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Equation of state for multicomponent classical plasmas

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An equation of state for D-dimensional ν-component classical plasmas that interpolates very effectively between the "Debye-Huckle" and "ion-sphere" limits is derived. Extensive analysis for three-dimensional ($D=3$) two-component ($\nu=2$) plasmas is presented.

I. INTRODUCTION

Very effective exact lower bounds for the correlation (internal) energy of classical D-dimensional one-component plasmas have been obtained recently[1] by combining the Ewald hybrid expression for the correlation energy (with optimized auxiliary functions) with Mermin's inequality for the structure factor. The optimized Ewald auxiliary functions describe the interaction energy between two uniformly charged D-dimensional spheres at distance r, and play a key role for strongly coupled plasmas. Here we use a similar approach to derive a new approximate equation of state for plasma mixtures which is adequate for arbitrary values of the plasma coupling parameter, and should be useful for applications.

The classical multicomponent plasma is a D-dimensional ν-component system of charges $Q_i e$, concentrations $x_i=N_i/N$, total ion number density $n=N/V$, at a given temperature $\beta=(k_BT)^{-1}$, imbedded in a uniform neutralizing background of charge density $-\rho_b=-ne\langle Q\rangle$ (the notation used is $\langle Q^s\rangle=\sum_i x_i Q_i^s$) and interacting via the D-dimensional Coulomb potentials

$$u_{ij}(r)=Q_iQ_je^2\phi_D(r)\ ,$$

where $\phi_D(r)$ is the solution of the D-dimensional Poisson equation.[2–4] Define the plasma coupling parameter $\gamma_D=\beta e^2 a_{\mathrm{WS}}^{2-D}$, where a_{WS} is the D-dimensional ion-sphere (Wigner-Seitz) radius, and denote the one-component plasma (OCP) correlation energy per ion (in temperature units) by $(\beta U/N_{\mathrm{OCP}})=u_{\mathrm{OCP}}^{(D)}(\gamma_D)$.

Exact lower bounds for the correlation energy of the mixture are given by the results of the Debye-Huckle[5] (DH) and ion-sphere[6,7] (IS) approximations:

$$u_{\mathrm{mix}}^{(D)}=\left[\frac{\beta U}{N}\right]_{\mathrm{mix}}\geq u_{\mathrm{mix,DH}}^{(D)},u_{\mathrm{mix,IS}}^{(D)}\ . \tag{1}$$

The DH result is effective for weak coupling ($\gamma_D<<1$) while the IS result is effective for strong coupling ($\gamma_D>>1$). For $D=3$ and with the usual notation $\gamma_3=\Gamma$ we have

$$u_{\mathrm{mix,DH}}^{(3)}=-\frac{\sqrt{3}}{2}(\Gamma\langle q^2\rangle^{3/2}$$

and

$$u_{\mathrm{mix,IS}}^{(3)}=-\tfrac{9}{10}\Gamma\langle Q\rangle^{1/3}\langle Q^{5/3}\rangle\ .$$

The weak- and strong-coupling limits are thus represented by a "one-fluid" equation of state (EOS):

$$u_{\mathrm{mix,\ one\ fluid}}^{(D)}=u_{\mathrm{OCP}}^{(D)}(\gamma_D Q_{\mathrm{eff}}^2)\ , \tag{2}$$

with

$$Q_{\mathrm{eff}}^2=\begin{cases}Q_{\mathrm{eff,DH}}^2=\langle Q^2\rangle & \text{for } \gamma_D>>1\\ Q_{\mathrm{eff,IS}}^2=\langle Q\rangle^{1-2/D}\langle Q^{1+2/D}\rangle & \text{for } \gamma_D>>1\end{cases}\ .$$

A one-fluid EOS for strong coupling, with $Q_{\mathrm{eff,IS}}$, was derived by assuming a scaled form for the Ornstein-Zernike direct correlation functions.[8]

Numerical data in 3D, from the solution of the hypernetted chain (HNC) equations and from Monte Carlo (MC) simulations, have shown that the excess free energy of mixing at constant charge density (i.e., constant $\Gamma'=\Gamma\langle Q\rangle^{1/3}$ in 3D) is very small for strongly coupled plasmas. By assuming that it is zero one obtains an EOS which is better than the one-fluid EOS for strong coupling. The result, termed the "linear law," reads[9]

$$u_{\mathrm{mix,linear}}^{(3)}=\sum_i x_i u_{\mathrm{OCP}}^{(3)}(\Gamma\langle Q\rangle^{1/3}Q_i^{5/3})\ . \tag{3}$$

In this paper we derive an EOS for plasma mixtures which is nearly as accurate as (3) for strong coupling (i.e., much better than the one-fluid EOS), gives the IS and DH results in the appropriate limits, and, in general, interpolates very well between these limits.

In Sec. II we display the main features of the "Ewald hybrid" approach for the plasma correlation energy, while the best available exact lower bounds are derived in Sec. III. The new approximate EOS is derived in Sec. IV and is tested against MC and HNC data in 3D. Detailed analysis of the EOS for 3D-plasma mixtures is presented in Sec. V where, in particular, results for the two-component plasma are reviewed and used to further test the validity of the new approximate EOS. Some concluding remarks are contained in Sec. IV.

