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Linear mixing rule in screened binary ionic mixtures

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We examine the validity of the empirical "linear mixing rule" for the determination of the thermodynamic properties of screened binary ionic mixtures interacting with effective *density*- and *temperature*-dependent screened Coulomb potentials. Comparison with hypernetted-chain calculations reveals generally good agreement and further verifies the reliability of the linear law, even when the response of the finite-temperature electron gas is taken into account.

I. INTRODUCTION

For many years the study of binary ionic mixtures (BIM) has been of interest because of their immediate application to diverse astrophysical problems as well as to inertial-confinement experiments in plasma physics. Phase separation of elements in these strongly coupled multi-ionic plasma can occur, in principle, in the interior of low-mass stellar objects. Hydrogen-helium phase separation, in particular, has been studied extensively[1,2] and is believed to occur in the interior of the giant planets. Calculations have also been performed for more asymmetric mixtures[3] ($Z_2/Z_1=3-8$) but, until recently, no attempt has been made to look extensively at the possibility of phase separation in highly asymmetric mixtures ($Z_2/Z_1 \geq 8$). Such mixtures may be encountered in quite different astrophysical objects. Brown dwarfs, for example, are promising candidates for H-Fe phase separation,[4] and He-Fe phase separation can occur in the crust of neutron stars. The possibility of Fe-C phase separation as an energy source in cooling white dwarfs[5] has also to be explored. For these reasons the investigation of the phase diagram of such plasmas is of primary interest and indeed requires very accurate calculations of the equations of state of the corresponding ionic mixtures.

The BIM model is a straightforward generalization of the well-known one-component plasma model (OCP), and consists of a mixture of point ions of charges Z_1 and Z_2 (and corresponding masses m_1 and m_2) embedded in a rigid, uniform, neutralizing background of electrons. Hansen and collaborators[1,3] have shown that the contribution of the ionic fluid to the thermodynamics of the plasma at constant temperature T and charge density ρ' can be expressed, to a high degree of accuracy, as a linear interpolation between the thermodynamic functions of the respective pure phases. The excess (nonideal) free energy of the mixture, as well as the other thermodynamic quantities of the ionic fluid, can be expressed by the simple statement

$$\frac{F}{NkT}=f(\Gamma',x_1)$$
$$\simeq x_1 f(\Gamma_1,x_1=1)+(1-x_1)f(\Gamma_2,x_1=0) \ , \qquad (1)$$

where the different parameters will be defined in Sec. II. Equation (1) is referred to as the "linear mixing rule" (LMR) and its use simplifies appreciably the calculation of the thermodynamics of the plasma, in particular the determination of the phase diagram of the mixture. The apparent validity of the linear rule has been demonstrated recently to a very high level of accuracy for a fully ionized carbon and oxygen fluid, and also for solid mixtures near the phase transition.[6] More recently, DeWitt *et al.*[7] have explored the accuracy of Eq. (1) for the BIM for extremely asymmetric mixtures ($Z_2/Z_1=16,24$) by performing hypernetted-chain (HNC) calculations. Again they found the agreement to be good, in fact to about 1% of the thermal energy. In all of these calculations the electron neutralizing background is considered to be completely rigid, i.e., characterized by a dielectric constant equal to unity.

As the density decreases, however, the polarization of the electron gas by the ionic charge distribution must surely be taken into consideration. It can be approximately accounted for by introducing the dielectric function of the electrons. The result is a screened binary ionic mixture (SBIM) in which the ions interact via effective *screened* potentials. It is believed that the phase separation in the different ionic mixtures discussed above would then arise in part from the electron screening of the ions, a contribution that tends to destabilize the mixture.[1] Given this, it is necessary to take into account the response of the electron gas in the calculation of the thermodynamic properties of such ionic mixtures. In turn it is of interest to examine the possible validity of the LMR for such *screened* mixtures. In most situations of interest, the electron gas is just *partially* degenerate, i.e., the degeneracy parameter $\theta=kT/kT_F$ is quite far from zero, so that we are also required to consider the temperature dependence of the screened potentials. To data, the only attempt that has been made to include the response of the electron gas at finite temperature in the phase diagram of a screened binary ionic mixture is the treatment by Iyetomi and Ichimaru.[8] Their work, however, is very restricted in scope and has been applied to solar conditions only, where the ionic plasma is weakly coupled ($\Gamma \sim 5 \times 10^{-2}$).

