulomb interactions.

A recent free-energy model for charged-Yukawa mixtures [23] enables us to obtain, to very high accuracy, the equation of state of bulk dense-plasma mixtures. The excess free energy for the mixture is given by an average of those for two appropriately chosen single component Yukawa systems, as an extension of the Coulomb ''linear mixing rule'' to Yukawa charges. In view of the high accuracy of this approximation, deviations from the Coulomb or Yukawa ''mixing rules'' can be meaningfully determined only by simulations which are accurate to roughly one part in 10^5 (i.e., provide *about* five significant figures for the potential energy). An additional self-consistent density functional theory for the structure provides between three to five figures of accuracy for the energy when compared with the recent ultrahigh accuracy simulations [33,34] for both the one-component and binary Coulomb plasma mixtures. The simulations results for the tiny deviations from ''linear mixing'' are accurately represented [35] by the hypernetted-chain approximation, and by an analytic variational hard-sphere model, which, ironically, provide only two figures of accuracy for the potential energy. In turn, the density functional theory, with all its exceptional high accuracy, cannot provide correctly the deviations from the ''mixing rules'', and the reason for this will be discussed. However, by combining the results of the density functional theory with those of the analytic variational model or the hypernetted-chain equation for the deviations from the ''mixing rules,'' the most accurate simulation results for the structure and equation of state of the Coulomb and Yukawa systems can be reproduced with unprecedented high accuracy. Preliminary accounts of parts of the present work were given before [35,36].

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II. COULOMB AND YUKAWA ‘‘MIXING RULES’’

We consider classical binary mixtures ($i=1,2$) consisting of N_i positively charged, $Z_i e>0$, $Z_2 \geqslant Z_1$, point particles interacting through the Yukawa pair potentials

$$\frac{u_{ij}(r)}{k_B T}=Z_i Z_j \Gamma \frac{e^{-\alpha r}}{r}. \tag{1}$$

Measuring distances in units of the total Wigner-Seitz radius $a=(3/4\pi n)^{1/3}$, where $n=N/V\equiv(N_1+N_2)/V$ is the total number density, define $\Gamma=e^2/ak_B T$ as the conventional plasma coupling parameter, where T is the temperature. The inverse screening length α can be density and temperature dependent. For a one-component Yukawa system, with $Z_i=1$, the potential energy, in units of $Nk_B T$, is a function of two variables: $u\equiv U/Nk_B T=u(\Gamma,\alpha)$. For the mixture it depends also on the charges and on the relative concentrations $x\equiv x_2=N_2/N=1-x_1$, $U_{\mathrm{mix}}/Nk_B T=u_{\mathrm{mix}}(x,Z_1,Z_2,\Gamma,\alpha)$.

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 for unscreened plasma mixtures is the empirical ‘‘*linear mixing rule*’’ [15,16]. 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 [17] and moderately screened [2] binary ionic mixtures, is based on the ‘‘ion-sphere’’ model, which provides an Onsager type [37] exact lower bound for the potential energy of the mixture, as first proven by Lieb and Narnhofer [38]. The linear-mixing rule was first verified by extensive hypernetted-chain calculations, which provide a very useful tool for developing such theories [5,15,16], and it was only later validated by the heavy simulations [5] which were required.

A nontrivial generalization of the linear-mixing rule to Yukawa interactions was achieved recently. For the case of binary Yukawa mixtures the approximate scaling law has the form [23]

$$u_{\mathrm{mix}}(x,Z_1,Z_2,\Gamma,\alpha)=(1-x)u(\Gamma_1,\alpha_1)+xu(\Gamma_2,\alpha_2), \tag{2}$$

where ($i=1,2$)

$$\Gamma_i=(Z_i^2/\lambda_i)\Gamma, \quad \alpha_i=\alpha\lambda_i \tag{3}$$

and where the λ_i are obtained from the solution of the following set of *nonlinear* coupled algebraic equations

$$\lambda_i^3=\frac{Z_i Q(\alpha\lambda_i)}{(1-x)Z_1 Q(\alpha\lambda_1)+xZ_2 Q(\alpha\lambda_2)}, \quad i=1,2. \tag{4}$$

The plasma is weakly, moderately, or strongly coupled according to whether $\Gamma_{\mathrm{eff}}=x_1\Gamma_1+x_2\Gamma_2 \ll 1$, ~ 1, or $\gg 1$, respectively. The function

$$Q(t)=\frac{2t^3}{3[e^t(t-1)+e^{-t}(t+1)]}\leqslant 1$$

has the following physical meaning: The Yukawa intermolecular potential has the special property [23] that the potential outside a spherically symmetric uniform distribution of charge Z_i inside a sphere of radius λ_i, retains the Yukawa form, but the charge is renormalized by the factor $1/G(\alpha\lambda_i)$, i.e., $\Phi(r\geqslant\lambda_i)=Z_i/Q(\alpha\lambda_i)e^{-\alpha r}/r$. The Gauss-Newton theorem for the Coulomb potential ($\alpha=0$) is manifestly satisfied by $Q(0)=1$, $\lambda_i=(Z_i/\langle Z\rangle)^{1/3}$, and in this Coulomb limit the Yukawa mixing rule corresponds to the ‘‘linear-mixing rule’’ [15] approximation for unscreened plasmas

$$\begin{aligned} u_{\mathrm{mix}}(x,Z_1,Z_2,\Gamma,\alpha=0)=(1-x)u(\Gamma_1,\alpha=0) \\ +xu(\Gamma_2,\alpha=0), \end{aligned} \tag{5}$$

where ($i=1,2$)

$$\Gamma_i=Z_i^{5/3}\langle Z\rangle^{1/3}\Gamma. \tag{6}$$

The Yukawa mixing rule has a simple physical meaning in the context of the Thomas-Fermi model for the equation of state of mixtures of elements, as discussed in [23].

This Yukawa mixing rule (sometimes referred to as the ‘‘nonlinear’’-mixing rule, due to the nonlinearity of the equations for determining the λ_i) should be verified eventually by simulations but, similarly to the past experience with the Coulomb 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 [23] for binary mixtures it was found that the Yukawa mixing rule holds to an accuracy of about 0.1% for a wide range of values for the physically relevant parameters, namely, values of $\alpha\leqslant 3$, charge ratios $Z_1/Z_2\leqslant 30$, and effective couplings $\Gamma_{\mathrm{eff}}=(\Sigma_i x_i\Gamma_i)e^{-\alpha}\leqslant 200$. 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. The linear-mixing rule can be applied also for Yukawa mixtures, i.e., using $R_i^3=Z_i/\langle Z\rangle$, but it is overall much less accurate than the full solution of the nonlinear equations (4). From the physics point of view, the Yukawa mixing rule for screened plasmas is a significant improvement over the linear rule, and its improvement over the linear-mixing rule becomes more significant as α or Γ increase.