II. EWALD HYBRID EXPRESSIONS FOR THE CORRELATION ENERGY

A useful approach for understanding the equation of state for plasmas is based on scaling arguments applied in the context of the Ewald hybrid expression for the correlation (internal) energy.[1,8] Let $\theta_{ij}(r)$ be arbitrary functions for which the Fourier transforms $\widetilde{\theta}_{ij}(k)$ exist, then the correlation energy can be written in the following form:

$$u=B[\theta]+W_1[g,\theta]+W_2[S,\theta] \,, \tag{4}$$

where

$$B[\theta]=-\tfrac{1}{2}n\sum_{ij}x_ix_j\int[\theta_{ij}(r)+\beta e^2Q_iQ_j\phi_D(r)]d\vec{r}+\tfrac{1}{2}(2\pi)^{-D}\sum_{i}x_i\int\widetilde{\theta}_{ii}(k)d\vec{k} \,, \tag{5}$$

$$W_1[g,\theta]=\tfrac{1}{2}n\sum_{ij}x_ix_j\int g_{ij}(r)[\theta_{ij}(r)+\beta e^2Q_iQ_j\phi_D(r)]d\vec{r} \,, \tag{6}$$

and

$$W_2[S,\theta]=\tfrac{1}{2}(2\pi)^{-D}\sum_{ij}(x_ix_j)^{1/2}\int S_{ij}(\vec{k})[-\widetilde{\theta}_{ij}(k)]d\vec{k} \,, \tag{7}$$

while $S_{ij}(\vec{k})$ denotes the structure factors related to the pair functions $h_{ij}(\vec{r})=g_{ij}(\vec{r})-1$ by

$$S_{ij}(\vec{k})=\delta_{ij}+n(x_ix_j)^{1/2}\widetilde{h}_{ij}(\vec{k}) \,. \tag{8}$$

A good description of the equation of state in the strong-coupling regime will be given by $u \simeq B[\theta]$, provided $\theta_{ij}(r)\cong c_{ij}(r)$, where $c_{ij}(r)$ denotes the direct correlation functions. The result obtained with $\theta_{ij}(r)=c_{ij}(r)$ and by assuming $W_i[g,c]=0$, namely: $u_{\text{GMSA}}=B[c]+\frac{1}{2}$, has been termed the "generalized mean-spherical approximation" (GMSA).[10] Choosing the functions $\theta_{ij}(r)$ such that $W_1[g,\theta]\geq 0$ and $W_2[S,\theta]\geq 0$ we obtain an exact lower bound $\beta U/N\geq B[\theta]$. The best such bound[1] is the IS result obtained by the choice

$$\theta_{ij}^{(\text{IS})}(r)=-\beta\psi_{ij}^{(D)}(r) \,, \tag{9}$$

where $\psi_{ij}^{(D)}$ is the electrostatic interaction energy between two uniformly charged D-dimensional balls of total charge Q_ie and radii d_i [the balls are denoted $b(d_i)$]:

$$\psi_{ij}^{(D)}(r)=\int_{b(d_i)}d\vec{x}\int_{b(d_j)}d\vec{y}\,\rho_i(|\vec{x}|)\rho_j(|\vec{y}-\vec{r}|)\phi_D(|\vec{x}-\vec{y}) \,, \tag{10}$$

where

$$\rho_i(\omega)=\begin{cases}\overline{\rho}_i & \text{if } \omega<d_i\\ 0 & \text{if } \omega>d_i\end{cases} \tag{11}$$

while $\overline{\rho}_i=Q_ie$ (volume of the "i" ball), and all distances are scaled by a_{WS}. The most important features of (9), from the standpoint of the equation of state for the mixture, are[1] (i) the *separation* of the components

$$B[-\beta\psi]=-\gamma_D\alpha_D\sum_{i}x_i\left[\left[\frac{D-2}{D}\right]\langle Q\rangle Q_id_i^2+\frac{2}{D}Q_i^2d_i^{2-D}\right] , \tag{12}$$

where α_D is the IS "Madelung constant" (e.g., $\alpha_3=\frac{9}{10}$), and (ii) the scaling property

$$\psi_{ii}^{(D)}(r)=Q_i^2e^2d_i^{2-D}\psi_{\mathrm{OCP}}^{(D)}(r/d_i)\ ,\tag{13}$$

where $d^{2-D}\psi_{\mathrm{OCP}}^{(D)}(r/d)$ is the function [Eq. (10)] for identical balls of radius d and until total charge.

III. EXACT LOWER BOUNDS FOR THE CORRELATION ENERGY

Using Mermin's inequality[5] for the structure factor of the OCP,

$$S(\vec{k})\geq S_{\mathrm{RPA}}(k)=[1+n\tilde{\phi}_D(k)]^{-1}\ ,\tag{14}$$

one obtains the following exact lower bound:

$$u_{\mathrm{OCP}}^{(D)}\geq B[-\beta\psi_{\mathrm{OCP}}^{(D)}]+W_2[S_{\mathrm{RPA}},-\beta\psi_{\mathrm{OCP}}^{(D)}]\equiv BW_{2,\mathrm{OCP}}^{(D)}\ .\tag{15}$$

The scaling property of ψ leads to the following result:

$$BW_{2,\mathrm{OCP}}^{(D)}(\gamma_D,d)=-\gamma_D\left[\alpha_D\frac{D-2}{D}d^2+d^{2-D}F_D(\lambda d)\right]\ ,\tag{16}$$

where $\lambda=(k_{\mathrm{DH}}a_{\mathrm{WS}})=\sqrt{D\gamma_D}$ and

$$F_D(x)=\tfrac{1}{2}(2\pi)^{-D}x^D\int_0^\infty\frac{k_{D/2-1}(xy)}{(xy)^{D/2-1}}\psi_{\mathrm{OCP}}^{(D)}(y)dy\ ,\tag{17}$$

while

$$K_{D/2-1}(\lambda r)=\frac{1}{\lambda^{D/2-1}}\int_0^\infty\frac{k^{D/2}}{k^2+\lambda^2}J_{D/2}(kr)dk$$

and $J_{D/2}(x)$ is the Bessel function.

The "best" bound is obtained by maximizing $BW_2^{(D)}$ with respect to d,

$$\left.\frac{\partial BW_{2,\mathrm{OCP}}^{(D)}(\gamma_D,d)}{\partial d}\right|_{d=d_{\mathrm{best,OCP}}}=0\ ,$$

or

$$d^D+\frac{D}{2\alpha_D(D-2)}[F_D(\lambda d)(2-D)+(\lambda D)F_d'(\lambda d)]\,|_{d=d_{\mathrm{best,OCP}}}=0\tag{18}$$

to get $d_{\mathrm{best,OCP}}(\lambda)$, and finally

TABLE I. Lower bounds for the correlation (internal) energy for the three-dimensional one-component plasma, compared with Monte Carlo data.