The purpose of this paper is to examine (and in fact verify) the validity of the LMR, (1) when the response of the electron gas is taken into account in the effective ionic interaction, and (2) when finite-temperature effects are included in the dielectric response of the electrons, i.e., when the ions interact with both temperature- and density-dependent screened Coulomb potentials. We consider three mixtures with different charge ratios, ranging from a symmetric case ($Z_2/Z_1 \sim 1$) to a highly asymmetric case ($Z_2/Z_1 \gg 1$). For each mixture we span a wide range of values for the coupling parameter Γ_i and the degeneracy parameter θ. This work is to be viewed as the first step towards an extensive study of the phase diagrams of the ionic mixtures mentioned above.

II. THE MODEL

We consider a mixture of N_1 ions of charge $Z_1 e$ and N_2 ions of charge $Z_2 e$ in a volume V. Here $N_1+N_2=N$. The number concentrations are $x_1=N_1/N$ and $x_2=1-x_1$; the partial mean number densities are $\rho_1=N_1/V$, $\rho_2=N_2/V$. The average charge density is $\rho'=\rho_1 Z_1+\rho_2 Z_2=\rho\langle Z\rangle$, where $\langle Z\rangle$ is the mean charge $x_1 Z_1+x_2 Z_2$, and $\rho=N/V=\rho_1+\rho_2$ is the total ionic number density. We define, respectively, the mean interionic distance a and the mean interelectronic distance a' by $a=(3/4\pi\rho)^{1/3}$ and $a'=(3/4\pi\rho')^{1/3}=a/\langle Z\rangle^{1/3}$. The density parameter for the quantum electron gas is given as usual by $r_s=a'/a_0$, where a_0 is the Bohr radius. The electronic and ionic coupling parameters are also defined, respectively, by

$$\Gamma'=e^2/a'kT=\Gamma\langle Z\rangle^{1/3}=\frac{0.543r_s}{\theta};\quad \Gamma_i=\Gamma'\langle Z^{5/3}\rangle\ , \tag{2}$$

where

$$\Gamma=e^2/akT\ .$$

We restrict ourselves to densities sufficiently high (i.e., values of r_s sufficiently small) that ion-electron coupling remains weak compared to the kinetic contribution of the electrons. Under these conditions (typically $r_s \le 1$), the linear-response approximation can be used. We also use the adiabatic approximation for the response of the electron gas; i.e., the static limit is assumed valid in the determination of the electronic dielectric function. The validity of the adiabatic approximation has been assessed recently[9] even in the domain of low electronic degeneracy ($\theta \ge 1$), where the finite-temperature effects of the electrons are expected to be important. With this assumption we can integrate over the electronic coordinates, and the fluid under consideration can then be viewed as a superposition of a uniform electronic background and a screened binary ionic fluid. The SBIM is then characterized by the following effective ionic Hamiltonian:[8,10]

$$H=E_e+\hat{K}_i+\hat{V}_\iota\ , \tag{3}$$

with

$$\hat{V}_i=\frac{1}{2V}\sum_{k'}\frac{4\pi e^2}{k^2}\left[\frac{\rho'_{\mathbf{k}}\rho'_{-\mathbf{k}}}{\epsilon(k,w=0)}-N\langle Z^2\rangle\right]\ . \tag{4}$$

In Eq. (3), E_e is the energy of the rigid electron gas, i.e., the jellium model, $\hat{K}_\iota$ represents the kinetic energy of the ions, and $\hat{V}_i$ the effective potential energy after the electron trace is taken. Here $\rho'_{\mathbf{k}}=Z_1\rho_{1\mathbf{k}}+Z_{2\rho_{2\mathbf{k}}}$, where the $\rho_{i\mathbf{k}}$ are the Fourier components of the ion number fluctuations. The dielectric function $\epsilon\equiv\epsilon(k,T,V,w=0)$ is the finite-temperature static Lindhard function, evaluated in the random-phase approximation (RPA). It follows that the Hamiltonian (3) is now both density and temperature dependent. For the two lowest densities considered in our calculations ($r_s=0.5$ and 1), we include a local-field correction (LFC) in the dielectric function in order to take into account nonlinear correlation effects between the electrons beyond the RPA. The LFC used is the one derived by Utsumi and Ichimaru,[11] but is corrected in order to include temperature dependence at long wavelength.[9] The excess internal energy U^{ex} and pressure P^{ex} of the temperature-dependent SBIM characterized by the Hamiltonian following from (4) are calculated within the framework of the hypernetted-chain equations and are given by