III. DEVIATIONS FROM THE ‘‘MIXING RULES’’

With the increasing possible accuracy attainable by the simulations it became possible to consider the relatively very small deviations from the linear-mixing approximation which, however, turn out to have very important consequences for the predicted phase diagrams [39,40]. Due to the extremely long runs required, there are relatively few results of that high accuracy [33,34], and limited to only Coulomb mixtures. Thus, even though the theory is general and applies to both Coulomb and Yukawa charges, the numerical comparisons with simulations for mixtures in this paper concentrate on unscreened plasmas. For unscreened plasmas, the linear-mixing (LM) ‘‘rule’’ takes the form,

$$u_{\mathrm{LM}}(\xi,x,\Gamma_1)=(1-x)u^{\mathrm{OCP}}(\Gamma_1)+xu^{\mathrm{OCP}}(\Gamma_2=\Gamma_1\xi^{5/3}), \tag{7}$$

where $\xi=Z_2/Z_1\geqslant 1$ is the charge ratio, and $u^{\mathrm{OCP}}(\Gamma)=u(\alpha=0,\Gamma)$ represents the internal energy for the unscreened one-component plasma (OCP). Since u_{LM} is already a good approximation for the potential energy of the binary ionic mixture (BIM) u^{BIM} the analysis of u^{BIM} customarily proceeds by considering the ''deviations from linear mixing''

$$\Delta u^{\mathrm{BIM}}=u^{\mathrm{BIM}}-u_{\mathrm{LM}}. \tag{8}$$

In view of the fact that Δu^{BIM} is relatively very small, very highly accurate equations of state for *both* the one-component plasma (OCP) *and* the binary ionic mixtures (BIM) are required for its accurate determination. Accurate simulation data for the BIM were provided by Ogata and co-workers [40], and by DeWitt and Slattery [41]. Very recently, ultrahigh accuracy results were presented [33,34] by DeWitt, Slattery, and Chabrier for both the BIM and the corresponding OCP energies, so that Δu^{BIM} could be accurately determined using Eqs. (7), (8). All these simulations agree very well with an analytic model, which thus provides a convenient representation for the equation of state of the mixture, and is expected to be more reliable than a plain fit for purposes of interpolations and extrapolations of the data.

The model is based on the idea to consider the well known variational hard-sphere model [42,43] separately for the mixture and for the one-component systems with Γ_1, and Γ_2, and to calculate the *deviation* from linear-mixing entirely within the model. The expectation is that inaccuracies of the model will cancel out between the results for the mixture and for linear mixing, to yield accurate values for Δu^{BIM}.

The model excess free energy (in Nk_BT units) for the Coulomb plasma is written in the form (see Appendix A)

$$f_{\mathrm{ex}}(\eta,q,\Gamma_e,Z_1,Z_2,x)=f_{\mathrm{ex}}^{\mathrm{PYV}}(\eta,q,x)+u_{\mathrm{PY}}(\eta,q,\Gamma_e,Z_1,Z_2,x), \tag{9}$$

where $f_{\mathrm{ex}}^{\mathrm{PYV}}$ is the excess free energy for the hard-sphere binary mixture as obtained from the Percus-Yevick ''virial'' (PYV) equation of state [45], and u_{PY} is the excess (potential) energy obtained by the standard energy integral but using the Percus-Yevick (PY) radial distribution functions [45], and can be expressed analytically. The variational parameters are the total hard-sphere packing fraction η and the ratio between the two hard-sphere diameters q. The optimal values of the parameters η_0, q_0 are obtained by minimizing f_{ex}. The reason for choosing the PY-virial entropy is that for the OCP it provides the paradigm [43] for the functional form used to fit the Monte Carlo data. It yields [43] the following asymptotic large Γ expansion:

$$u_{\mathrm{PY}}(\eta_0(\Gamma),\lambda,\Gamma,Z_1=1,Z_2,x=0)=-0.9\Gamma+0.971\Gamma^{0.25}-0.5+\cdots, \tag{10}$$

TABLE I. Deviations from ''linear mixing'' for binary ionic mixtures (BIM), as calculated by Monte Carlo (MC) simulations [33], [34], by the variational model (VAR), and by the hypernetted-chain approximation (HNC). The entries marked by a star employ the BIM simulations of Ogata and co-workers [40].

Z_2	Γ_1	x_2	$\Delta u^{\mathrm{BIM,MC}}$	$\Delta u^{\mathrm{BIM,VAR}}$	$\Delta u^{\mathrm{BIM,HNC}}$
3	10	0.01	0.000 60±0.000 18	0.000 75	0.000 74
3	10	0.02	0.001 04±0.000 18	0.001 49	0.001 04
3	10	0.05	0.002 06±0.000 21	0.003 54	0.003 20
3	10	0.10	*0.006±0.001	0.006 21	0.005 83
3	10	0.20	*0.010±0.0011	0.0108	0.0094
3	10	0.50	*0.012±0.0021	0.0139	0.0107
3	15	0.01	0.000 38±0.000 22	0.000 74	0.000 78
3	15	0.05	0.002 25±0.000 25	0.003 49	0.003 40
3	15	0.10	*0.003 51±0.001	0.006 38	0.005 91
3	15	0.20	*0.008±0.0111	0.0106	0.009 12
3	15	0.50	*0.008±0.0021	0.0135	0.0099
3	20	0.01	0.000 97±0.000 31	0.000 71	0.000 71
3	20	0.05	0.002 81±0.000 26	0.003 40	0.003 36
3	20	0.10	*0.006±0.001	0.006 21	0.005 83
3	20	0.20	*0.005±0.002	0.0103	0.008 96
3	20	0.50	*0.007±0.002	0.0132	0.0094
5	10	0.01	0.001 44±0.000 21	0.001 83	0.002 01
5	10	0.05	0.006 88±0.000 22	0.008 60	0.008 82
5	10	0.10	0.012 66±0.000 28	0.015 37	0.0149
5	10	0.20	0.018 55±0.000 40	0.02439	0.021 49
5	10	0.50	0.019 67±0.000 84	0.02852	0.0209
8	10	0.01	0.002 66±0.000 19		

featuring the form

$$u^{\mathrm{OCP}}(\Gamma)=a\Gamma+b\Gamma^s+c, \tag{11}$$

which can be conveniently used to fit both the simulations and hypernetted-chain (HNC) results for $\Gamma\geqslant 1$. It was proven [44] that within the HNC approximation, which neglects the bridge functions, $a=-0.9$ and $s=0.5$. The very recent high accuracy Monte Carlo results have been fitted, for $\Gamma\geqslant 1$, by DeWitt, Slattery, and Chabrier [33]

$$a=-0.899\,126,\quad b=0.607\,12,$$

$$c=-0.279\,98,\quad s=0.321\,308$$

with a standard deviation of $\sigma=\pm 0.0045$, which is [33] ''the most accurate fitting function for the OCP energy at the present time.'' It is known [24] that the leading asymptotic large Γ term of the above hard-sphere (Percus-Yevick) variational model for plasma mixtures obeys the linear-mixing rule, and in view of the nature of the asymptotic expansion, the deviations from linear mixing are expected to be relatively small. It was already found [35] that the results of this analytic model for Δu^{BIM} are very similar to those obtained within the hypernetted-chain (HNC) approximation, featuring always positive deviations from linear mixing.

The Δu^{BIM} results from the analytic variational model and from the hypernetted-chain approximation are compared with the simulations in Table I, and in Figs. 1–4. The overall agreement between the theories and the simulations is very good, yet the Γ_1 dependence of the simulations results is larger than predicted by the theoretical models. The models predict that the deviations from linear mixing are always positive, in agreement with the simulations. The models pre-

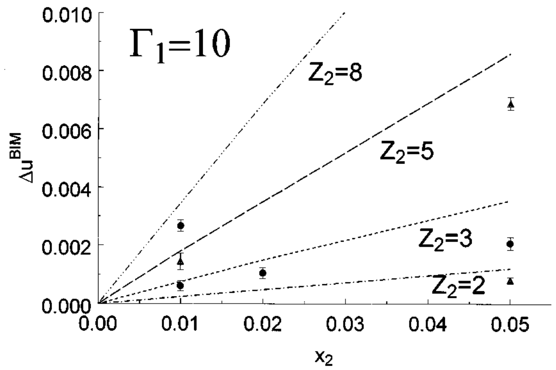

FIG. 1. Deviations from ''linear mixing'' for binary ionic mixtures $\delta u^{\rm BIM}$ for different charge ratios $Z_2(Z_1=1)$, for small concentrations x_2 of the larger charge $Z_2>Z_1=1$, for $\Gamma_1=10$. The symbols represent the simulation results, and the lines are the results of the variational model (see the text and Table I).

dict (Fig. 4) linear dependence of $\Delta u^{\rm BIM}$ on x_2 for small relative concentrations of the larger charge (see also Ref. [16]).

