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# Coherent approach to critical demixing in strongly coupled binary ionic mixtures. I. Weak electron-ion coupling and stability requirements

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We analyze the minimal conditions required to build up a coherent and neutral-like description of critical phenomena in strongly coupled binary mixtures of pointlike positive charges. One is thus led to bridge the gap between the microscopic approach dealing with the divergence of the ionic structure factors $S_{\alpha\beta}(k)$ in the $k \to 0$ limit and the thermodynamic one deduced as usual from the Gibbs free-energy function. We emphasize the fundamental role played by the electronic polarization. Namely, modeling the plasma in the so-called polarized binary ionic mixture which accounts for the electronic density fluctuations through a static dielectronic function $\epsilon(k)$, we show that the ionic mixture may be properly described as a mixture of "pseudoatom" if $\epsilon(k)$ fulfills the compressibility sum rule while the weak electron-ion coupling hypothesis is assumed to be valid. Conversely, the binary ionic mixture model, with no electronic polarization at all, appears to be inappropriate to the microscopic approach, as a consequence of the rigid character of the electron background.

## I. INTRODUCTION

From a general point of view, studies of critical phase separation in binary ionic mixtures may be developed along two different routes. The first one deals with the thermodynamic properties of the system via the following standard equation:

$$\left[ \frac{\partial^2 g}{\partial c_1^2} \right]_{T,p} = 0 , \tag{1.1}$$

which results from the usual interdiffusion stability condition.[1] $g = G/N$ denotes here the Gibbs free energy per atom, $T$ and $p$ are the temperature and the pressure, and $c_\alpha$ ($\alpha = 1,2$), the concentration numbers. The Greek indices denote the type of component. Solutions of Eq. (1.1) provide a line of critical temperature $T_c(c_1)$ which corresponds to the spinodal decomposition curve (see Fig. 1). Only the higher critical point $T_c$ is physically accessible. The proper demixing curve is deduced from the free-energy isotherms by means of the usual double tangent construction (Fig. 1) and gives the compositions of the coexisting stable phases. Note that the quantity $(\partial^2 g/\partial c_1^2)_{T,p}$ plays the same role as the inverse isothermal compressibility $K^{-1}$ in the liquid-gas critical transition.[2]

The second route is based on the main characteristics of the critical regime, that is, the emergence of a long-range tail in the pair distribution functions $g_{\alpha\beta}(r)$ appropriate to the mixture, and the onset of large concentration fluctuations. Consequently, the long-wavelength limit of the partial structure factors $S_{\alpha\beta}(k)$, and some of their linear combinations, exhibit a singular behavior, the analysis of which allows us to study demixing within a microscopic framework. The link with thermodynamics is achieved through a small number of fundamental relationships expressing the structure factors at zero wave vector in terms of related thermodynamical quantities. Some of the latter have been derived by Bhatia and Thornton,[3] who got the following important result:

$$\lim_{k \to 0} S_{cc}(k) = k_B T \left[ \left[ \frac{\partial^2 g}{\partial c_1^2} \right]_{T,p} \right]^{-1} . \tag{1.2}$$

$S_{cc}(k)$ here stands for the concentration-concentration structure factor which we will detail later. Equation (1.2) provides a rigorous statement which is valid whenever the left- and right-hand sides are exact. It is worth mentioning that the coherence between the microscopic and thermodynamic approaches which it implies generally fails if an approximate description of the system under consideration is to be used.

In the present paper we consider an extension of the above coherent scheme to critical phenomena in strongly coupled binary ionic mixtures. Here we are confronted with a three-component system composed of two classical ionic species embedded in a highly degenerate electron gas. We will restrict our analysis to the case of fully ionized point-like ions and assume the weak electron-ion coupling hypothesis (WCH) to be fulfilled, an assumption which imposes an upper limit on the electronic parameter $r_s$ (typically $r_s \lesssim 1.5$ in the $H^+$-$He^{2+}$ mixture).