$$U^{\mathrm{ex}}=\langle E\rangle+\beta\left\langle\frac{\partial E}{\partial\beta}\right\rangle_V\ , \tag{5a}$$

$$\begin{aligned} u^{\mathrm{ex}}=\frac{\beta U^{\mathrm{ex}}}{N}=&\ \frac{1}{2}\frac{\beta}{(2\pi)^3}\langle Z^2\rangle\int d\mathbf{k}\,v(k)[S_z(k)-1]+\frac{1}{2}\frac{\beta}{(2\pi)^3}\langle Z^2\rangle\int d\mathbf{k}\,v(k)\left[\frac{1}{\epsilon(k)}-1\right]S_z(k)\\ &+\frac{1}{2}\frac{\beta}{(2\pi)^3}\langle Z^2\rangle\int d\mathbf{k}\,v(k)\left[\frac{\partial}{\partial\beta}\left[\frac{1}{\epsilon(k)}\right]\right]_V S_z(k)\ , \end{aligned} \tag{5b}$$

$$P^{\mathrm{ex}}=\tfrac{1}{3}\langle E\rangle-\left\langle\frac{\partial E}{\partial V}\right\rangle_\beta\ , \tag{5c}$$

and

$$\begin{aligned} p^{\mathrm{ex}}=\frac{\beta P^{\mathrm{ex}}}{\rho}=&\ \frac{1}{6}\frac{\beta}{(2\pi)^3}\langle Z^2\rangle\int d\mathbf{k}\,v(k)[S_z(k)-1]+\frac{1}{6}\frac{\beta}{(2\pi)^3}\langle Z^2\rangle\int d\mathbf{k}\,v(k)\left[\frac{1}{\epsilon(k)}-1\right]S_z(k)\\ &-\frac{1}{2}\frac{\beta}{(2\pi)^3}\langle Z^2\rangle\int d\mathbf{k}\,v(k)\left[V\frac{\partial}{\partial V}\left[\frac{1}{\epsilon(k)}\right]\right]_\beta S_z(k)\ . \end{aligned} \tag{5d}$$

Here $v(k)=4\pi e^2/k^2$, and $S_z(k)=\rho'_{\mathbf{k}}\rho'_{-\mathbf{k}}/N\langle Z^2\rangle$. The *interaction energy* is given by the first term on the right-hand side of Eq. (5a), or alternatively by the first two terms on the right-hand side of Eq. (5b). The interaction energy and internal energy are different for a quantum interacting system because of the excess kinetic term, i.e., because of the difference of kinetic energy between the interacting system and the noninteracting (perfect gas) system. This difference vanishes in the zero-temperature limit ($\theta=0$) and in the purely classical limit ($\theta \gg 1$). For the calculations of the excess free energy, we use the extended formula derived by Iyetomi and Ichimaru.[8]

III. RESULTS AND DISCUSSION

In Tables I–III, we summarize the results for the excess thermodynamic quantities of three different mixtures, namely H-He ($Z_2/Z_1=2$), H-O ($Z_2/Z_1=8$), and H-Fe ($Z_2/Z_1=24$). We have assumed that Fe ions have retained their most tightly bound 1*s* electrons. Our approach can be applied to cases where one (or both) ionic species are only partially ionized, provided the remaining ion core possesses a smaller radius than the distance of closest approach. For each mixture we carry out HNC calculations for different concentrations, but over a range of the degeneracy parameter θ. The two limits corresponding to the rigid electron gas, i.e., the BIM model, and the zero-temperature screened binary mixture,[12] are recovered respectively, by setting $r_s \to 0$ and $\theta \to 0$. We establish the accuracy of our HNC calculations by making comparison with the results of Monte Carlo (MC) simulations[1,12] carried out, in both limits, for the H-He mixture, again taken over an extended range of both coupling parameter Γ ($1 \le \Gamma \le 80$) and density parameter r_s ($0.5 \le r_s \le 1.5$). Our results always agree to within less than 1% with the Monte Carlo results. There, is however, a noticeable ($\sim 20\%$) discrepancy in the comparison with the MC results of Hubbard and DeWitt[12] in the limit of *small* values of Γ ($\Gamma < 2$). This discrepancy is attributed to two factors, namely the declining accuracy of the MC method at small Γ (when the Debye radius becomes larger than the unit-cell dimension, leading to a distortion of the results by the periodic boundary condition), and to the approximate mean-square fit of the MC results in this region.[13]

In each case we compare the HNC results with the linear interpolation given by Eq. (1). The results of such a comparison are summarized in Tables I–III for the three different mixtures. The numbers in parenthesis indicate the *relative* departure from the linear mixing rule, defined as $(f-\langle f\rangle)/f$, where f is the thermodynamic function derived from the HNC calculations and $\langle f\rangle$ is given by Eq. (1).