Extensive simulation data for Yukawa mixtures is not yet available, but our calculations predict that the deviations from the Yukawa linear mixing are always *positive*, and change very slowly with α. It is also interesting to note here that (like for the Coulomb plasma) the deviations from the Yukawa linear mixing within the hypernetted-chain (HNC) approximation [23] are similar in magnitude to those obtained by the variational model, and are also always *positive*. As discussed in detail in [35,46,47], and in [18,33,34], our results contradict those of Ogata and co-workers, who found [40] negative deviations from linear mixing in the limit of small concentrations of the larger charge ($x_2<\sim0.1$). The claimed consequences for the enhancement factors and for the phase diagrams [40,48] appear to be irrelevant.

IV. SELF-CONSISTENT DENSITY FUNCTIONAL THEORY

Density functional methods played a key role in providing the now emerging comprehensive picture of the complex thermodynamic behavior of fluids in confined geometries. As a quite general approach to the equilibrium properties of nonuniform fluids, the density functional method has proven to be one of the more successful and widely applicable approaches to a variety of interfacial phenomena like adsorption, wetting, and freezing [49].

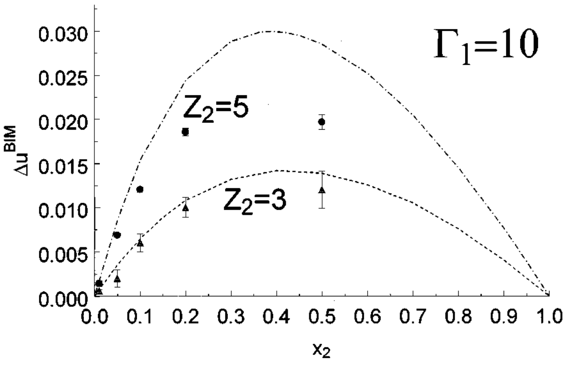

FIG. 2. Deviations from ''linear mixing'' for binary ionic mixtures $\Delta u^{\rm BIM}$ for different charge ratios Z_2 $(Z_1=1)$, as a function of the concentrations x_2 of the larger charge $Z_2>Z_1=1$, for $\Gamma_1=10$. The symbols represent the simulation results, and the lines are the results of the variational model (see the text and Table I).

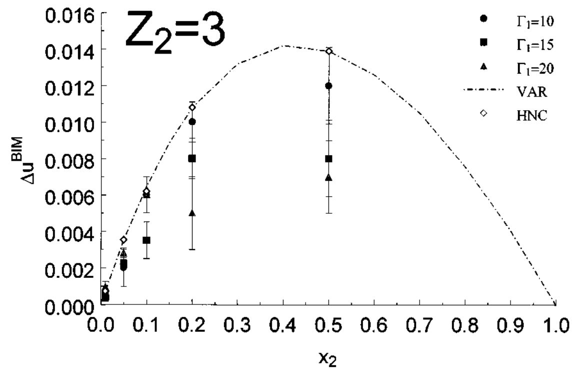

FIG. 3. Deviations from ''linear mixing'' for binary ionic mixtures $\Delta u^{\rm BIM}$ for $Z_2=3$ and $Z_1=1$, as a function of the concentrations x_2 of the larger charge $Z_2>Z_1=1$, for different values of Γ_1. The full symbols represent the simulation results. The open diamonds represent the HNC results for $\Gamma_1=10$, and the lines are the results of the variational model for $\Gamma_1=10$. The theoretical results do not vary appreciably with Γ_1 (see the text and Table I).

The density profiles $\{\rho_m(\vec{r})\}$ for the fluid subject to external potentials $\{u_m(\vec{r})\}$ which couple to the particles of type $\{m;\ m=1,2,\ldots,M\}$ are obtained by solving the Euler-Lagrange equations

$$\delta\Omega[\{\rho_m(\vec{r})\}]/\delta\rho_i(\vec{r})=0, \quad i=1,2,\ldots,M, \tag{12}$$

which correspond to the minimization of the grand potential $\Omega[\{\rho_m(\vec{r})\}]$,

$$\Omega[\{\rho_m(\vec{r})\}]=F_{\rm id}[\{\rho_m(\vec{r})\}]+F_{\rm ex}[\{\rho_m(\vec{r})\}] + \sum_i \int d\vec{r}\, \rho_i(\vec{r})[u_i(\vec{r})-\mu_i], \tag{13}$$

where μ_i are the chemical potentials. The ideal-gas free energy is given by the exact relation

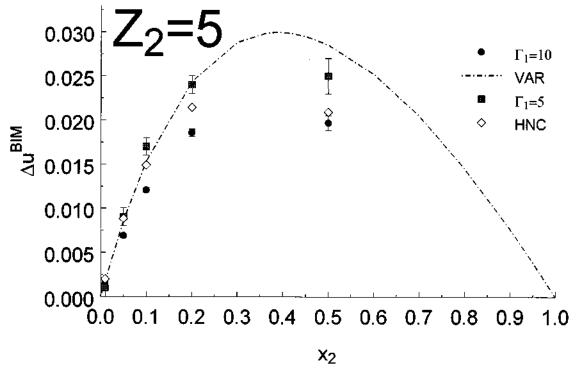

FIG. 4. Same as Fig. 3, but for $Z_2=5$ and $Z_1=1$.

$$F_{\mathrm{id}}[\{\rho_m(\vec{r})\}]=k_BT\sum_i\int d\vec{r}\,\rho_i(\vec{r})\{\ln[\rho_i(\vec{r})\lambda_i^3]-1\}, \tag{14}$$

where $\lambda_i=(h^2/2\pi m_i k_BT)^{1/2}$ are the de Broglie wavelengths. The central quantity in the density functional theory for nonuniform fluids is the excess (over ''ideal-gas'' contributions) free-energy $F_{\mathrm{ex}}[\{\rho_m(\vec{r})\}]$ which originates in interparticle interactions. It is a unique functional of the spatially varying one particle densities, $\{\rho_m(\vec{r})\}$, which is in general unknown.

A hierarchy of direct correlation functions $c^{(n,\mathrm{FD})}$ is given by *functional derivatives* (FD) of the excess free-energy functional. In particular, the one particle ($n=1$, the excess chemical potential) and pair ($n=2$) direct correlation functions are

$$k_BTc_i^{(1,\mathrm{FD})}(\vec{r}_1)=-\frac{\delta F_{\mathrm{ex}}[\{\rho_m(\vec{r})\}]}{\delta\rho_i(\vec{r}_1)}=-\mu_{i,\mathrm{ex}}[\{\rho_m(\vec{r})\};\vec{r}_1], \tag{15}$$

$$k_BTc_{ij}^{(2,\mathrm{FD})}(\vec{r}_1,\vec{r}_2)=-\frac{\delta F_{\mathrm{ex}}[\{\rho_m(\vec{r})\}]}{\delta\rho_i(\vec{r}_1)\,\delta\rho_j(\vec{r}_2)}. \tag{16}$$

In the language of density functional theory, when given the excess free-energy functional F_{ex}, the exact equations for the pair correlation functions of the bulk fluid can be written in the modified hypernetted-chain form, with the bridge function given through the bridge functional which is related to the free-energy functional [24]. A key role is played by the fundamental-measure excess free-energy functional for hard spheres [50–53] from which the ''universal'' bridge functional (see below) is derived in explicit form.