		Exact bounds			
Γ	MC data Ref. 14	DH	IS	Eq. (17)	Totsuji (Ref. 11)
0.1	−0.0258	−0.0274		−0.026 92	−0.026 93
0.5	−0.2383	−0.3062		−0.265 5	−0.266 9
1	−0.573	−0.8660		−0.650 3	−0.657 2
2	−1.320		−1.80	−1.491 8	−1.518
4	−2.927		−3.60	−3.245 1	−3.322
10	−7.992		−9.00	−8.600 4	−8.854
15	−12.309		−13.50	−13.085 3	−13.49
20	−16.668		−18.00	−17.575 8	−18.14
100	−87.500		−90.00	−89.538 1	−92.55

$$u^{(D)}_{\text{best,OCP}}(\gamma_D)=BW^{(D)}_{2,\text{OCP}}[\gamma_D,d_{\text{best,OCP}}(\lambda)]\ .$$

$u^{(D)}_{\text{best,OCP}}(\gamma_D)$ is an exact lower bound that interpolates between the DH bound (to which it equals for $\gamma_D \ll 1$) and the IS bound (to which it equals for $\gamma_D \gg 1$), which is effective for arbitrary values of γ_D. Denoting $G=(2d)^{-1}$, the 3D result is

$$BW_{2,\text{OCP}}(\Gamma,G)=\Gamma\left[\frac{3}{40}G^{-2}-\frac{6}{5}G\mathscr{F}\left[\frac{\sqrt{3\Gamma}}{G}\right]\right], \tag{19}$$

where

$$\mathscr{F}(x)=1-\frac{10}{x^2}+\frac{30}{x^3}-\frac{120}{x^5}+\frac{30}{x^3}e^{-x}+\frac{120}{x^4}e^{-x}+\frac{120}{x^5}e^{-x}\ . \tag{20}$$

The results obtained by maximizing this lower bound are summarized in Table I.

Mermin's inequality for plasma mixtures takes the form[11]

$$\sum_{ij}(x_ix_j)^{1/2}Q_iQ_jS_{ij}(\vec{k})\geq\langle Q^2\rangle\frac{k^2}{k^2+\lambda_{\text{mix}}^2}\ , \tag{21}$$

where $\lambda_{\text{mix}}=(D\gamma_D\langle Q^2\rangle)^{1/2}$. It is possible to use this inequality to obtain a rigorous bound like (16) by taking $Q_{ij}(r)=-Q_iQ_je^2d^{2-D}\psi^{(D)}_{\text{OCP}}(r/d)$ (i.e., using essentially a single auxiliary function):

$$u^{(D)}_{\text{mix}}\geq-\gamma_D\left[\alpha_D\frac{D-2}{D}\langle Q\rangle^2d^2+\langle Q^2\rangle d^{2-D}F_D(\lambda_{\text{mix}}d)\right]\ . \tag{22}$$

The best such bound is determined by

$$\left[\left[\frac{\langle Q\rangle^2}{\langle Q^2\rangle}\right]^{1/D}d\right]^D+\frac{D}{2\alpha_D(D-2)}[(2-D)F_D(\lambda_{\text{mix}}d)+(\lambda_{\text{mix}}d)F'_D(\lambda_{\text{mix}}d)]=0\ ,$$

and by comparison with (18) the solution is

$$d_{\text{best,mix}}=\left[\frac{\langle Q^2\rangle}{\langle Q\rangle^2}\right]^{1/2}d_{\text{best,OCP}}\left[\lambda_{\text{mix}}\left[\frac{\langle Q^2\rangle}{\langle Q\rangle^2}\right]^{1/D}\right]\ ,$$

so that the best bound from (22) has the form

$$u^{(D)}_{\text{best,mix}}=\frac{\langle Q\rangle^2}{\langle Q^2\rangle}u^{(D)}_{\text{best,OCP}}\left[\gamma_D\frac{\langle Q^2\rangle^{1+2/D}}{\langle Q\rangle^{4/D}}\right]\ . \tag{23}$$

Note that the relation (23) between the bounds for the OCP and the mixture will be obtained for any auxiliary function with a scaled form $d^{2-D}\theta(r/d)$. Totsuji[4,11,12] tried various Ewald auxiliary functions that do have that form but did not recognize the significance of both the functions ψ_{ij} and the scaling property.

The bound (23) improves upon the bounds given by Totsuji[11] and especially it does give the IS Madelung constant for $\gamma_D \gg 1$, but it fails to be effective in strong coupling due to the inadequate charge averaging, i.e., $Q^2_{\text{eff}}=\langle Q\rangle^{2-4/D}\langle Q^2\rangle^{4/D}$. As discussed by Totsuji,[11] the bound (23) gives the correct DH behavior for $\gamma_D \ll 1$ and improves upon the DH and IS bounds in the region of weak and intermediate coupling.

IV. APPROXIMATE EQUATION OF STATE FOR PLASMA MIXTURES

The exact bound (23) suggests an approximate EOS for the mixture of the form

$$u^{(D)}_{\text{mix}}=\frac{\langle Q\rangle^2}{\langle Q^2\rangle}u^{(D)}_{\text{OCP}}\left[\gamma_D\frac{\langle Q^2\rangle^{1+2/D}}{\langle Q\rangle^{4/D}}\right]\ . \tag{24}$$

The main deficiency of this OES is its failure to feature the IS charge averaging. A parametric representation of the correlation energy via the Ewald hybrid expression will be able to interpolate between the DH and IS limits, provided we retain the separation of components as featured by $B[-\beta\psi]$ in Eq. (12). This approach calls for a ν-parameter fit (e.g., the ν radii of the "balls", for the case of a ν-component plasma, but scaling considerations and the separation of components lead to simplified results. At this stage we no longer seek exact bounds but rather hints for an EOS for the mixture.