The principal conclusion is that the absolute difference between the thermodynamic functions as derived from the HNC calculations and those given by the LMR is *always small* ($\lesssim 0.07$). This difference, nevertheless, becomes a sizable fraction of the energy of the mixture, so that its relative importance increases in the limit of small Γ. It is also interesting to point out that this difference in energy, which can eventually lead to phase separation in the mixture, becomes positive in the regime of strong coupling ($\Gamma \gg 1$). This point will be clarified below. These results indicate strongly that the LMR is still extremely accurate for the SBIM model, i.e., for ionic mixtures interacting by means of screened Coulomb potentials, even in the case of very asymmetric mixtures.

The physical explanation for this striking feature is the following: It is very well known that for $\Gamma > 1$, the dominant term in the energy of a BIM is the common approximation to the Madelung energy $E_M=-0.9\Gamma_i$.[7,12] This term follows from the use of the ion sphere model[14] $E_{\mathrm{IS}}=-0.9\Gamma'\langle Z^{5/3}\rangle$, a result which states that each ion interacts only with the uniform background in its "ion-sphere," i.e., a sphere of radius $a_\alpha/a=(Z_\alpha/\langle Z\rangle)^{1/3}$, such that the background charge contained in it exactly cancels the charge Z_α of the ion. This result also yields, in fact, a lower bound to the energy for the BIM, and also leads to an immediate understanding of the LMR (1). Now from the definition of the *screened* binary ionic mixture model, the ion-electron interaction is weak compared to the kinetic contribution of the electrons, and can therefore be treated essentially as a perturbation of the bare ion-ion interaction. Therefore we can expect the ion-sphere contribution to remain dominant in the SBIM in the regime of strong coupling and can also expect, in consequence, the LMR to be accurate in this regime. This point has been verified by Hubbard and DeWitt for the H-He mixture.[12]

Accordingly, any departure from the LMR must be attributed to the thermal contribution. The thermal energy is normally obtained by subtracting off the Madelung (ion sphere) energy. When this is done the leading term in the thermal energy, in the strong-coupling regime, behaves as $\Gamma^{1/n}$, where n is believed to be equal to 3 in Monte Carlo calculations,[3] and has been shown to be equal to 2 in the HNC approximation.[15] When the response of the electron gas is taken into account, the thermal energy includes two further contributions, namely the ionic contribution, which is positive[3,12] for large values of Γ, (and which yields a positive value for $f-\langle f\rangle$ for large Γ, as mentioned above), and the thermal contribution arising from the ion-electron interaction, whose sign is not determined and which also depends on the ionic concentration. The ionic contribution is the thermal energy arising from lattice vibrations in a crystal, whereas the ion-electron part can be seen as the equivalent of a temperature-dependent band-structure energy. Any departure from the LMR in the case of a SBIM must then depend on a partial compensation between these two contributions.

As the temperature or degeneracy parameter θ increases at constant density, the coupling parameter Γ_i decreases. In the region of weak coupling ($\Gamma < 1$), the Madelung energy no longer dominates, and there is no clear distinction between static and thermal energy. The correlation energy of the fluid tends towards its Debye Hückel limit, which is proportional to $-(\Gamma\langle Z^2\rangle)^{3/2}$. This term is obviously nonlinear in concentration, and then a departure from the LMR is both expected and found in this region.

Two other features can be observed from our results.

TABLE I. Excess internal energy u^{ex}, excess pressure p^{ex}, and excess Helmholtz free energy f^{ex} per ion in units of kT for the H-He mixture. For each concentration and value of θ, the first line is the HNC result, whereas the second line is the linear interpolation given by Eq. (1). X_H denotes the relative concentration of hydrogen. The number in parenthesis gives the relative difference between these two values. (a) $r_s=0.2$, (b) $r_s=0.5$, (c) $r_s=1$.