Up to now the important problem of critical phase separation in such dense Coulombic systems[4-12] has been handled through the thermodynamical equation (1.1) in connection with the determination of a miscibility gap within ionic mixtures of astrophysical interest, such as the hydrogen-helium one building up the fluid phase in the deep interior of giant planets.[13] Using a hard-sphere reference system, Stevenson[4] has first noted that the $H^+$-$He^{2+}$ mixture in a *responding* electron gas separates under the physical conditions of temperature and pressure prevailing in Jupiter. In his calculation he made use of thermodynamic perturbation theory carried out up to second order to describe the response of the electron gas. A similar hard-sphere perturbative approach, based on a linear response model with Thomas-Fermi and Debye-Hückel screening, was derived later by Firey and Ashcroft.[5] Hansen, Torrie, and Vieillefosse[6] (HTV) and Pollock and Adler[8] reached the same conclusion as that of Stevenson but within the framework of the binary ionic mixture (BIM) model where the electron gas is taken as nonresponding and mechanically rigid. HTV have also shown that electronic polarization corrections, as well as quantum corrections, introduced linearly in a perturbative manner, result in a marked shift of the critical point location, although the position of the demixing curve is not drastically affected on average. This feature is explained by the smallness of the excess (nonideal) free energy of mixing, typically less than 1% of the internal energy for the $H^+$-$He^{2+}$ mixture, a quantity which turns out to be crucial for the accurate determination of phase diagrams. An extension of HTV's results to highly disymmetric mixtures has been produced by Brami, Hansen, and Joly.[7] In a more recent work, Hubbard and DeWitt[9] have directly incorporated the electronic polarization within the interionic potential. Therefore the reference system here has to be enlarged to the so-called polarized BIM (PBIM) model where the electron background is now allowed to respond to ionic fluctuations. Finally we mention the works of MacFarlane and Hubbard[10-12] who computed the free energy of mixing of alloys at high pressure, both in the fluid and solid phases, carrying out the calculation of the electron response within the framework of the Thomas-Fermi-Dirac (TFD) theory. The latter, which allows for a *strong electron response*, were used to account for the partial ionization character of elements with higher charge number than hydrogen. The authors have shown that their TFD results predict a *smaller deviation* from ideal mixing than the perturbation theory does, even for the hydrogen-helium alloy. They concluded that the latter might be fully stable against phase separation in the metallic zone of Jupiter and Saturn.

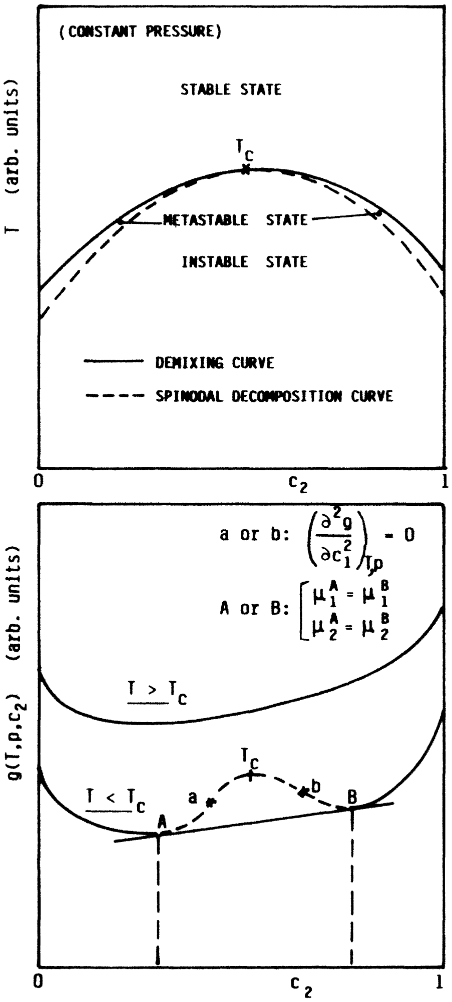

FIG. 1. Schematic of Gibbs free-energy variations with respect to concentration $c_2$. The spinodal curve corresponds to the locus of points $a$ and $b$ $[(\partial^2 g/\partial c_1^2)_{T,p}=0]$. The demixing curve pertains to the locus of points $A$ and $B$. It corresponds to the standard double tangent construction, and expresses the chemical potentials' equalities.