Consider the following parametric representation (i.e., approximation) for the correlation energy:

$$BW_{2,\mathrm{mix}}^{(D)}=B[-\beta\psi]+W_2[S_{\mathrm{RPA}},-\beta\psi] , \tag{25}$$

which, with the structure factors in the DH [i.e., random-phase-approximation (RPA)] limit,

$$S_{\mathrm{RPA},ij}(k)=\delta_{ij}-\frac{Q_iQ_j}{\langle Q^2\rangle}(x_ix_j)^{1/2}\frac{\lambda_{\mathrm{mix}}^2}{k^2+\lambda_{\mathrm{mix}}^2} , \tag{26}$$

provides the analog of (15) for mixtures (without being an exact bound). After some algebra we get

$$\begin{aligned}BW_{2,\mathrm{mix}}^{(D)}=&-\gamma_D\left[\alpha_D\sum_i x_i\frac{D-2}{D}\langle Q\rangle Q_id_i^2+\sum_i Q_i^2d_i^{2-D}F_D(\lambda_{\mathrm{mix}}d_i)\right]\\&-\frac{1}{2}\frac{(2\pi)^{-D}}{\langle Q^2\rangle}\sum_{ij}x_ix_jQ_i^2Q_j^2\int\frac{\lambda_{\mathrm{mix}}^2}{k^2+\lambda_{\mathrm{mix}}^2}\tfrac{1}{2}[\tilde{\rho}_i(k)-\tilde{\rho}_j(k)]^2d\vec{k} .\end{aligned} \tag{27}$$

Note that if $\tilde{\rho}_i(k)=\tilde{\rho}_j(k)$ for all i,j (that is all d_i's are equal) we retrieve the result (22). Thus, the "mixed" term in (27) has a relatively small effect for weak and intermediate coupling. From the results for the OCP (Table I) we see that, for strong coupling, the term $W_2[S_{\mathrm{RPA}},-\beta\psi]$ produces only small changes on the results with $B[-\beta\psi]$ alone. In view of these observations we ignore the mixed term in (22) and remain with a parameter representation in which the contribution of each component (i.e., parameter) is separate from the others:

$$\bar{u}_{\mathrm{mix}}^{(D)}=-\gamma_D\sum_i x_i\left[\alpha_d\frac{D-2}{D}\langle Q\rangle Q_id_i^2+Q_i^2d_i^{2-D}F_D(\lambda_{\mathrm{mix}}d_i)\right] . \tag{28}$$

The problem of maximizing this expression

$$0=\frac{\partial\bar{u}_{\mathrm{mix}}^{(D)}}{\partial d_i},\quad i=1,\ldots,\nu \tag{29}$$

reduces to that for a single component, and we obtain

$$d_{i,\mathrm{best}}=\left[\frac{Q_i}{\langle Q\rangle}\right]^{1/D}d_{\mathrm{best,OCP}}\left[\lambda_{\mathrm{mix}}\left[\frac{Q_i}{\langle Q\rangle}\right]^{1/D}\right] .$$

Note that $d_i=a_{\mathrm{WS}}(Q_i/\langle Q\rangle)^{1/D}$ is the result of the "ion-sphere" model for the radius of the (charge neutral) ion sphere around an ion of type i. Finally, the solution of (28) and (29) gives

$$\bar{u}_{\mathrm{mix,best}}^{(D)}=\sum_i x_i\frac{Q_i\langle Q\rangle}{\langle Q^2\rangle}u_{\mathrm{best,OCP}}^{(D)}\left[\gamma_D\langle Q\rangle^{1/D}\frac{\langle Q^2\rangle Q_i^{2/D}}{\langle Q\rangle}\right] , \tag{30}$$

where $u_{\mathrm{best,OCP}}^{(D)}$ is the solution of (16) and (18). Note that as an approximate EOS for plasma mixtures, Eq. (30) interpolates between the DH and IS rigorous bounds.

Denoting the excess free energy per ion by $(\beta F^{\mathrm{ex}}/N)=f$, then Eq. (30) suggest the following approximate relation between the EOS of the mixture and that for the OCP:

$$f_{\mathrm{mix}}^{(D)}=\sum_i x_i\frac{Q_i\langle Q\rangle}{\langle Q^2\rangle}f_{\mathrm{OCP}}^{(D)}\left[\gamma_D\langle Q\rangle^{1/D}\frac{\langle Q^2\rangle Q_i^{2/D}}{\langle Q\rangle}\right] . \tag{31}$$

Computer simulation data and HNC results are available (in the literature) for binary ionic mixtures (two-component plasma) in 3D. For $D=3$

TABLE II. Comparison of the HNC free and internal energies (Ref. 13) with the values obtained by the linear law (2), and the new equations (28) and (29) for $Q_1=1$, and various values of Q_2, Γ, and x_1.

Q_2	Γ	x_1	$-f_{\rm HNC}$	$-f_{\rm linear}$	$-f_{\rm new}$	$-u_{\rm HNC}$	$-u_{\rm linear}$	$-u_{\rm new}$
2	5	0.5	8.693	8.710	8.731	9.638	9.644	9.669
2	40	0.75	54.911	54.933	55.049	57.438	57.441	57.514
3	1	0.75	1.5708	1.5956	1.599	1.8741	1.8854	1.904
3	10	0.75	20.854	20.9034	21.036	22.289	22.3005	22.406
3	10	0.5	37.111	37.1623	37.280	39.090	39.1005	39.191
3	10	0.25	55.280	55.3133	55.381	57.804	57.8091	57.859
8	1.6758	0.9	6.1025	6.2069	6.317	6.6683	6.6964	6.825
8	4	0.95	8.5372	8.6191	8.833	9.2649	9.2812	9.469
8	4	0.9	15.573	15.701	15.960	16.546	16.573	16.791
8	10	0.95	22.750	22.848	23.282	24.019	24.040	24.338