X_{H}	θ	Γ_i	$-u^{\text{ex}}$	$-f^{\text{ex}}$	$-p^{\text{ex}}$
			(a) $r_s=0.2$		
1	5	0.022	0.4797×10^{-2}	0.3273×10^{-2}	0.1577×10^{-2}
	1	0.109	0.429×10^{-1}	0.3193×10^{-1}	0.1324×10^{-1}
	0.5	0.217	0.1001	0.7898×10^{-1}	0.295×10^{-1}
	0.05	2.172	1.5123	1.288	0.4704
0.75	5	0.033	0.8867×10^{-2}	0.6063×10^{-2}	0.2919×10^{-2}
			0.9025×10^{-2} (1.8)	0.6180×10^{-2} (1.9)	0.2972×10^{-2} (1.8)
	1	0.168	0.783×10^{-1}	0.5862×10^{-1}	0.2434×10^{-1}
			0.7925×10^{-1} (1.2)	0.5950×10^{-1} (1.5)	0.2469×10^{-1} (1.4)
	0.5	0.335	0.1809	0.144	0.540×10^{-1}
			0.1826 (0.9)	0.1458 (1.2)	0.5468×10^{-1} (1.2)
	0.05	3.35	2.5277	2.2184	0.7859
			2.5300 (0.1)	2.2262 (0.3)	0.7875 (0.2)
0.25	5	0.057	0.1737×10^{-1}	0.1191×10^{-1}	0.5726×10^{-2}
			0.1748×10^{-1} (0.6)	0.1199×10^{-1} (0.7)	0.5763×10^{-2} (0.6)
	1	0.286	0.1513	0.114	0.4734×10^{-1}
			0.1519 (0.4)	0.1146 (0.5)	0.4758×10^{-1} (0.5)
	0.5	0.571	0.3465	0.2783	0.1045
			0.3477 (0.3)	0.2795 (0.4)	0.105 (0.5)
	0.05	5.71	4.5635	4.0971	1.4205
			4.5653 (0)	4.1026 (0.1)	1.4216 (0)
0	5	0.069	0.2171×10^{-1}	0.149×10^{-1}	0.7158×10^{-2}
	1	0.345	0.1883	0.1422	0.5903×10^{-1}
	0.5	0.69	0.4303	0.3464	0.1302
	0.05	6.895	5.583	5.0408	1.7387
			(b) $r_s=0.5$		
1	10	0.027	0.6814×10^{-2}	0.4616×10^{-2}	0.2254×10^{-2}
	5	0.054	0.1851×10^{-1}	0.1275×10^{-1}	0.6068×10^{-2}
	1	0.2715	0.1561	0.1196	0.4762×10^{-1}
	0.1	2.715	2.0621	1.845	0.6024
0.75	10	0.042	0.1255×10^{-1}	0.8532×10^{-2}	0.4153×10^{-2}
			0.1275×10^{-1} (1.6)	0.8689×10^{-2} (1.8)	0.4223×10^{-2} (1.7)
	5	0.084	0.3382×10^{-1}	0.2344×10^{-1}	0.111×10^{-1}
			0.3427×10^{-1} (1.3)	0.2382×10^{-1} (1.6)	0.1125×10^{-1} (1.3)
	1	0.419	0.2769	0.215	0.0849
			0.2782 (0.5)	0.2169 (0.9)	0.0854 (0.6)
	0.1	4.191	3.4458	3.156	1.000
			3.4454 (0)	3.1604 (0.1)	1.0023 (0.2)
0.5	10	0.057	0.1847×10^{-1}	0.1259×10^{-1}	0.6115×10^{-2}
			0.187×10^{-1} (1.2)	0.1276×10^{-1} (1.4)	0.6192×10^{-1} (1.2)
	5	0.113	0.4953×10^{-1}	0.3448×10^{-1}	0.1627×10^{-1}
			0.5003×10^{-1} (1)	0.3489×10^{-1} (1.2)	0.1643×10^{-1} (1)
	1	0.567	0.3989	0.3121	0.1226
			0.4004 (0.4)	0.3141 (0.6)	0.1232 (0.5)
	0.1	5.667	4.8291	4.4709	1.4005
			4.8287 (0)	4.4758 (0.1)	1.4023 (0.1)
0.25	10	0.071	0.245×10^{-1}	0.1673×10^{-1}	0.8111×10^{-2}
			0.2464×10^{-1} (0.5)	0.1684×10^{-1} (0.6)	0.8161×10^{-2} (0.6)
	5	0.143	0.6548×10^{-1}	0.457×10^{-1}	0.2151×10^{-1}
			0.6579×10^{-1} (0.5)	0.4597×10^{-1} (0.6)	0.2162×10^{-1} (0.5)
	1	0.714	0.5216	0.4101	0.1606
			0.5225 (0.2)	0.4114 (0.3)	0.161 (0.2)
	0.1	7.143	6.2123	5.788	1.8011
			6.2120 (0)	5.7912 (0)	1.8022 (0)

Table I. (*Continued*).