In contradistinction to the thermodynamic approach, only a few works have been devoted to the study of demixing at a microscopic level in Coulombic systems,[14,15] by paying attention to the divergent behavior in the long-wavelength limit of the partial structure factors. This method has been applied first by Stroud[14] to the alkali metals with some success, on the basis of a mean-field approximation for the $S_{\alpha\beta}(k)$ and an empty-core variety for the $e^-$-ion pseudopotentials. In dense-plasma physics, on the other hand, previous attempts such as that of Baus[15] have shown that the critical *microscopic* features of an unscreened Coulombic binary mixture (i.e., the BIM) are partly akin to those of an uncharged fluid mixture. Baus's conclusion, however, is reached by hypothesizing an *ad hoc* Ornstein-Zernike behavior for the static concentration fluctuations, a conjecture which proves erroneous as demonstrated in Sec. III of the present paper and in Sec. II of the following one. Another BIM of considerable astrophysical interest is the $H^+$-$Fe^{24+}$ mixture, located at the center of the sun. Its potential demixing properties have been sometimes discussed[16,17] in relation to the observed discrepancy in the number of solar-produced neutrinos escaping towards the earth. This explains that several microscopic approaches to the corresponding equilibrium properties have been developed. This includes nodal expansions[16] correcting the Debye static correlations with $\hbar$ effective interactions, as well as static ion-ion correlations[17] derived from the so-called hypernetted-chain (HNC) integral equation. However, the relevant neutralizing electron background remains mostly classical, while the present work is dedicated to the investigation of BIM neutralized by a nearly completely degenerate jellium.

In this work we investigate the problem of demixing in strongly coupled binary ionic mixtures in a way which ensures that the coherence between the thermodynamic and microscopic approaches as detailed in the preceding is preserved. We analyze the long-wavelength behavior of the ionic structure factors both in the BIM and the

PBIM models within the framework of the theory of thermodynamic fluctuations[18,19] (TTF). The polarization is introduced within the linear-response approximation (LRA) through a static dielectric function $\epsilon(k)$, at any $r_s$ value compatible with the weak electron-ion coupling hypothesis. Our claim is that the electron background should be allowed through polarization to follow the enhanced ionic fluctuations near criticality in order to observe demixing *at a microscopic level.* More specifically, it follows from our TTF analysis that the PBIM critical properties may completely reduce to those of a neutral binary fluid mixture provided the function $\epsilon(k)$ fulfills the compressibility sum rule,[20,21] while a superposition approximation scheme is used for the thermodynamic variables of the plasma. The analogy between the PBIM and an uncharged fluid mixture extends also to the stability conditions of the system as well as to the entire compressibility sum rule. On the other hand, the BIM appears to be *fully stable* against demixing, i.e., without any expected divergence of the $S_{\alpha\beta}(k)$. This result is explained by the presence of a Coulombic energy term which prevents the ionic density fluctuations to build up indefinitely.

This paper is organized as follows. The main features of our TTF analysis are displayed in Sec. II. We first introduce the basic notations together with the description of the plasma in the superposition approximation scheme. Next we introduce a small number of thermodynamical relationships. The suitable second-order differentials of entropy which form the groundwork of the TTF are then derived. Their long-wavelength behavior is discussed through the properties of an effective potential $\Delta\hat{v}(k)$ which turns out to play a central role in our analysis. The stability conditions of the system, which directly arise from the expression for the entropy variation, are discussed in Sec. III. In Sec. II of the following paper, we apply the methods of the TTF to derive the expression of the direct correlation functions $\hat{C}_{\alpha\beta}(k)$ and that of the structure factors $S_{\alpha\beta}(k)$ in the long-wavelength (or hydrodynamical) limit and then set up a few sum rules. Finally, numerical results based on the HNC approximation for the $S_{\alpha\beta}(k)$ are displayed in Sec. III of the following paper, for the $H^+$-$He^{2+}$ mixture. These results confirm the stability of the BIM and the possibility to observe a "microscopic" demixing in the PBIM. A preliminary account of parts of this work has already been given elsewhere.[22]

## II. CONSEQUENCES OF THE WEAK ELECTRON-ION COUPLING HYPOTHESIS

### A. Notations

We consider a mixture of $N_i=\sum_{\alpha=1}^{2}N_{i\alpha}$ ions with charge number $Z_\alpha$ ($\alpha=1$ refers to the smallest charge) and $N_e$ electrons in a volume $V$. The ionic component is characterized by the ionic number densities $n_i=\lim_{V\to\infty}(N_i/V)$ and $n_{i\alpha}=\lim_{V\to\infty}(N_{i\alpha}/V)$. The concentration numbers are $c_\alpha=N_{i\alpha}/N_i$.

We choose the ion-sphere radius $a_i=[3/(4\pi n_i)]^{1/3}$ as the unit of length and we define the classical plasma parameter as $\Gamma=\beta e^2/a_i$, where $\beta=1/k_BT$. The electron gas is characterized by the usual dimensionless parameter $r_s=a_e/a_0$, where $a_0$ is the Bohr radius and $a_e=[3/(4\pi n_e)]^{1/3}$ is the electron sphere radius deduced as usual from the electronic number density $n_e=\lim_{V\to\infty}(N_e/V)$.