Eq. (31) yields

$$f^{(3)}_{\rm mix}=\sum_i x_i \frac{Q_i\langle Q\rangle}{\langle Q^2\rangle} f^{(3)}_{\rm OCP}\left[\Gamma\langle Q\rangle^{1/3}\frac{\langle Q^2\rangle Q_i^{2/3}}{\langle Q\rangle}\right], \tag{32}$$

$$u^{(3)}_{\rm mix}=\sum_i x_i \frac{Q_i\langle Q\rangle}{\langle Q^2\rangle} u^{(3)}_{\rm OCP}\left[\Gamma\langle Q\rangle^{1/3}\frac{\langle Q^2\rangle Q_i^{2/3}}{\langle Q\rangle}\right]. \tag{33}$$

The results of this approximate EOS for various binary ionic mixtures in the strong-coupling regime, for both MC and HNC, compared with direct MC or HBC calculations (respectively), are presented in Tables II and III. For the OCP EOS we take the following fits:

$$u^{(3)}_{\rm OCP,HNC}(\Gamma)=\Gamma^{3/2}\left[\frac{A_1}{(B_1+\Gamma)^{1/2}}+\frac{A_2}{B_2+\Gamma}+\frac{A_3}{(B_3+\Gamma)^{3/2}}\right], \tag{34}$$

with

$$A_1=-0.902\,165,\quad B_1=-0.599\,750\,,$$

$$A_2=0.295\,087,\quad B_2=0.847\,639\,,$$

$$A_3=-0.050\,775,\quad B_3=1.003\,474\,,$$

for HNC,[13] while for MC we use[14,15]

$$u^{(3)}_{\rm OCP,MC}(\Gamma)=-0.897\,91\Gamma+0.952\,77\Gamma^{1/4}-0.817\,65+0.189\,02\Gamma^{-1/4} \tag{35}$$

in the range $\Gamma\geq 1$. We find that Eqs. (32) and (33) are, in general, much more accurate than the one-fluid EOS, and are neraly as accurate as the linear law. Additional tests are provided in Sec. V.

V. DETAILED ANALYSIS FOR $D=3$

In this section we put on quantitative basis the qualitative statement that the accuracy of the equa-

TABLE III. Comparison of Monte Carlo and HNC internal energies (Ref. 15) with the values obtained by the linear law (2) and the new equation (29) for $Q_1=1$ and various values of Q_2, Γ, and x_1. Note that in all cases considered in this table the one-fluid equation of state gives the same values for the internal energy, namely, $u=-16.4985$ for HNC and -16.6273 for Monte Carlo.

				HNC			MC	
Q_2	Γ	x_1	$-u_{\rm HNC}$	$-u_{\rm linear}$	$-u_{\rm new}$	$-u_{\rm MC}$	$-u_{\rm linear}$	$-u_{\rm new}$
2	12.0	0.75	16.5507	16.5564	16.5975	16.8813	16.6667	16.7115
2	8.3511	0.5	16.5503	16.5566	16.5900	16.6872	16.6659	16.7019
2	6.2936	0.25	16.5298	16.5344	16.5516	16.6706	16.6481	16.6664
10	1.0905	0.25	16.9232	16.9713	17.0924	17.0321	17.0613	17.1912
10	0.4768	0.5	16.7816	16.8205	16.8705	16.9033	16.9224	16.9821
10	0.2876	0.75	16.6376	16.6593	16.6765	16.7743	16.7766	16.7936

tion of state for a $(\nu+1)$-component plasma is similar to the accuracy claimed for the screening factors for nuclear reaction rates in ν-component plasmas. The analysis presented here in order to further test the accuracy of our new EOS, should prove useful for a proper interpretation of computer simulation data.

A. General relations

The excess free energy per ion for a ν-component plasma depends on ν-independent variables, which in view of the accuracy of the linear law are chosen to be $\Gamma'=\Gamma\langle Q\rangle^{1/3}$ and $\{x_i, i=1,\ldots,\nu-1\}$:

$$\frac{\beta F^{\mathrm{ex}}(\nu)}{n}=f_{(\nu)}(\Gamma',x_1,\ldots,x_{\nu-1})$$

$(=f_{(\nu)}$ in short notations). The correlation energy

$$\frac{\beta U_{(\nu)}}{N}=\Gamma'\left[\frac{\partial f_{(\nu)}}{\partial \Gamma'}\right]_{x_1,\ldots,x_{\nu-1}}=u_{(\nu)}(\Gamma',x_1,\ldots,x_{\nu-1})$$

$(=u_{(\nu)}$ in short notations). The OCP results are thus denoted by $f_{\mathrm{OCP}}=f_{(1)}$, $u_{\mathrm{OCP}}=u_{(1)}$. Various approximations like the one-fluid, linear (24), or (31) are written in a form which is symmetric in all concentations x_i, $i=1,\ldots,\nu$, that is , the extra variable x_ν is included explicitly despite the fact that it depends on the other via $x_\nu=1-\sum_{i=1}^{\nu-1}x_i$. Thus define the symmetric form

$$\frac{\beta F^{\mathrm{ex}}(\nu)}{N}=f^S_{(\nu)}(\Gamma',x_i,\ldots,x_\nu)\ ,$$

and note that

$$\left[\frac{\partial f_{(\nu)}}{\partial x_i}\right]_{\Gamma',x_j\neq x_i}=\left[\frac{\partial f^S_{(\nu)}}{\partial x_i}\right]_{\Gamma',x_j\neq x_j}-\left[\frac{\partial f^S_{(\nu)}}{\partial x_\nu}\right]_{\Gamma',x_j\neq x_\nu}. \tag{36}$$