X_H	θ	Γ_i	$-u^{ex}$	$-f^{ex}$	$-p^{ex}$
0	10	0.086	0.3058×10^{-1}	0.2091×10^{-1}	0.1013×10^{-1}
	5	0.172	0.8155×10^{-1}	0.5704×10^{-1}	0.268×10^{-1}
	1	0.862	0.6447	0.5087	0.1988
	0.1	8.62	7.5953	7.1066	2.2022
			(c) $r_s=1$		
1	10	0.054	0.1894×10^{-1}	0.1292×10^{-1}	0.6253×10^{-2}
	5	0.109	0.5074×10^{-1}	0.3536×10^{-1}	0.1657×10^{-1}
	1	0.543	0.4004	0.3169	0.1202
	0.1	5.43	4.6656	4.3842	1.3075
0.75	10	0.084	0.3455×10^{-1}	0.2374×10^{-1}	0.1141×10^{-1}
			0.350×10^{-1} (1.3)	0.2411×10^{-1} (1.5)	0.1156×10^{-1} (1.3)
	5	0.168	0.9139×10^{-1}	0.6439×10^{-1}	0.2987×10^{-1}
			0.9218×10^{-1} (0.9)	0.6519×10^{-1} (1.2)	0.3014×10^{-1} (0.9)
	1	0.838	0.6966	0.560	0.2095
			0.6972 (0)	0.5623 (0.4)	0.2099 (0.2)
	0.1	8.382	7.7703	7.4261	2.1384
			7.7642 (0)	7.4236 (0)	2.1392 (0)
0.25	10	0.143	0.6681×10^{-1}	0.4624×10^{-1}	0.2208×10^{-1}
			0.6712×10^{-1} (0.5)	$0.465\times10^{\ 1}$ (0.6)	0.2218×10^{-1} (0.4)
	5	0.286	0.1745	0.1243	0.571×10^{-1}
			0.1751 (0.3)	0.1249 (0.4)	0.5729×10^{-1} (0.3)
	1	1.429	1.2903	1.0515	0.3891
			1.2907 (0)	1.05312 (0.1)	0.3894 (0.1)
	0.1	14.287	13.9657	13.5042	3.8015
			13.9614 (0)	13.5025 (0)	3.8027 (0)
0	10	0.172	0.8318×10^{-1}	0.577×10^{-1}	0.2749×10^{-1}
	5	0.345	0.2165	0.1547	0.7086×10^{-1}
	1	1.724	1.5875	1.2985	0.4791
	0.1	17.24	17.06	16.5419	4.6334

TABLE II. Same as Table I for the H-O mixture. (a) $r_s=0.2$, (b) $r_s=0.5$.

X_H	θ	Γ_i	$-u^{ex}$	$-f^{ex}$	$-p^{ex}$
			(a) $r_s=0.2$		
0.75	5	0.19	0.1059	0.771×10^{-1}	0.3501×10^{-1}
			0.1111 (5)	0.8173×10^{-1} (6)	0.3673×10^{-1} (5)
	1	0.95	0.7733	0.6302	0.2441
			0.788 (1.9)	0.6507 (3.2)	0.2496 (2.2)
	0.5	1.9	1.6582	1.439	0.5023
			1.6763 (1)	1.4709 (2.2)	0.5106 (1.6)
	0.05	19.005	18.0846	17.3609	5.3411
			18.062 (0.1)	17.4165 (0.3)	5.3528 (0.2)
0.25	5	0.527	0.3215	0.2367	0.1063
			0.3237 (0.7)	0.2386 (0.8)	0.107 (0.7)
	1	2.633	2.272	1.8797	0.720
			2.2784 (0.3)	1.8883 (0.45)	0.7223 (0.3)
	0.5	5.267	4.8209	4.2411	1.4692
			4.8288 (0.2)	4.2548 (0.3)	1.4728 (0.2)
	0.05	52.671	51.170	49.648	15.1124
			51.1613 (0)	49.6735 (0)	15.1176 (0)
0	5	0.695	0.430	0.3171	0.1422
	1	3.475	3.0235	2.5071	0.9587
	0.5	6.95	6.405	5.6467	1.9539
	0.05	69.504	67.711	65.802	20.0

Table II. (*Continued*).