For convenience, we introduce the short notation[23]

$$\overline{Y^\nu}=c_1Y_1^\nu+c_2Y_2^\nu \tag{2.1}$$

for any average concentration number over the variable $Y_\alpha$. The electroneutrality condition is thus expressed as $N_e=\overline{Z}N_i$, or equivalently, $a_i=a_e\overline{Z}^{1/3}$. Also we denote by $z_\alpha=Z_\alpha/\overline{Z}$ a reduced charge number.

We define $\lambda=(9\pi/4)^{1/3}$ as a numerical constant and we denote[23] by $\hat{\alpha}=3-\alpha$, the complementary value of the index $\alpha$. Finally, we introduce the symbol $\epsilon_{\alpha\beta}$ defined as $\epsilon_{\alpha\beta}=1$ if $\alpha=\beta$ and $\epsilon_{\alpha\beta}=-1$ if $\alpha\neq\beta$.

From the preceding notations, we see that the thermodynamic state of the binary ionic mixture under consideration is entirely determined in terms of the set of independent parameters $(\Gamma,r_s,c_1)$. Alternatively, one can choose $(\Gamma',r_s,c_1)$, where $\Gamma'=\beta e^2/a_e=\Gamma\overline{Z}^{1/3}$ defines another plasma parameter.

In the following we will have to consider the local fluctuations of the thermodynamic variables around their equilibrium values. This local character will be introduced simply through the explicit dependence over the space variable $\mathbf{r}$, or $\mathbf{k}$, in the Fourier space, except for the local number densities, which will be denoted explicitly as $\rho_i(\mathbf{r})$, $\rho_{i\alpha}(\mathbf{r})$, and $\rho_e(\mathbf{r})$.

### B. Superposition approximation scheme

As previously stated, we restrict ourselves to the case of a classical and strongly coupled binary ionic component interacting weakly with a highly degenerate neutralizing electron gas. The latter assumption is written in terms of the degeneracy parameter $\alpha=T/T_F$ as

$$\alpha=T/T_F=\frac{2}{\lambda^2}\frac{r_s}{\Gamma'}=0.54\frac{r_s}{\Gamma'}\ll 1\ , \tag{2.2}$$

where $T_F$ is the Fermi temperature.

Equation (2.2) imposes an upper limit over the electronic parameter $r_s$ which gets obviously enhanced in the strong-coupling regime $\Gamma\gg 1$ of present interest. As a result, the electron-gas properties are entirely described in terms of the electronic parameter $r_s$ when the condition (2.2) applies.

The validity of the WCH is ensured when the average $e^-$-ion Coulombic energy remains smaller than the Fermi energy,

$$\frac{\overline{Z}e^2}{a_e}\lesssim E_F\Longrightarrow r_s\lesssim\frac{\lambda^2}{2\overline{Z}}=\frac{1.84}{\overline{Z}}\ . \tag{2.3}$$

The condition (2.3), which is obviously fulfilled for $r_s\lesssim 1$ in the $H^+$-$He^{2+}$ mixture, enables us to envision the plasma in the superposition approximation scheme where the thermodynamic variables of the whole system are written as the sum of the ionic and electronic components, respectively. Thus, with evident notations, we get

$$\begin{aligned} &p = p_e + p_i, \quad && G = G_e + G_i, \\ &K^{-1} = K_e^{-1} + K_i^{-1}, \quad && S = S_e + S_i, \\ &\ldots, && \ldots, \end{aligned} \tag{2.4}$$

for the pressure, the inverse isothermal compressibility, the Gibbs free energy, the entropy, etc. Moreover, the electronic and ionic variables are assumed to depend only on the state variables of each component separately. As a particular example, we get for the pressure and the chemical potentials.

$$\begin{aligned} &p = p_e(n_e), \quad \mu_e = \mu_e(n_e), \\ &p_i = p_i(n_{i\alpha}, T), \quad \mu_{i\alpha} = \mu_{i\alpha}(n_{i\alpha}, T), \end{aligned} \tag{2.5}$$

choosing $T$ and the density numbers as independent variables.