When the external potential is obtained by fixing a *test particle* of type t at the origin $u_i(\vec{r})=\phi_{ti}(r)$ where $\phi_{ti}(r)$ is the corresponding pair potential between particles of types t and i in the fluid, then the density profiles $\rho_i(r)$ normalized to unity at larger r, correspond to the pair distribution functions in the bulk uniform fluid $g_{ti}(r)=\rho_i(r)/\rho_{i,0}$, where $\{\rho_{m,0}\}$ are the average densities of the bulk fluid. The test particle limit of the exact density profile equations takes the form [24,36,52]

$$g_{ti}(r)=\exp\biggl(-\frac{\phi_{ti}(r)}{k_BT}-\overline{b_{ti}}(r)+\sum_j\rho_{j,0}\int d\vec{r}\,'c_{ji}(|\vec{r}-\vec{r}\,'|)h_{tj}(r')\biggr), \tag{17}$$

where $h_{tj}(r)=g_{tj}(r)-1$, and $c_{ij}(r)$ are the uniform fluid, bulk limit of the direct correlation functions as obtained from the second functional derivative (FD) of the excess free-energy functional. The *symmetrized* bridge function.

$$\overline{b_{ti}}(r)=\frac{x_ib_{ti}(r)+x_tb_{it}(r)}{x_t+x_i} \tag{18}$$

is obtained as the appropriate weighted bulk average of the bridge functions $b_{ij(r)}$, which are derived from the *bridge functional* $B_i[\{\rho_{m,0}\};\{\rho_m(\vec{r})\};\vec{r}]$ by using $\rho_i(\vec{r})=\rho_{i,0}g_{ti}(r)$

$$b_{ti}(r)=B_i[\{\rho_{m,0}\};\{\rho_{m,0}g_{tm}(r)\};r]. \tag{19}$$

The *exact* free-energy functional must obey the ''test particle self-consistency'': the exact $g_{ij}(r)$'s as obtained from the solution of the coupled density profile equations (17) and (18) are identical to those obtained from the Ornstein-Zernike relations

$$h_{ti}(r)=c_{ti}(r)+\sum_j\rho_{j,0}\int d\vec{r}\,'c_{ji}(|\vec{r}-\vec{r}\,'|)h_{tj}(r'). \tag{20}$$

The bridge functional is defined as follows [24]: Separate the free energy into a ''second order'' part and a ''bridge'' part,

$$F_{\mathrm{ex}}[\{\rho_{m,0}\};\{\rho_m(\vec{r})\}]=F_{\mathrm{ex}}^{(2)}[\{\rho_{m,0}\};\{\rho_m(\vec{r})\}]+F_{\mathrm{ex}}^{(B,\mathrm{ref})}\times[\{\rho_{m,0}\};\{\rho_m(\vec{r})\}], \tag{21}$$

where $F_{\mathrm{ex}}^{(2)}[\{\rho_{m,0}\};\{\rho_m(\vec{r})\}]$ is the second order functional of the system and $F_{\mathrm{ex}}^{(B,\mathrm{ref})}[\{\rho_{m,0}\};\{\rho_m(\vec{r})\}]$ generates the bridge functional of the *reference* system (which can also be the original system at hand)

$$B_i^{\mathrm{ref}}[\{\rho_{m,0}\};\{\rho_{m,0}g_{tm}(r)\};\vec{r}]=\frac{\mu_{i,\mathrm{ex}}^{\mathrm{ref}}[\{\rho_m(r)\};r]}{k_BT}-\frac{\mu_{i,\mathrm{ex}}^{\mathrm{ref}}[\{\rho_{m,0}\}]}{k_BT}+\Sigma_j\rho_{j,0}\int d\vec{r}\,'c_{ij}^{(2,\mathrm{FD}),\mathrm{ref}}[\{\rho_{m,0}\};(|\vec{r}-\vec{r}\,'|)]\times(g_{tj}(r')-1)\}. \tag{22}$$

The resulting coupled equations (17)–(20), for both $\{g_{ij}(r)\}$ and $\{c_{ij}(r)\}$, in which the bridge functions are obtained from the exact bridge functionals Eq. (22) should provide the exact pair correlations. Given approximate (''reference'') bridge functionals, the same set of equations defines the reference bridge functional approximation, which also optimizes the second order free-energy functional when starting from the corresponding approximate (''reference'') free-energy functional. Given explicit ''reference'' bridge functionals, the coupled equations (17)–(20) represent a well defined approximation for the pair correlation functions. It is possible to *optimize the reference-system parameters*, by using the following equations (see Appendix B), which are the same as derived by Lado [60] in the context of the modified hypernetted-chain theory [19]:

$$\sum_{ij}\rho_{i,0}\rho_{j,0}\int d\vec{r}[g_{ij}(\vec{r})-g_{ij}^{\mathrm{ref}}(\vec{r})]\,\delta\overline{b_{ij}^{\mathrm{ref}}}(\{g_{lm}\};\vec{r})=0. \tag{23}$$

For simple fluids, interacting via Lennard-Jones (LJ) type potentials, or plasmas of point charges interacting through the Coulomb or Yukawa potentials similar results are obtained by the simplified form [24]

$$\sum_{ij}\rho_{i,0}\rho_{j,0}\int d\vec{r}[g_{ij}(\vec{r})-g_{ij}^{\mathrm{ref}}(\vec{r})]\overline{b_{ij}^{\mathrm{ref}}}(\{g_{lm}\};\vec{r})=0. \tag{24}$$

For a correct description of phase boundaries it is best to optimize the reference potential parameters by imposing thermodynamic consistency (e.g., ‘‘energy-compressibility’’ consistency, and see below).

In practice, the reference bridge functional calculations all start from the same model free energy for the hard-body fluids, and thus from the same reference bridge functionals. The self-consistent method is thus operationally equivalent to the approximation that the bridge functional is *universal*, and is given (e.g.) by that derived from the fundamental-measure free-energy functional for the hard-sphere fluid [50–53]. Thus we replace the $g_{ij}^{\mathrm{ref}}(r)$ in the Lado equations by the results obtained by the Ornstein-Zernike equation using $c_{ij}^{(2,\mathrm{FD}),\mathrm{ref}}$, namely, $g_{ij}^{(OZ,\mathrm{FD}),\mathrm{ref}}$, which, in the case of the fundamental-measure functional for hard-spheres, turn out to be just the well known Percus-Yevick hard-sphere correlation functions.

The hard-sphere ‘‘universal’’ bridge functional, and the corresponding optimized free-energy functional have been tested (directly and also implicitly) very successfully, for a variety of hard and soft pair interactions and external potentials, by comparison with computer simulations of density profiles for a large variety of situations where size or packing effects play an important role and by comparison with experiments on colloids and emulsions which address the challenging question of phase separation in asymmetric binary hard-sphere mixtures [50–59,24]. As special cases for the general method, accurate results [58] were obtained also for the bulk pair correlation functions for a variety of potentials, for both one-component systems and mixtures. ‘‘Universality of the bridge functional’’ [24] for general nonuniform fluids generalizes ‘‘universality of the bridge functions’’ [19]. The application of this general method to the special cases of charged particles and to plasmas is in accord with the asymptotic strong coupling limit of integral equation theories for the pair structure (‘‘Onsager limit’’) [47,61]. The fundamental-measure excess free-energy functional extends the scaled particle [62] and scaled field-particle [63] theories to inhomogeneous hard particle mixtures. By capturing the correct geometric features it provides an accurate universal bridge functional for bulk simple fluid mixtures, and may well do the same [53] for nonspherical molecular fluids.

Perhaps the most striking tests for repulsive soft potentials is provided by the plasmas [24] (point charges!). When the recent extra-long simulations results for binary ionic mixtures [33,34] became available, the self-consistent density functional method has been applied to these important systems, to find excellent agreement with the simulations. The results for the potential energy are compared with the simulations, and with the hypernetted-chain theory, in Tables II and III. Between three to five figures of accuracy for the bulk potential energy are achieved by the density functional theory, without any adjustable parameters. A typical example of the high accuracy for the pair correlation functions is given in Fig. 5. Similar accuracy for the energy and pair correlation function is achieved for the one-component plasma (OCP). Accurate results for the energy of the one-component Yukawa system were recently tabulated [20]. The self-consistent density functional theory results agree to better than a few parts in 10^4 with all these simulations results for the energy of the Yukawa system in the fluid state. Like in the modified HNC calculations using a universal bridge function [19], the density functional theory results for the compressibility equation of state are much more sensitive to the reference-system parameters (e.g., the ‘‘bridge’’ effective packing fraction) than the corresponding results for the energy. Thus, if thermodynamic consistency is desired, it can be imposed (instead of the Lado criterion) in order to determine the ‘‘bridge’’ effective packing. This procedure will yield almost identical results for the energy as obtained from the Lado equations, but will also provide much more accurate results for the compressibility.