x_H	θ	Γ_i	$-u^{ex}$	$-f^{ex}$	$-p^{ex}$
			(b) $r_s=0.5$		
0.75	10	0.238	0.1447	0.1057	0.4799×10^{-1}
			0.1509 (4.3)	0.1116 (5)	0.050 (4)
	5	0.475	0.3565	0.269	0.1173
			0.3664 (2.8)	0.2805 (4)	0.1207 (2.8)
	1	2.376	2.4762	2.0676	0.7593
			2.4818 (0.2)	2.096 (1.4)	0.7629 (0.5)
	0.1	23.756	26.3237	25.6753	6.926
			26.2417 (0.3)	25.6549 (0)	6.919 (0.1)
0.5	10	0.448	0.2902	0.2139	0.9624×10^{-1}
			0.2951 (1.7)	0.2185 (2.2)	0.9788×10^{-1}
	5	0.896	0.7064	0.5392	0.2326
			0.7143 (1.1)	0.5483 (1.7)	0.2353 (1.1)
	1	4.48	4.8026	4.0495	1.4752
			4.8076 (0.1)	4.0724 (0.5)	1.4783 (0.2)
	0.1	44.798	50.488	49.4806	13.2408
			50.4213 (0.1)	49.4648 (0)	13.2356 (0)
0.25	10	0.658	0.4367	0.3230	0.1448
			0.4392 (0.6)	0.3255 (0.8)	0.1457 (0.6)
	5	1.317	1.058	0.8112	0.3484
			1.0622 (0.4)	0.816 (0.6)	0.3499 (0.4)
	1	6.584	7.1305	6.0366	2.1919
			7.1333 (0)	6.0489 (0.2)	2.1936 (0)
	0.1	65.839	74.6369	73.283	19.5549
			74.6009 (0)	73.2748 (0)	19.5522 (0)
0	10	0.869	0.5834	0.4325	0.1935
	5	1.738	1.4101	1.0838	0.4645
	1	8.688	9.459	8.0253	2.9089
	0.1	86.8i8	98.7805	97.0487	25.8688

The first is that the departure from the LMR is greater for the asymmetric mixtures, as we would have expected, because of the important difference in coupling between the two components. The second is that the departure from linearity seems to be more important when the element with the smallest charge is dominant in the mixture. This behavior has also been previously observed in the BIM[7] and can be explained within a purely geometrical argument:[7] When the concentration of ions Z_1 is much larger than the concentration of ion Z_2, with $Z_1 \ll Z_2$, all the ion spheres of charge Z_1, are packed in a volume given approximately by $V - N_2 r_s^3 Z_2$, where V is the total volume, and the second term is the volume occupied by the ion spheres of charge Z_2. Thus, when $N_1 \gg N_2$, we can expect important overlapping between the ion spheres Z_1, and hence to corresponding multipole effects, which lead to a departure of LMR.

Finally, it is apparent that electronic screening leads to a more unstable system than the corresponding ionic mixture embedded in a *rigid* electron background. The reason is this: In terms of density operators, the Hamiltonian of the system can be written as

$$H = \hat{T}_\alpha + \hat{T}_\beta + \int d\mathbf{r} \int d\mathbf{r} v(\mathbf{r}-\mathbf{r}') \times [Z_\alpha^2 \hat{\rho}_{\alpha\alpha}^{(2)}(\mathbf{r},\mathbf{r}') + Z_\alpha Z_\beta \hat{\rho}_{\alpha\beta}^{(2)}(\mathbf{r},\mathbf{r}') + Z_\beta^2 \hat{\rho}_{\beta\beta}^{(2)}(\mathbf{r},\mathbf{r}')] , \quad (6)$$

where

$$\hat{\rho}_{\alpha\alpha}^{(2)} = \sum_{i=1}^{N_\alpha} \delta(\mathbf{r}-\mathbf{r}_i^\alpha) \sum_{j\neq 1}^{N_\alpha} \delta(\mathbf{r}'-\mathbf{r}_j^\alpha)$$

are the two-particle density operators.

The term $v(\mathbf{r})$ denotes the interaction potential, i.e., the bare Coulomb potential $\mathbf{v}(\mathbf{r}) = e^2/\mathbf{r}$ for the BIM, or the screened Coulomb potential $v(\mathbf{r}) = (e^2/\mathbf{r}) f(r)$ for the SBIM $[f(r) < 1]$. Note in particular that the *form* of the Hamiltonian does not change at the level of linear screening. There is only *one* additional length scale common to *all* ions, namely the electronic screening length, whose value depends on the electron density and temperature only. Thus the mixing entropy should not be affected when considering the differences between BIM or the SBIM models. In the latter, however, the ionic contribution to the pressure ceases to be negligible in comparison to the electronic contribution as r_s and θ take finite values. The condition of equal pressures for the coexisting phases leads then to different charge densities of these phases and to a nonadditivity of volumes, and this in turn leads to phase separation. We expect this effect to be particularly important for very asymmetric mixtures.