We shall use the notation $\partial f_{(\nu)}/\partial x_i$ for

$$\left[\frac{\partial f_{(\nu)}}{\partial x_i}\right]_{\Gamma',x_j\neq x_i}.$$

The screening factor $H_{ij}^{(\nu)}(0)=\lim_{r\to 0}[g_{ij}(r)e^{\beta u_{ij}(r)}]$ can be also defined thermodynamically by the following free-energy difference[1,16]:

$$\begin{aligned}H_{ij}^{(\nu)}(0)=&Nf^S_{(\nu)}(\Gamma',x_1,\ldots,x_\nu)\\&-(N-1)f^S_{(\nu+1)}\left[\Gamma',x_1+\frac{x_1}{N-1},x_2+\frac{x_2}{N-1},\ldots,\right.\\&\left.x_i+\frac{x_i}{N-1}-\frac{1}{N-1},\ldots,x_j+\frac{x_j}{N-1}-\frac{1}{N-1},\ldots,x_\nu+\frac{x_\nu}{N-1},x_{\nu+1}\right],\end{aligned}$$

where $Q_{\nu+1}=Q_i+Q_j$ and $x_{\nu+1}=1/(N-1)$. This relation can be written as

$$\begin{aligned}H_{ij}^{(\nu)}(0)&=f^S_{(\nu)}+\lim_{x_\nu\to 0}\left[-\left[\sum_{i=1}^{\nu}x_i\frac{\partial f^S_{(\nu+1)}}{\partial x_i}\right]+\frac{\partial f^S_{(\nu+1)}}{\partial x_i}+\frac{\partial f^S_{(\nu+1)}}{\partial x_j}-\frac{\partial f^S_{(\nu+1)}}{\partial x_{\nu+1}}\right]\\&=f^S_{(\nu)}-\left[\sum_{i=1}^{\nu}x_i\frac{\partial f_{(\nu)}}{\partial x_i}\right]+\frac{\partial f^S_{(\nu)}}{\partial x_i}+\frac{\partial f^S_{(\nu)}}{\partial x_j}-\lim_{\substack{x_{\nu+1}\to 0\\ Q_{\nu+1}=Q_i+Q_j}}\left[\frac{\partial f^S_{(\nu+1)}}{\partial x_{\nu+1}}\right].\end{aligned} \tag{37}$$

Defining

$$\mu_{Q_l}^{(\nu)}=f_{(\nu)}^{S}+\lim_{x_{\nu+1}\to 0}\left[-\left[\sum_{i=1}^{\nu}x_i\frac{\partial f_{(\nu+1)}^{S}}{\partial x_i}\right]+\frac{\partial f_{(\nu+1)}^{S}}{\partial x_l}\right] \tag{38}$$

we obtain a convenient and symmetric result for the symmetric forms for the EOS:

$$H_{ij}^{(\nu)}(0)=\mu_{Q_i}^{(\nu)}+\mu_{Q_j}^{(\nu)}-\mu_{Q_i+Q_j}^{(\nu)}\ . \tag{39}$$

The chemical potential for an ion of type i in the ν-component plasma is given by

$$\begin{aligned}\beta\mu_i^{(\nu)}&=\frac{\partial}{\partial N_i}(Nf_{(\nu)})\\&=\frac{\partial f_{(\nu)}^{S}}{\partial x_i}+\frac{1}{3}u_{(\nu)}\left[\frac{Q_i}{\langle Q\rangle}+1\right]\ .\end{aligned} \tag{40}$$

Thus we have

$$\begin{aligned}\frac{\partial f_{(\nu)}^{S}}{\partial x_i}&=\beta\mu_i^{(\nu)}-\beta\mu_{(\nu)}\\&\quad-(\beta\mu_{(\nu)}-f_{(\nu)})\frac{Q_i}{\langle Q\rangle}\ ,\end{aligned} \tag{41}$$

$$\begin{aligned}\frac{\partial f_{(\nu)}}{\partial x_i}&=(\beta\mu_i^{(\nu)}-\beta\mu_\nu^{(\nu)})\\&\quad+(f_{(\nu)}-\beta\mu_{(\nu)})\left[\frac{Q_i}{\langle Q\rangle}-\frac{Q_\nu}{\langle Q\rangle}\right]\ ,\end{aligned} \tag{42}$$

and

$$\mu_{Q_l}^{(\nu)}=\beta\mu_l^{(\nu)}-(\beta\mu_{(\nu)}-f_{(\nu)})\frac{Q_l}{\langle Q\rangle}\ , \tag{43}$$

where the total chemical potential is

$$\beta\mu_{(\nu)}=\sum_{i=1}^{\nu}x_i\beta\mu_i^{(\nu)}=f_{(\nu)}+\tfrac{1}{3}u_{(\nu)}\ . \tag{44}$$

From (39) and (43) we finally obtain the following expression for the screening factors:

$$H_{ij}^{(\nu)}(0)=\beta\mu_i^{(\nu)}+\beta\mu_j^{(\nu)}-\lim_{\substack{x_{\nu+1}\to 0\\ Q_{\nu+1}=Q_i+Q_j}}[\beta\mu_{\nu+1}^{(\nu+1)}]\ . \tag{45}$$

The HNC energy equation of state is highly accurate (see, e.g., Table II), and the chemical potentials $\beta\mu_i^{(\nu)}$ (via the "energy" EOS) can be calculated, in HNC, directly in terms of the structure functions:

$$\beta\mu_i^{(\nu)}=\sum_{j=1}^{\nu}x_j\left[\tfrac{3}{2}\int_0^{\infty}h_{ij}(r)[h_{ij}(r)-c_{ij}(r)]r^2dr-3\int_0^{\infty}\left[c_{ij}(r)+\frac{\Gamma Q_iQ_j}{r}\right]r^2dr\right]\ , \tag{46}$$

where r is in units of a_{WS} (and thus $n=3/4\pi$). Note, however, that HNC theory is thermodynamically inconsistent and the result obtained from (45) and (46) (which should be a very good approximation to the exact results) does not agree with the direct structural definition of HNC theory,

$$[H_{ij}^{(\nu)}(0)]_{\mathrm{HNC}}=-1-[c_{ij}(0)]_{\mathrm{HNC}}\ . \tag{47}$$

The modified HNC (MHNC) theory, with the hard-sphere (HS) bridge functions,[8,17,18] does bring the structural definition

$$\begin{aligned}[H_{ij}^{(\nu)}(0)]_{\mathrm{MHNC}}&=-1-[c_{ij}(0)]_{\mathrm{MHNC}}\\&\quad-[B_{ij}^{\mathrm{HS}}(0)]_{\mathrm{MHNC}}\end{aligned} \tag{48}$$

into agreement with the thermodynamic expression (45), but small discrepancies should remain. As discussed, however, in Ref. 17 the thermodynamic definition (45) when evaluated with the EOS of the MHNC theory is within the noise of the best available Monte Carlo calculations.