TABLE II. Potential energies for the one component plasma (OCP) as calculated by Monte Carlo (MC) simulations [33], [34], by the density functional theory (DFT), and by the hypernetted-chain approximation (HNC).

Γ	$u^{\mathrm{OCP,MC}}$	$u^{\mathrm{OCP,DFT}}$	$u^{\mathrm{OCP,HNC}}$
1	−0.572 05±0.000 05	−0.571 81	−0.570 45
5	−3.756 96±0.000 10	−3.764 62	−3.732 07
10	−7.998 37±0.000 14	−8.004 97	−7.935 44
20	−16.673 27±0.000 16	−16.6986	−16.5377
40	−34.259 40±0.000 26	−34.2932	−33.9992
80	−69.727 42±0.000 41	−69.7612	−69.2636
160	−141.039 63±0.000 69	−141.023	−140.257

Using the density functional theory I also reconfirmed (see Table IV) the Hansen-Verlet rule [64] about the value of the maximum value of the structure factor at freezing,

TABLE III. Potential energies for the binary ionic mixtures (BIM) as calculated by Monte Carlo (MC) simulations [33], [34], by the density functional theory (DFT), and by the hypernetted-chain approximation (HNC). The entries marked by a star denote the BIM simulations of Ogata and co-workers [40].

Z_2	Γ_1	x_2	$u^{\mathrm{BIM,MC}}$	$u^{\mathrm{BIM,DFT}}$	$u^{\mathrm{BIM,HNC}}$
3	10	0.01	−8.458 74±0.000 11	−8.4628	−8.393
3	10	0.02	−8.919 27±0.000 11	−8.934	−8.850
3	10	0.05	−10.300 53±0.000 14	−10.297	−10.221
3	10	0.10	−12.602±0.001*	−12.592	−12.508
3	10	0.20	−17.208±0.001*	−17.201	−17.082
3	10	0.50	−31.035±0.002*	−31.032	−30.815
3	15	0.01	−13.012 04±0.000 18	−13.0166	−12.907
3	15	0.05	−15.790 68±0.000 26	−15.7850	−15.668
3	15	0.10	−19.265±0.001*	−19.252	−19.120
3	15	0.20	−26.212±0.001*	−26.199	−26.026
3	15	0.50	−47.066±0.002*	−47.057	−46.752
3	20	0.01	−17.601 88±0.000 26	−17.6033	−17.461
3	20	0.05	−21.318 34±0.000 19	−21.3100	−21.156
3	20	0.10	−25.963±0.001*	−25.948	−25.776
3	20	0.20	−35.260±0.002*	−35.237	−35.017
3	20	0.50	−63.145±0.002*	−63.126	−62.749
5	10	0.01	−9.204 14±0.000 15	−9.203 26	−9.134
5	10	0.05	−14.027 53±0.000 15	−14.0081	−13.929
5	10	0.10	−20.058 40±0.000 17	−20.0301	−19.926
5	10	0.20	−32.123 99±0.000 23	−32.0974	−31.924
5	10	0.50	−68.339 13±0.000 32	−68.3609	−67.940
8	10	0.01	−10.756 98±0.000 18	−10.7466	−10.680

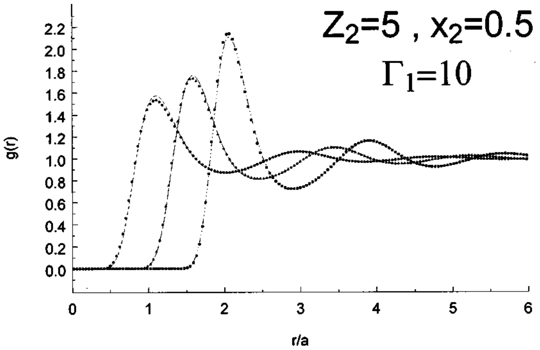

FIG. 5. Pair correlation functions $g_{ij}(r)$ for the equimolar ($x_1=x_2=0.5$) binary ionic mixture of $Z_2=5$ and $Z_1=1$, at $\Gamma_1=10$. The symbols represent the Monte Carlo data of DeWitt, Slattery, and Chabrier [33], [34] and the lines are the results of the self-consistent density functional theory (see the text).

$S(k)_{\mathrm{MAX}}\sim 3$ at freezing. Since the density functional theory employs a universal bridge functional, which was derived for hard spheres, I also obtain at each case the value of an effective hard-sphere packing fraction η associated with the optimal (self-consistent) bridge function (see Table III). For all the freezing points in the literature for all potentials, the value of the bridge parameter (i.e., the reference-system effective packing) η is very close to its hard-sphere value of $\eta=0.5$. This is a nice confirmation of the ''bridge freezing rule'' [65]: $b(r=0)\approx 50$ at freezing. It will be interesting to check this rule for two dimensional systems, for which the ''bridge freezing rule'' is expected [65] to hold as well.

It is also interesting to observe that the self-consistent bridge functions have the property that their asymptotic large distance form also provides an excellent description of the functions at intermediate distances (Fig. 6). This property was observed [66] for the pair correlation functions $h(r)$ of various model simple fluids. A long standing question concerns the sign of the bridge functions. The bridge functions that are obtained for the hard spheres by regarding the Percus-Yevick analytic results as a solution to the modified hypernetted-chain equation [19] are positive definite. The bridge functions that are obtained from the self-consistent density functional theory results and the ''universal'' bridge functional were up to now found to be positive in all our numerical calculations for simple fluids and plasmas. Moreover, a systematic search of the output of the bridge functional for input pair correlation functions from the Percus-Yevick result for hard spheres, has shown (Fig. 7) that the resulting bridge functions are positive for all input functions corresponding to the hard-sphere fluid. Although indicative, these results still leave open the general question regarding the sign of the bridge functions.

TABLE IV. Self-consistent density functional theory: maximum of the structure factor $S_{\max}(k)$ and the ''bridge'' effective packing fraction at freezing, $(\eta_B)_{\mathrm{freezing}}$, for different interaction potentials.

Inverse-power potentials, $\frac{\phi(r)}{k_BT}=\frac{\epsilon}{k_BT}\left(\frac{\sigma}{r}\right)^n,\ \frac{\epsilon}{k_BT}=1$			
n	$\rho\sigma^3$	$(\eta_B)_{\mathrm{freezing}}$	$S_{\max}(k)$
1	($\Gamma=171$)	0.5011	3.00
4	4.94	0.4767	2.69
6	2.292	0.4918	2.97
12	1.151	0.4825	2.86
∞	0.943	0.5042	3.25
Yukawa potential			
α	Γ	$(\eta_B)_{\mathrm{freezing}}$	$S_{\max}(k)$
0	171	0.5011	3.00
1	220	0.4992	3.00
1.83	400	0.5001	3.07
3.34	1800	0.4938	3.02
Lennard-Jones (12-6) potential: $\frac{\phi(r)}{k_BT}=\frac{4\epsilon}{k_BT}\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$			
k_BT/ϵ	$\rho\sigma^3$	$(\eta_B)_{\mathrm{freezing}}$	$S_{\max}(k)$
100	2.601	0.4812	2.85
2.74	1.113	0.4719	2.78