Finally, the superposition approximation must be supplemented by the electroneutrality constraint. The differential of the Gibbs free energy

$$\begin{aligned} &dG = dG_e + dG_i , \\ &dG_e = -S_e dT + V\,dp_e + \mu_e dN_e , \\ &dG_i = -S_i dT + V\,dp_i + \sum_{\alpha=1}^{2} \mu_{i\alpha} dN_{i\alpha} , \end{aligned} \tag{2.6}$$

yields

$$dG = -S\,dT + V\,dp + \sum_{\alpha=1}^{2} \tilde{\mu}_{i\alpha} dN_{i\alpha} , \tag{2.7a}$$

with

$$\tilde{\mu}_{i\alpha} = \mu_{i\alpha} + Z_\alpha \mu_e . \tag{2.7b}$$

The $\tilde{\mu}_{i\alpha}$'s define the effective chemical potentials of the whole system which may thus be described as an effective two-component one. Moreover, from Eqs. (2.1)–(2.7), it is easily shown that there exists a one-to-one correspondence between the variables related to the entire system and that of the ionic component alone,

$$\{T, p_i, n_{i\alpha}, \mu_{i\alpha}, \ldots\} \Longleftrightarrow \{T, p, n_{i\alpha}, \tilde{\mu}_{i\alpha}, \ldots\} . \tag{2.8}$$

The thermodynamic state of the plasma may then be described in both types of representation and this possibility will be steadily worked out in this paper. It is worth mentioning that the superposition approximation scheme (2.4) and (2.5) holds equally well for the local variables by assuming a local thermodynamic equilibrium (LTE) hypothesis. When the latter is supplemented with a local electroneutrality criterion, the bijection rule (2.8) applies to the local variables too.

### C. Basic thermodynamical relationships

A small number of thermodynamical relationships which will be currently used in the sequel are summarized in the present section. Some detailed derivations are given in Appendix A. For convenience we adopt a lower-case letter for all the intensive variables, along the notation

$$\begin{aligned} &A = A_i + A_e \quad (a_i = A_i/N_i, \quad a_e = A_e/N_e) , \\ &a = A/N_i = a_i + \bar{Z} a_e . \end{aligned} \tag{2.9}$$

#### 1. *Gibbs-Duhem relations and related expressions*

The Gibbs free energies $g_i = G_i/N_i$ and $g = G/N_i$ are expressed as

$$g_i = \sum_{\alpha=1}^{2} c_\alpha \mu_{i\alpha}, \quad g = \sum_{\alpha=1}^{2} c_\alpha \tilde{\mu}_{i\alpha} . \tag{2.10}$$

When choosing the set $(T, p_i, c_1)$ or $(T, p, c_1)$ as independent variables, their first-order differential reads

$$\begin{aligned} &dg_i = -s_i dT + v\,dp_i + \mu_c dc_1 \quad \text{with} \quad \mu_c = \mu_{i1} - \mu_{i2} , \\ &dg = -s\,dT + v\,dp + \tilde{\mu}_c dc_1 \quad \text{with} \quad \tilde{\mu}_c = \tilde{\mu}_{i1} - \tilde{\mu}_{i2} . \end{aligned} \tag{2.11}$$

$v = V/N_i = 1/n_i$ defines the mean ionic volume while $\mu_c$ and $\tilde{\mu}_c$ are the chemical potentials conjugated of the charge number concentration $c_1$. Alternatively, one can choose the charge number concentration $c_0 = c_1 Z_1/\bar{Z}$ in lieu of $c_1$. We get

$$d\left[\frac{g_i}{\bar{Z}}\right] = -\frac{s_i}{\bar{Z}} dT + \frac{dp_i}{n_e} + \mu_{c_0} dc_0$$

$$\text{with } \mu_{c_0} = \frac{Z_2 \mu_{i1} - Z_1 \mu_{i2}}{Z_1 Z_2} , \tag{2.12a}$$

$$d\left[\frac{g}{\bar{Z}}\right] = -\frac{s}{\bar{Z}} dT + \frac{dp}{n_e} + \tilde{\mu}_{c_0} dc_0$$

$$\text{with } \tilde{\mu}_{c_0} = \frac{Z_2 \tilde{\mu}_{i1} - Z_1 \tilde{\mu}_{i2}}{Z_1 Z_2} , \tag{2.12b}$$

$$\tilde{\mu}_{c_0} \equiv \mu_{c_0} , \tag{2.12c}$$

$\tilde{\mu}_{c_0}$ being a conjugate of the charge concentration number $c_0$.