B. Binary ionic mixtures ($\nu=2$)

Let $\Gamma_1=\Gamma' Q_1^{5/3}$ and $\Gamma_2=\Gamma' Q_2^{5/3}$, then the free energy of the two-component plasma in the linear approximation is

$$\begin{aligned}f_{(2),\mathrm{linear}}&=x_1f_{(1)}(\Gamma_1)\\&\quad+(1-x_1)f_{(1)}(\Gamma_2)\ ,\end{aligned} \tag{49}$$

and the small deviations from the linear law, $\Delta f_{(2)}$, may be defined

$$\Delta f_{(2)}=f_{(2)}-f_{(2),\mathrm{linear}}\ . \tag{50}$$

In the limits $x_1\to 0$ or $x_2\to 0$, the free energy of the binary mixture is determined by the slopes at infinitely small dilutions p_1 and p_2:

$$f_{(2)}(\Gamma',x_1)=f_{(1)}(\Gamma_1)+p_1x_2+O(x_2^2)\ ,$$
$$f_{(2)}(\Gamma',x_1)=f_1(\Gamma_2)-p_2x_2+O(x_1^2)\ , \quad (51)$$

where

$$p_1=-\lim_{x_2\to 0}\left[\frac{\partial f_2}{\partial x_2}\right]=p_1\left[\Gamma_1,\frac{Q_2}{Q_1}\right]\ ,$$
$$p_2=\lim_{x_1\to 0}\left[\frac{\partial f_2}{\partial x_2}\right]=p_2\left[\Gamma_2,\frac{Q_2}{Q_1}\right]\ . \quad (52)$$

For $Q_2>Q_1$ the slopes p_1 and p_2 are both positive, and in the linear approximations are given by

$$(p_1)_{\text{linear}}=(p_2)_{\text{linear}}=p_l\equiv f_{(1)}(\Gamma_2)-f_{(1)}(\Gamma_1)\ . \quad (53)$$

Extensive HNC calculations[13] yield always $\Delta f_{(2)}\geq 0$, $\Delta p_1\equiv p_1-p_l\geq 0$, $\Delta p_2\equiv p_l-p_2\geq 0$. The high accuracy of the linear law is measured by

$$\left|\frac{\Delta p_1}{p_1}\right|<<1$$

and

$$\left|\frac{\Delta p_2}{p_2}\right|<<1\ .$$

The simplest Padé approximant for $\Delta f_{(2)}$ with the correct limiting behavior (51), namely,

$$\Delta f_{(2),\text{Padé}}=(\Delta p_1)\frac{x_2-x_2^2}{1+[(\Delta p_1-\Delta p_2)/\Delta p_2]x_2}\ , \quad (54)$$

is in remarkable agreement with the HNC results for binary mixtures.[13] For $\Gamma_1\gtrsim 1$ we find from the HNC data that $\Delta p_2\cong(Q_1/Q_2)\Delta p_1$, so that roughly

$$\Delta f_{(2)}\cong(\Delta p_1)\frac{x_2-x_2^2}{1+[(Q_2/Q_1)-1]x_2}\lesssim\Delta p_1\ .$$

Thus in HNC, the deviations from the linear law for $\Gamma_1\gtrsim 1$, have essentially the magnitude of Δp_1 and a form with asymmetry characterized by $(Q_2/Q_1)-1$. The maximum of $\Delta f_{(2)}$ occurs at about

$$x_2\cong\frac{(Q_2/Q_1)^{1/2}-1}{(Q_2/Q_i)-1}\ ,$$

with the value of

$$(\Delta f_{(2)})_{\max}\cong(\Delta p_1)\frac{[(Q_2/Q_1)^{1/2}-1]^2+1}{[(Q_2/Q_1)-1]^2}\ ,$$

which turns out to be roughly independent of Q_2/Q_1 for the same Γ_1.

Of special significance in this context are the results for p_1 when $Q_2/Q_1=2$ [denoted $p_1(\Gamma_1, Q_2/Q_1=2)$]. In that case we have

$$p_1\left[\Gamma_1,\frac{Q_2}{Q_1}=2\right]=f_{(1)}(\Gamma_1)-H^{(1)}(r=0;\Gamma_1)\ , \quad (55)$$

where $H^{(1)}(r=0;\Gamma_1)$ is the screening factor for a one-component plasma for $\Gamma=\Gamma_2$. Recall that in the linear approximation

$$H^{(1)}_{\text{linear}}(r=0;\Gamma_1)=2f_{(1)}(\Gamma_1)-f_{(1)}(2^{5/3}\Gamma_1)\ , \quad (56)$$

and the correction to (56) is given by

$$\Delta H^{(1)}\equiv H^{(1)}(r=0;\Gamma_1)-H^{(1)}_{\text{linear}}(r=0;\Gamma_1)=-\left[p_2\left[\Gamma_i;\frac{Q^2}{Q_1}=2\right]-p_l\right]=-\Delta p_1\left[\Gamma_2;\frac{Q_2}{Q_1}=2\right]\ . \quad (57)$$

Comparison with Eq. (54) and the discussion following it shows how the values of $H^{(1)}(r=0;\Gamma)$ and $f_{(1)}(\Gamma)$ practically determine the EOS of the two-component plasma [i.e., $f_{(2)}(\Gamma',x_1)$].