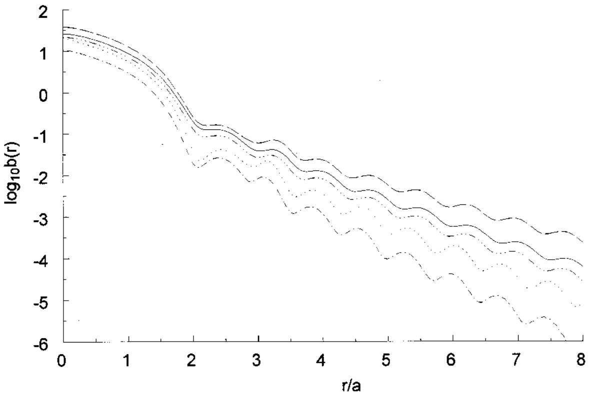

FIG. 6. Bridge functions $b(r)$ on logarithmic scale, for different one component systems, as obtained from the self-consistent density functional theory. The reference bridge parameter (the radius, R, or the corresponding effective packing, $\eta_B=4\pi\rho R^3/3$, is determined by the Lado equations (see the text). The different lines correspond to (from top to bottom):

Potential	Density-temperature	Bridge effective packing, $\eta_B=4\pi\rho R^3/3$
Yukawa	$\Gamma=350$, $\alpha=1.8$	0.4933
Coulomb	$\Gamma=100$	0.4374
Yukawa	$\Gamma=350$, $\alpha=2.4$	0.4437
hard-sphere	$\rho^*=\rho\sigma^3=0.8$ (i.e., $\eta=0.4189$)	0.4310
Lennard-Jones	$\rho^*=\rho\sigma=0.8$, $T^*=k_BT/\varepsilon=2$	0.3781

V. CONCLUSION

The self-consistent density functional theory presented above, as based on the fundamental-measure hard-sphere bridge functional, is the most accurate available ''first principles'' theory for the structure and the equation of state of classical plasmas. An additional major advantage of this theory is that its application to the bulk plasma represents

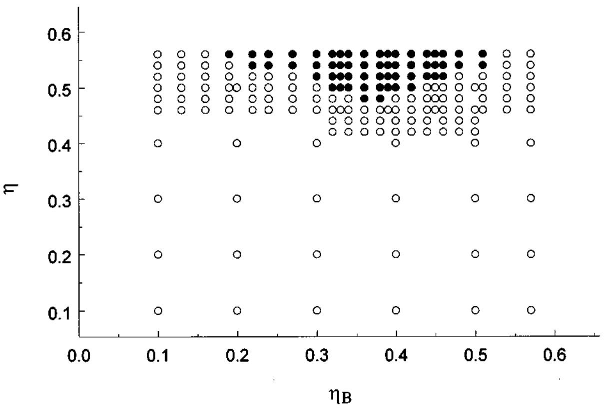

FIG. 7. Onset of negative values of the bridge function. The bridge function $b(r/a,\eta,\eta_B)$ was obtained from the bridge functional with reference bridge parameter (the effective packing) η_B and Percus-Yevick pair correlation functions, for hard spheres at packing fraction η, as input. The bridge function is positive for all cases marked by empty circles, while for the cases marked by full circles it begins to have negative values for $r/a\approx 2$.

just a special case of its applicability to general inhomogeneous fluids and plasmas. In particular, it was already found successful [24] in reproducing simulation results for a OCP against a hard wall (essentially the same as for the OCP with a jump discontinuity of the compensating background charge density).

Despite its high accuracy (better than a few parts in 10^4) for the energy, the above density functional theory is not capable of providing accurate results for the tiny deviations from the ''mixing rules'' (representing a few parts in 10^5 of the energy), while much less accurate theories like the variational model and the hypernetted-chain approximation, can describe correctly these deviations. The reason for this is apparently the internal ''coherence'' within these models, by which the relatively large errors for the one component system and for the mixtures (larger than a few parts in 10^3) cancel out when applied for calculating the deviations from the ''mixing rule.'' This ''coherence'' is apparently lost by the more sophisticated and more accurate density functional theory.

The following semiempirical model for the equation of state for fluid multicomponent plasmas, with or without Yukawa screening, is thus proposed: Combine (i) the ''mixing rule'' approximation calculated with an accurate equation of state for the one-component system as obtained from simulations, together with (ii) the deviations from the ''mixing rule'' calculated from the variational hard-sphere model (with the Percus-Yevick pair correlation functions, and the Percus-Yevick ''virial'' entropy):

$$f_{\text{ex}}^{(\text{mix})}=(f_{\text{mixing rule}})_{\text{from fit for one-component system}}+(\Delta f_{\text{ex}}^{(\text{mix})})_{\text{from variational Hard-sphere-model}}. \tag{25}$$

In particular, for the unscreened OCP we can use the DeWitt-Slattery-Chabrier fit [33,34]

$$f^{\text{OCP}}(\Gamma)=a\Gamma+\frac{1}{s}\,b\Gamma^{s}+c\,\ln\Gamma+d \tag{26}$$

with the parameters quoted above. As we have seen above, this model agrees well with the simulations data for the binary ionic mixture. Given a good representation for the potential energy of the one-component Yukawa system the model, in its general form [19], is applicable to arbitrary fluid multicomponent Yukawa mixtures, and supplements the Yukawa ''mixing rule'' developed [23] on the basis of the asymptotic strong coupling properties.

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APPENDIX A: VARIATIONAL HARD-SPHERE MODEL FOR YUKAWA AND COULOMB PLASMA MIXTURES

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 $g_{ij}(r)$

$$u=\frac{U}{Nk_BT}=\frac{n}{2}\sum_{i,j}x_ix_j\int g_{ij}(r)\,\frac{\phi_{ij}(r)}{k_BT}\,d^3r, \tag{A1}$$

where $x_i=N_i/N$ are the number concentrations. For the Yukawa potential $u_{ij}(r)/k_BT=Z_iZ_j\Gamma e^{-\alpha r}/r$ this takes the special form

$$u=\frac{U}{Nk_BT}=\frac{3\Gamma}{2}\sum_{i,j}Z_iZ_jx_ix_j\hat{G}_{ij}(\alpha), \tag{A2}$$

where $\hat{G}_{ij}(\alpha)=\int_0^\infty rg_{ij}(r)e^{-\alpha r}dr$ is the Laplace transform of $[rg_{ij}(r)]$. In the Coulomb limit, $\alpha=0$ we have to subtract the contribution of the uniform compensating background charge density, and the potential energy is related to our energy expression u by using $[g_{ij}(r)-1]$ instead of $g_{ij}(r)$ in (A1) and (A2), i.e.,

$$u=\lim_{\alpha=0}\frac{3\Gamma}{2}\sum_{ij}x_ix_jZ_iZ_j\left(\hat{G}_{ij}(\alpha)-\frac{1}{\alpha^2}\right). \tag{A3}$$

The variational excess free energy [42,43] (in Nk_BT units) is based on the Gibbs-Bogoliubov-Feynman inequality, and takes the form

$$f_{\text{ex}}(\alpha,\eta,q,\Gamma_e,Z_1,Z_2,x)=f_{\text{ex}}^{\text{HS}}(\eta,q,x)+u_{\text{HS}}(\alpha,\eta,q,\Gamma_e,Z_1,Z_2,x), \tag{A4}$$

where $f_{\rm ex}^{\rm HS}$ is the excess free energy for the hard-sphere binary mixture, and $u_{\rm HS}$ is the excess (potential) energy obtained by the standard expression but using the hard-sphere radial distribution functions in the energy integral. The variational parameters are the total hard-sphere packing fraction η and the ratio between the two hard-sphere diameters q. The optimal values of the parameters η_0,q_0 are obtained by minimizing $f_{\rm ex}$

$$\frac{\partial f_{\rm ex}(\alpha,\eta,q,\Gamma_e,Z_1,Z_2,x)}{\partial\eta}=0;$$

$$\frac{\partial f_{\rm ex}(\alpha,\eta,q,\Gamma_e,Z_1,Z_2,x)}{\partial q}=0. \tag{A5}$$