From the well-known Gibbs-Duhem relationships,

$$\sum_{\alpha=1}^{2} c_\alpha d\mu_{i\alpha} - v\,dp_i + s_i dT = 0 , \tag{2.13a}$$

$$\sum_{\alpha=1}^{2} c_\alpha d\tilde{\mu}_{i\alpha} - v\,dp + s\,dT = 0 , \tag{2.13b}$$

one deduces

$$\sum_{\alpha=1}^{2} c_\alpha \left[\frac{\partial \mu_{i\alpha}}{\partial c_\beta}\right]_{T,p_i} = 0, \quad \sum_{\alpha=1}^{2} c_\alpha \left[\frac{\partial \tilde{\mu}_{i\alpha}}{\partial c_\beta}\right]_{T,p} = 0 . \tag{2.14}$$

These relations permit us to link the second-order derivative of the Gibbs free energy to the first one of the chemical potentials $\mu_c$ (or $\tilde{\mu}_c$) and $\mu_{c_0}$ as follows:

$$\left[\frac{\partial^2 g_i}{\partial c_1^2}\right]_{T,p_i} = \left[\frac{\partial \mu_c}{\partial c_1}\right]_{T,p_i} = \bar{Z}(z_1 z_2)^2 \left[\frac{\partial \mu_{c_0}}{\partial c_0}\right]_{T,p_i} , \tag{2.15a}$$

$$\left(\frac{\partial^2 g}{\partial c_1^2}\right)_{T,p}=\left(\frac{\partial\tilde{\mu}_c}{\partial c_1}\right)_{T,p}=\bar{Z}(z_1z_2)^2\left(\frac{\partial\tilde{\mu}_{c_0}}{\partial c_0}\right)_{T,p}\ . \qquad (2.15b)$$

Another important relation reads (Appendix A)

$$\bar{Z}(z_1z_2)^2\beta\left(\frac{\partial\mu_{c_0}}{\partial c_0}\right)_{T,n_e}=\beta\left(\frac{\partial^2 g_i}{\partial c_1^2}\right)_{T,p_i}+\delta'^2\frac{K_0}{K_i}$$
$$=\beta\left(\frac{\partial^2 g}{\partial c_1^2}\right)_{T,p}+\tilde{\delta}'^2\frac{K_0}{K}\ , \qquad (2.16a)$$

which implies

$$\beta\left(\frac{\partial^2 g_i}{\partial c_1^2}\right)_{T,p_i}=\beta\left(\frac{\partial^2 g}{\partial c_1^2}\right)_{T,p}-\tilde{\delta}'^2\frac{K_0}{K}\frac{K_i}{K_e}\ . \qquad (2.16b)$$

The expansion coefficients $\delta'$ and $\tilde{\delta}$ are detailed in the sequel [Eq. (2.26)].

### 2. *Compressibility relationships*

We denote the kinetic (ideal) compressibility of the ionic component as $K_0=\beta/n_i$ and we introduce the short notation

$$\mu_{\alpha\beta}=\left(\frac{\partial\mu_{i\alpha}}{\partial n_{i\beta}}\right)_{T,n_{i\gamma}\neq n_{i\beta}}\ ,$$
$$\tilde{\mu}_{\alpha\beta}=\left(\frac{\partial\tilde{\mu}_{i\alpha}}{\partial n_{i\beta}}\right)_{T,n_{i\gamma}\neq n_{i\beta}}\ . \qquad (2.17)$$

In terms of the derivatives $\mu_{\alpha\beta}$ and $\tilde{\mu}_{\alpha\beta}$, the inverse isothermal compressibilities are (see Appendix A)

$$\frac{K_0}{K_i}=\beta\left(\frac{\partial p_i}{\partial n_i}\right)_{T,c_1}=\beta n_i\sum_{\alpha\beta=1}^{2}c_\alpha c_\beta\mu_{\alpha\beta}\ , \qquad (2.18a)$$

$$\frac{K_0}{K}=\beta\left(\frac{\partial p}{\partial n_i}\right)_{T,c_1}=\beta n_i\sum_{\alpha\beta=1}^{2}c_\alpha c_\beta\tilde{\mu}_{\alpha\beta}\ . \qquad (2.18b)$$

According to the usual definition of the electronic compressibility,

$$\frac{K_0}{K_e}=\bar{Z}\beta\left(\frac{\partial p_e}{\partial n_e}\right)_T\equiv\bar{Z}\beta n_e\left(\frac{\partial\mu_e}{\partial n_e}\right)_T\ , \qquad (2.19)$$

the relation linking together $\mu_{\alpha\beta}$ and $\tilde{\mu}_{\alpha\beta}$ reads

$$\tilde{\mu}_{\alpha\beta}=\mu_{\alpha\beta}+\frac{z_\alpha z_\beta}{\beta n_i}\frac{K_0}{K_e}\ . \qquad (2.20)$$