TABLE III. Same as Table I for the H-Fe mixture. (a) $r_s=0.2$, (b) $r_s=0.5$.

X_H	θ	Γ_i	$-u^{ex}$	$-f^{ex}$	$-p^{ex}$
			(a) $r_s=0.2$		
0.75	5	1.1	0.917	0.7419	0.3034
			0.934 (1.8)	0.7611 (2.5)	0.3091 (1.8)
	1	5.503	5.9347	5.1191	1.8587
			5.9588 (0.4)	5.1757 (1.1)	1.8689 (0.5)
	0.5	11	12.4231	11.2445	3.6619
			12.4388 (0.1)	11.3152 (0.6)	3.6754 (0.4)
0.25	5	3.258	2.7864	2.270	0.9220
			2.7925 (0.2)	2.2769 (0.3)	0.9241 (0.2)
	1	16.292	17.7817	15.4425	5.5765
			17.7908 (0.05)	15.4631 (0.1)	5.5803 (0.07)
	0.5	32.583	37.1102	33.7616	10.9622
			37.1162 (0.02)	33.7678 (0.02)	10.9598 (0.02)
0	5	4.337	3.7218	3.0348	1.2316
	1	21.686	23.7067	20.6069	7.436
	0.5	43.372	49.455	45.0238	14.6131
			(b) $r_s=0.5$		
0.75	10	1.376	1.2199	0.9855	0.4045
			1.2389 (1.5)	1.0086 (2.3)	0.4108 (1.5)
	5	2.7515	2.8387	2.3138	0.9335
			2.8617 (0.8)	2.352 (1.6)	0.9413 (0.8)
	1	13.758	19.4332	16.3936	5.8526
			19.4054 (0.1)	16.4421 (0.3)	5.8484 (0)
0.5	10	2.724	2.4575	1.9963	0.8149
			2.471 (0.5)	2.0126 (0.8)	0.8194 (0.5)
	5	5.449	5.6684	4.6642	1.8710
			5.7049 (0.3)	4.6913 (0.6)	1.8766 (0.3)
	1	27.243	38.6743	32.7296	11.6521
			38.6547 (0)	32.7646 (0.1)	11.6493 (0)
0.25	10	4.073	3.6962	3.0083	1.2257
			3.7031 (0.2)	3.0167 (0.3)	1.228 (0.2)
	5	8.146	8.5396	7.0167	2.809
			8.562 (0.3)	7.0306 (0.2)	2.8118 (0.1)
	1	40.729	57.914	49.0691	17.4516
			57.904 (0)	49.0871 (0)	17.4501 (0)
0	10	5.4215	4.9352	4.0207	1.6366
	5	10.843	11.3913	9.3699	3.7471
	1	54.215	77.1533	65.4096	23.2509

IV. CONCLUSION

We have examined the thermodynamic functions of binary ionic mixtures whose ions interact by means of density- and temperature-dependent screened potentials. In this case the electron screening is not treated via perturbation theory, but is included directly in the interionic potential. We considered three different mixtures, ranging from symmetric mixtures ($Z_2/Z_1 \sim 1$) to very asymmetric mixtures ($Z_2/Z_1 \gg 1$), and have explored a large domain of density and temperature for the electron gas. We find that the so-called "linear mixing rule" remains valid when the electron response is taken into account in the interionic potential, at any density, even though the departure from linearity can reach a few percent for the asymmetric mixtures in the region of weak degeneracy for the electron gas. We propose a physical explanation for this behavior based on a simple additional length scale. These results can be useful in calculating thermodynamic properties and phase diagrams in stellar and giant planets interiors, neutron star crusts, and in deriving approximations for the thermodynamic functions of screened binary mixtures at finite temperature.

In our calculation, we assumed the degree of ionization to be constant for a given mixture. This is true for a given pressure and temperature. As the temperature varies along a phase diagram, the degree of ionization, and then the charge ratio, might change, but our approach will still be valid since it can be applied to partially ionized mixtures, as mentioned in Sec. III. The sensitivity of the phase diagram to the temperature is a much more complicated problem, one which will be examined in detail in a subsequent work.

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