With the exact hard-sphere input this gives an exact upper bound to the excess free energy. With approximate input, e.g., the Percus-Yevick pair correlations, and the Percus-Yevick virial excess free energy, this provides a model approximation for the excess free energy, which is convenient to apply since the Laplace transforms of the hard-sphere pair correlations in the Percus-Yevick approximation are given analytically [45]. In view of a misprint in the paper by Lebowitz [45], and in order to make the present paper self-contained, we hereby give the complete set of relations which yields the desired expression for the energy integral using the Percus-Yevick pair correlations for spheres of total packing fraction η, and size ratio q. Define $x_2=x$, $x_1=1-x_2$, and since we use the Wigner-Seitz radius as our unit of length, the density is $\rho=3/4\pi$. Define $\rho_1=x_1\rho$, $\rho_2=x_2\rho$, $\eta_1=\pi\rho_1/6$, $\eta_2=\pi\rho_2/6$, then the hard-sphere radii are given by, $R_2=[\eta/(\eta_1 q^3+\eta_2)]^{1/3}$, $R_1=qR_2$, and define also $R_{12}=(R_1+R_2)/2$. The input parameters are thus: $\alpha,x,q,\Gamma,\eta,Z_1,Z_2$.

(a) *Energy integral for Yukawa mixtures*: $u_{\rm PY}(\alpha,\eta,q,\Gamma,Z_1,Z_2,x)$

$$h=36\eta_1\eta_2(R_2-R_1)(R_2-R_1),$$

$$L_1=12\eta_2\left[\left(1+\frac{1}{2}\ \eta\right)+\frac{3}{2}\ \eta_1R_1R_1(R_2-R_1)\right]R_2\alpha^2$$
$$+[12\eta_2(1+2\eta)-hR_1]\alpha+h,$$

$$L_2=12\eta_1\left[\left(1+\frac{1}{2}\ \eta\right)+\frac{3}{2}\ \eta_2R_2R_2(R_1-R_2)\right]R_1\alpha^2$$
$$+[12\eta_1(1+2\eta)-hR_2]\alpha+h,$$

$$S=h+[12(\eta_1+\eta_2)(1+2\eta)-h(R_1+R_2)]\alpha-18(\eta_1R_1^2$$
$$+\eta_2R_2^2)^2\alpha^2-6(\eta_1R_1^2+\eta_2R_2^2)(1-\eta)\alpha^3-(1-\eta)^2\alpha^4,$$

$$D=h-L_1\exp(\alpha R_1)-L_2\exp(\alpha R_2)+S\ \exp[\alpha(R_1+R_2)],$$

$$g_{11}=\alpha[h-L_2\exp(\alpha R_2)]/D/12/\eta_1,$$

$$g_{22}=\alpha[h-L_1\exp(\alpha R_1)]/D/12/\eta_2,$$

$$G=\left[\frac{3}{4}\ (\eta_2R_2^3-\eta_1R_1^3)(R_2-R_1)-R_{12}\left(1+\frac{1}{2}\ \eta\right)\right]\alpha,$$

$$g_{12}=(\eta_1\eta_2)^{1/2}\alpha^2\exp(\alpha R_{12})[G-(1+2\eta)]/D/(\eta_1\eta_2)^{1/2},$$

$$u_{\rm PY}(\alpha,\eta,q,\Gamma,Z_1,Z_2,x)=\frac{3}{2}\ \Gamma(x_1^2Z_1^2g_{11}+x_2^2Z_2^2g_{22}$$
$$+2x_1x_2Z_1Z_2g_{12}).$$

(b) *Percus-Yevick virial excess free-energy* $f_{\rm PYV}(\eta,q,x)$

$$A_3=(x_1R_1^3+x_2R_2^3),$$

$$A_2=(x_1R_1^2+x_2R_2^2),$$

$$A=3(x_1R_1+x_2R_2)A_2/A_3,$$

$$B=\frac{3}{2}\ A_2^3/A_3^2,$$

$$f_{\rm PYV}(\eta,q,x)=(2B-1)\ln(1-\eta)+(2B+A)\eta/(1-\eta).$$

(c) *Energy integral for the one-component Yukawa system*

$$L=12\eta\left[\left(1+\frac{1}{2}\ \eta\right)s+(1+2\eta)\right],$$

$$S=[(1-\eta)^2]s^3+6\eta(1-\eta)s^2+18\eta^2s-12\eta(1+2\eta),$$

$$g(\eta,s)=[(Ls/(12\eta)]/[L+S\ \exp(s)],$$

$$\sigma=2\eta^{1/3},$$

$$u(\eta,\Gamma,Z,\alpha)=\frac{3}{2}\ \Gamma Z^2\sigma^2g(\eta,\alpha\sigma).$$

(d) *Percus-Yevick virial excess free energy for the one-component system*

$$f_{\rm PYV}(\eta)=2\ \ln(1-\eta)+6\eta/(1-\eta).$$

(e) *Energy integral for the Coulomb plasma*

In the Coulomb limit of the Yukawa energies we have to cancel correctly divergent terms, and the energy is given through the following expressions:

$$h=36\eta_1\eta_2(R_2-R_1)(R_2-R_1),$$

$$a_1=[12\eta_2(1+2\eta)-hR_1],$$

$$b_1=12\eta_2\left[\left(1+\frac{1}{2}\ \eta\right)+\frac{3}{2}\ \eta_1R_1R_1(R_2-R_1)\right]R_2,$$

$$a_2=[12\eta_1(1+2\eta)-hR_2],$$

$$b_2=12\eta_1\left[\left(1+\frac{1}{2}\ \eta\right)+\frac{3}{2}\ \eta_2R_2R_2(R_1-R_2)\right]R_1,$$

$$a_3=-(1+2\eta),$$

$$b_3=\left[\frac{3}{4}\ (\eta_2R_2^3-\eta_1R_1^3)(R_2-R_1)-R_{12}\left(1+\frac{1}{2}\ \eta\right)\right],$$

$$c_1=[12(\eta_1+\eta_2)(1+2\eta)-h(R_1+R_2)],$$

$$c_2=-18(\eta_1R_1^2+\eta_2R_2^2)^2,$$

$$c_3=-6(\eta_1R_1^2+\eta_2R_2^2)(1-\eta),$$

$$c_4=-(1-\eta)^2,$$

$$\sigma_{12}=R_1+R_2,$$

$$w_4=c_4+c_3\sigma_{12}+c_2\sigma_{12}^2/2+c_1\sigma_{12}^3/6+h\sigma_{12}^4/24,$$

$$w_6=(c_4/2+c_3\sigma_{12}/6+c_2\sigma_{12}^2/24+c_1\sigma_{12}^3/120+h\sigma_{12}^4/720)\sigma_{12}^2,$$

$$d_4=w_4-\left[\frac{1}{2}\,b_1R_1^2+a_1R_1^3/6+hR_1^4/24\right]$$
$$-\left[\frac{1}{2}\,b_2R_2^2+a_2R_2^3/6+hR_2^4/24\right],$$

$$d_6=w_6-[b_1R_1^4/24+a_1R_1/24+hR_1/120]$$
$$-[b_2R_2^4/24+a_2R_2/24+hR_2/120],$$

$$t_1=-\left[b_1R_1+\frac{1}{2}\,R_1^2a_1+hR_1^3/6\right]\bigg/\,12/\eta_2,$$

$$t_2=-\left[b_2R_2+\frac{1}{2}\,R_2^2a_2+hR_2^3/6\right]\bigg/\,12/\eta_1,$$

$$t_3=\left[b_3R_{12}+\frac{1}{2}\,a_3R_{12}^2\right],$$

$$g_{22}=(t_1-d_6)/d_4,$$

$$g_{11}=(t_2-d_6)/d_4,$$

$$g_{12}=(t_3-d_6)/d_4,$$

$$u_{\mathrm{PY}}(\alpha=0,\eta,q,\Gamma,Z_1,Z_2,x)=u_{\mathrm{PY}}(\eta,q,\Gamma,Z_1,Z_2,x)$$
$$=\frac{3}{2}\,\Gamma(x_1^2Z_1^2g_{11}+x_2^2Z_2^2g_{22}+2x_1x_2Z_1Z_2g_{12}).$$