### 3. *Volumic expansion coefficients*

The transformation relations for the derivatives $\mu_{\alpha\beta}$ or $\tilde{\mu}_{\alpha\beta}$, when changing from the set of independent variables $(T,n_{i\alpha})$ to $(T,p_i,c_\alpha)$ or $(T,p,c_\alpha)$, are (Appendix A)

$$\mu_{\alpha\beta}=\frac{(1-c_\beta)}{n_i}\left(\frac{\partial\mu_{i\alpha}}{\partial c_\beta}\right)_{T,p_i}+\frac{v_\alpha v_\beta}{K_i}\ , \qquad (2.21a)$$

$$\tilde{\mu}_{\alpha\beta}=\frac{(1-c_\beta)}{n_i}\left(\frac{\partial\tilde{\mu}_{i\alpha}}{\partial c_\beta}\right)_{T,p}+\frac{\tilde{v}_\alpha\tilde{v}_\beta}{K}\ , \qquad (2.21b)$$

where $v_\alpha$ and $\tilde{v}_\alpha$ are partial ionic volumes

$$v_\alpha=\left(\frac{\partial V}{\partial N_{i\alpha}}\right)_{T,p_i,N_{i\gamma}\neq N_{i\alpha}}\ ,$$
$$\tilde{v}_\alpha=\left(\frac{\partial V}{\partial N_{i\alpha}}\right)_{T,p,N_{i\gamma}\neq N_{i\alpha}}\ , \qquad (2.22)$$

the additive properties of which, according to Euler's theorem, read

$$v=\sum_{\alpha=1}^{2}c_\alpha v_\alpha=\sum_{\alpha=1}^{2}c_\alpha\tilde{v}_\alpha \qquad (2.23a)$$

or

$$1=\sum_{\alpha=1}^{2}n_{i\alpha}v_\alpha=\sum_{\alpha=1}^{2}n_{i\alpha}\tilde{v}_\alpha\ . \qquad (2.23b)$$

The $v_\alpha$'s and $\tilde{v}_\alpha$'s are readily expressed in terms of the following volumic expansion coefficients:

$$\delta=\frac{1}{n_i}\left(\frac{\partial n_i}{\partial c_1}\right)_{T,p_i},\quad \tilde{\delta}=\frac{1}{n_i}\left(\frac{\partial n_i}{\partial c_1}\right)_{T,p}\ , \qquad (2.24)$$

so that

$$n_iv_1=1-c_2\delta,\quad n_i\tilde{v}_1=1-c_2\tilde{\delta},$$
$$n_iv_2=1+c_1\delta,\quad n_i\tilde{v}_2=1+c_1\tilde{\delta}. \qquad (2.25)$$

In addition to $\delta$ and $\tilde{\delta}$, it is useful to introduce the expansion coefficient $\delta'$ and $\tilde{\delta}'$, related to the electronic number density $n_e$,

$$\delta'=\frac{1}{n_e}\left(\frac{\partial n_e}{\partial c_1}\right)_{T,p_i},\quad \tilde{\delta}'=\frac{1}{n_e}\left(\frac{\partial n_e}{\partial c_1}\right)_{T,p}\ . \qquad (2.26)$$

It is then a straightforward matter to derive the following transformation relations:

$$\tilde{\delta}'/\delta'=K/K_i\ , \qquad (2.27)$$

$$\delta'=z_1-z_2+\delta,\quad \tilde{\delta}'=z_1-z_2+\tilde{\delta}\ , \qquad (2.28)$$

from which arise

$$\delta=\tilde{\delta}\frac{K_i}{K}-(z_1-z_2)\left(1-\frac{K_i}{K}\right) \qquad (2.29)$$

and

$$n_iv_\alpha=n_i\tilde{v}_\alpha\frac{K_i}{K}+\left(1-\frac{K_i}{K}\right)z_\alpha\ . \qquad (2.30)$$