The statement that

$$(\Delta f_{(2)})_{\text{Monte Carlo}}=(\Delta f_{(2)})_{\text{HNC}} \quad (58)$$

is within the accuracy of the best computer simulation data available at present. Since the corrections Δp_1, $\Delta f_{(2)}$ are relatively small in strong coupling, results leaning on the linear law will be strongly affected in all cases when one of the arguments, $\Gamma_i=\Gamma' Q_i^{5/3}\gtrsim\Gamma_{\text{sf}}$, where $\Gamma_{\text{sf}}\cong 170$ is the value of the solid-fluid transition for the OCP.

TABLE IV. (a) Slopes p_1 and p_2 (see text) of the free energy vs concentration curves in the HNC approximation, at constant Γ', as function of $\Gamma_1=\Gamma' Q_1^{5/3}$ and $\Gamma_2=\Gamma' Q_2^{5/3}$, for ionic charge ratios $Q_2/Q_1=2$. The HNC results are compared with the corresponding results via the linear law (p_l) and via the new equation of state ($p_{1,\text{new}},p_{2,\text{new}}$). (b) Same as (a) for $Q_2/Q_1=8$.

Γ_1	$-p_1$	$-p_{1,\text{new}}$	$-p_l$	Γ_2	$-p_2$	$-p_{2,\text{new}}$	$-p_l$
(a) $Q_2/Q_1=2$							
0.05	0.024 68	0.0247	0.027 96	1	0.3563	0.3519	0.3455
0.2	0.175 0	0.1774	0.191 0	2	0.8391	0.8270	0.8206
1	1.371 1	1.4137	1.424 6	5	2.4390	2.4044	2.4078
2	3.082 2	3.1822	3.154 2	10	5.2589	5.1935	5.2176
5	8.513 1	8.7665	8.609 5	20	11.072	10.960	11.021
10	17.839 8	18.2910	17.955 1	40	22.925	22.745	22.863
20	36.795	37.532	36.930	60	34.897	34.668	34.830
40	75.107	76.234	75.258	80	46.931	46.660	46.860
60	113.634	115.049	113.792	120	71.102	70.764	71.024
100	190.966	192.829	191.140	160	95.353	94.962	95.273
(b) $Q_2/Q_1=2$							
0.05	0.5300	0.5456	0.7925	5	3.2215	3.1771	3.1573
0.2	3.4046	3.7077	4.2018	10	7.0755	6.9828	6.9711
0.4	8.0176	9.0053	9.1761	20	15.114	14.942	14.960
1	23.169	26.706	24.792	40	31.631	31.340	31.421
2	49.574	57.308	51.500	80	65.250	64.793	64.984
5	130.666	148.671	132.956	120	99.184	98.603	98.886
10	267.442	298.014	270.040	160	133.278	132.596	132.957

After this discussion we should be able to see the picture based on the new EOS [Eq. (32)], by considering its predictions for p_1 and p_2, namely,

$$-(p_2)_{\text{new}}=\frac{Q_1}{Q_2}f_{(1)}\left[\Gamma_2\left[\frac{Q_1}{Q_2}\right]^{2/3}\right]-f_{(1)}(\Gamma_2)+\frac{Q_1}{Q_2}\left[\frac{Q_1}{Q_2}-1\right][f_{(1)}(\Gamma_2)-u_{(1)}(\Gamma_2)]\;, \tag{59}$$

$$(p_1)_{\text{new}}=\frac{Q_2}{Q_1}f_{(1)}\left[\Gamma_1\left[\frac{Q_2}{Q_1}\right]^{2/3}\right]-f_{(1)}(\Gamma_1)+\frac{Q_2}{Q_1}\left[\frac{Q_2}{Q_1}-1\right][f_{(1)}(\Gamma_1)-u_{(1)}(\Gamma_1)]\;. \tag{60}$$

These, together with the results of the linear law and direct HNC calculations, are presented in Table IV. Equation (32) is exact in the DH limit, is better than the linear law in the weak- and intermediate-coupling regimes ($\Gamma_1 \lesssim 1$), and is of nearly the same accuracy of the linear law in the strong-coupling regime.

VI. CONCLUSIONS

From a purely formal point of view our results can be summarized as follows. Suppose that a very accurate fit of the OCP internal energies can be obtained variationally by a one-parameter function:

$$u_{\text{OCP}}(\gamma_D,d)=-\gamma_D[Ad^2+d^{2-D}\mathcal{F}_D(\sqrt{D\gamma_D}d)]\;,$$

$$\left.\frac{\partial u_{\text{OCP}}(\gamma_D,d)}{\partial d}\right|_{d=\bar{d}}=0\;,\quad u_{\text{OCP,fit}}(\gamma_D)=u_{\text{OCP}}[\gamma_D,\bar{d}(\gamma_D)]\;,$$

where the constant A and the functional form $\mathcal{F}_D(x)$ serve as the fitting parameters. The accuracy of Eq.

(32) suggests that the internal energies for the mixtures can be nearly equally well fitted by

$$u_{\text{mix}}(\gamma_D,\{d_i\})=-\gamma_D\sum_i x_i\{A\langle Q\rangle Q_i d_i^2+Q_i^2 d_i^{2-D}\mathscr{F}_D[(D\gamma_D\langle Q^2\rangle)^{1/2}d_i]\}\,,$$

$$\left.\frac{\partial u_{\text{mix}}}{\partial d_i}\right|_{d_i=\bar{d}_i}=0\,,\quad u_{\text{mix,fit}}=u_{\text{mix}}(\gamma_D,\{\bar{d}_i\})\,,$$

with the same constant A and the same functional form $\mathscr{F}_D(x)$ as used for the OCP. We expect that appropriately modified "fitting" functionals, obtained perhaps from the Ewals hybrid scheme, should prove useful for studying electronic screening corrections for the OCP and, in particular, for plasma mixtures.

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