For the one-component plasma obtain

$$\sigma=2\,\eta^{1/3},$$

$$u_{\mathrm{PY}}(\eta,\Gamma,Z,\alpha=0)=u_{\mathrm{PY}}(\eta,\Gamma,Z)=\frac{3}{2}\,\Gamma Z^2\sigma^2\left[-\frac{1}{2}\left(1-\frac{1}{5}\,\eta\right.\right.$$
$$\left.\left.+\frac{1}{10}\,\eta^2\right)\bigg/\,(1+2\,\eta)\right].$$

APPENDIX B: OPTIMIZATION OF THE REFERENCE BRIDGE FUNCTIONAL PARAMETERS

Rewrite Eq. (21) in the form

$$F_{\mathrm{ex}}[\{\rho_{m,0}\};\{\rho_m(\vec r)\}]=F_{\mathrm{ex}}^{(\mathrm{ref})}[\{\rho_m(\vec r)\}]$$
$$+[F_{\mathrm{ex}}^{(2)}[\{\rho_{m,0}\};\{\rho_m(\vec r)\}]-F_{\mathrm{ex}}^{(2,\mathrm{ref})}$$
$$\times[\{\rho_{m,0}\};\{\rho_m(\vec r)\}]]. \tag{B1}$$

In the test particle limit for the density profile equations, the second order functional (i.e, without ‘‘bridge’’ contributions) corresponds to the hypernetted-chain (HNC) approximation [49]. Thus the approximation corresponds to the following approximation in the bulk fluid:

$$f=f^{(\mathrm{ref})}+f_{\mathrm{HNC}}-f_{\mathrm{HNC}}^{(\mathrm{ref})}, \tag{B2}$$

where $f=F_{\mathrm{ex}}/k_BT$, and f_{HNC} denotes the HNC approximation free-energy functional for the bulk fluid [67]

$$f_{\mathrm{HNC}}=\mathcal{F}+\frac{\rho}{4}\sum_{ij}x_ix_j\int h_{ij}^2(\vec r)d\vec r, \tag{B3}$$

where $\rho=\Sigma_j\rho_{j,0}$, is the total bulk density and $x_j=\rho_{j,0}/\rho$ are the relative concentrations. The so called ‘‘random-phase approximation free energy functional’’ is given by

$$\mathcal{F}=-\frac{\rho}{2}\sum_{ij}x_ix_j\int c_{ij}(\vec r)d\vec r+\frac{1}{2}\,(2\pi)^{-3}\sum_i x_i\int c_{ii}(\vec k)d\vec k$$
$$+\frac{1}{2\rho}\,(2\pi)^{-3}\int d\vec k\,\ln\det(\underline{\underline{1}}-\underline{C}), \tag{B4}$$

where $\underline{\underline{1}}$ is the unit matrix, and $\underline{C}$ is the matrix of direct correlation functions $(\underline{C})_{ij}=(x_ix_j)^{1/2}c_{ij}(\vec k)$. For pair correlation functions which obey the Ornstein-Zernike equations, and the HNC closure

$$g_{ij}(\vec r)=\exp\left(-\frac{\varphi_{ij}(\vec r)}{k_BT}+h_{ij}(\vec r)-c_{ij}(\vec r)\right) \tag{B5}$$

for some potentials $\varphi_{ij}(\vec r)$, the HNC functional has the property [67] that its variation with respect to variation of the potentials obeys

$$\delta f_{\mathrm{HNC}}=\frac{\rho}{2k_BT}\sum_{ij}x_ix_j\int g_{ij}(\vec r)\,\delta\varphi_{ij}(\vec r)d\vec r, \tag{B6}$$

which is the same relation as holds for the variation of the exact free energy with respect to variation in the potentials. We now recall that the bulk limit for the optimized free energy is the solution of the HNC equation with the reference bridge functional, i.e., $\varphi_{ij}^{\mathrm{ref}}=\phi_{ij}^{\mathrm{ref}}+\overline{b}_{ij}^{\mathrm{ref}}$, for $f_{\mathrm{HNC}}^{(\mathrm{ref})}$ in Eq. (B2), or $\varphi_{ij}=\phi_{ij}+\overline{b}_{ij}^{\mathrm{ref}}$ for f_{HNC} in Eq. (B2). Thus the variation of the approximate free energy f in Eq. (B3) with respect to variation in the reference potentials is

$$\delta f=\frac{\rho}{2k_BT}\sum_{ij}x_ix_j\int d\vec r$$
$$\times\begin{array}{l}(g_{ij}^{\mathrm{ref}}(\vec r)\,\delta\phi_{ij}^{\mathrm{ref}}(\vec r)+g_{ij}(\vec r)\,\delta\overline{b}_{ij}^{\mathrm{ref}}(\{g_{lm}\};\vec r)\\ \quad-g_{ij}^{\mathrm{ref}}(\vec r)[\,\delta\phi_{ij}^{\mathrm{ref}}(\vec r)+\delta\overline{b}_{ij}^{\mathrm{ref}}(\{g_{lm}^{\mathrm{ref}}\};\vec r)])\end{array}$$
$$=\frac{\rho}{2k_BT}\sum_{ij}x_ix_j\int d\vec r[g_{ij}(\vec r)\,\delta\overline{b}_{ij}^{\mathrm{ref}}(\{g_{lm}\};\vec r)$$
$$-g_{ij}^{\mathrm{ref}}(\vec r)\,\delta\overline{b}_{ij}^{\mathrm{ref}}(\{g_{lm}^{\mathrm{ref}}\};\vec r)]. \tag{B7}$$

The relative insensitivity of the bridge functional to differences in the shapes of the input pair correlation functions (which is the preassumption of the present method) implies that the difference $[\delta\overline{b}^{\rm ref}_{ij}(\{g_{lm}\};\vec{r}) - \delta\overline{b}^{\rm ref}_{ij}(\{g^{\rm ref}_{lm}\};\vec{r})]$ is relatively small, and to leading order in the variations we thus have

$$\delta f = \frac{\rho}{2k_BT}\sum_{ij} x_i x_j \int d\vec{r}[g_{ij}(\vec{r}) - g^{\rm ref}_{ij}(\vec{r})]\,\delta\overline{b}^{\rm ref}_{ij}(\{g_{lm}\};\vec{r}). \tag{B8}$$

Thus to optimize the parameters of the reference potential we should make f stationary and solve the following equations:

$$\sum_{ij} \rho_{i,0}\rho_{j,0}\int d\vec{r}[g_{ij}(\vec{r}) - g^{\rm ref}_{ij}(\vec{r})]\,\delta\overline{b}^{\rm ref}_{ij}(\{g_{lm}\};\vec{r}) = 0. \tag{B9}$$

Similar equations in the context of the reference HNC equation for the bulk were previously derived by Lado by a different method [60]. We thus refer to Eq. (B9) as the ''Lado equations''. For simple fluids, interacting via LJ type potentials, or plasmas of point charges interacting through the Coulomb or Yukawa potentials we found that the Lado equations Eq. (B9), or the simplified Lado equations which we proposed [24]

$$\sum_{ij} \rho_{i,0}\rho_{j,0}\int d\vec{r}[g_{ij}(\vec{r}) - g^{\rm ref}_{ij}(\vec{r})]\,\overline{b}^{\rm ref}_{ij}(\{g_{lm}\};\vec{r}) = 0 \tag{B10}$$

yield almost identical results.

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