## D. The second-order differential of entropy

The suitable thermodynamic potential required to describe the equilibrium properties of a fully isolated system is the entropy $S$. In the theory of thermodynamic fluctuation,[18,19] the probability of having a fluctuation $\delta a$ for a thermodynamic quantity $a$ around its equilibrium value $\langle a\rangle_{\rm av}$ is proportional to $\exp(\Delta S/k_B)$, where $\Delta S$ denotes the corresponding entropy variation. As a standard result, the TTF provides a powerful method to derive the static correlations $\langle \delta a,\delta b\rangle_{\rm av}$ within every couple of variables, the normalized average being computed with the weight function $\exp(\Delta S/k_B)$, while the entropy variation is expressed as a quadratic form in $\delta a$ and $\delta b$. In the following, we apply the TTF to the case of a *polarizable* ionic mixture, choosing the local ionic density fluctuations $\delta\rho_{i\alpha}(\mathbf{r})=\rho_{i\alpha}(\mathbf{r})-n_i$ as independent, the induced electronic density fluctuation $\delta\rho_e(\mathbf{r})=\rho_e(\mathbf{r})-n_e$ being computed in the linear-response approximation (LRA). We thus generalize to polarizable ionic mixture the TTF analysis of Vieillefosse and Hansen[24] for the OCP, which has been subsequently extended by Vieillefosse[25,26] to other Coulombic mixtures such as molten salts.

In a fully isolated polarized binary ionic mixture at fixed volume $V$ and temperature $T$, the local entropy variation per unit volume which arises from local but macroscopic density fluctuations reads

$$T\delta(\rho_i(\mathbf{r})s(\mathbf{r}))=\delta(\rho_i(\mathbf{r})u(\mathbf{r}))-\sum_{\alpha=1}^{2}\mu_{i\alpha}(\mathbf{r})\delta\rho_{i\alpha}(\mathbf{r}) -\mu_e(\mathbf{r})\delta\rho_e(\mathbf{r}) , \qquad (2.31)$$

where $u(\mathbf{r})$ and $s(\mathbf{r})$ are the local internal energy and entropy per ion, respectively.

Equation (2.31) is written under the assumption of the LTE hypothesis and its range of application is thus restricted only to the long-wavelength regime,

$$\lambda=\frac{2\pi}{k}\gg a_i \Longleftrightarrow k\ll a_i^{-1} , \qquad (2.32)$$

where $k$ stands for the current wave vector of the Fourier transform of any spatial fluctuation $\delta f(\mathbf{r})$, the latter being defined as

$$\delta\hat f(\mathbf{k})=\int_V d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}}\delta f(\mathbf{r}) \Longleftrightarrow \delta f(\mathbf{r})=\frac{1}{V}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\delta\hat f(\mathbf{k}) . \qquad (2.33)$$

It should be noted that the restrictive condition (2.32) applies only far from any critical transition. If this is not the case, $a_i$ must be replaced by some characteristic critical correlation length $\xi$, so that one expects the results of the TTF deduced from (2.31)–(2.33) to be valid only in the strict limit $k\to0$, i.e., in the vicinity of a critical point. This peculiar feature will be discussed further in the sequel.

The electronic density fluctuation in Eq. (2.31) is to be taken in the LRA, so that we get in Fourier space

$$\delta\hat\rho_e(\mathbf{k})=-\left[\frac{1}{\epsilon(k)}-1\right]\delta\hat\rho_{i0}(\mathbf{k}) , \qquad (2.34a)$$

with

$$\delta\hat\rho_{i0}(\mathbf{k})=\sum_{\alpha=1}^{2} Z_\alpha\delta\hat\rho_{i\alpha}(\mathbf{k}) . \qquad (2.34b)$$

$\delta\hat\rho_{i0}(\mathbf{k})$ denotes here the ionic charge-density fluctuation. The dielectric electronic function $\epsilon(k)$ is assumed to fulfill the usual perfect screening condition[27] $\epsilon(k)_{k\to0}\sim k^{-2}$, so that the electroneutrality law is then automatically ensured for the whole system through (2.34a). With the LTE criterion (2.32) it may also be extended to the local macroscopic subsystems of typical extension $\lambda^3$.

The second-order differential of the entropy is directly deduced from (2.31),

$$T(\rho_i(\mathbf{r})s(\mathbf{r})-n_is)=\delta(\rho_i(\mathbf{r})u(\mathbf{r}))+\tfrac{1}{2}\delta^2(\rho_i(\mathbf{r})u(\mathbf{r}))-\sum_{\alpha=1}^{2}\mu_{i\alpha}(\mathbf{r})\delta\rho_{i\alpha}(\mathbf{r})-\tfrac{1}{2}\sum_{\alpha=1}^{2}\delta\mu_{i\alpha}(\mathbf{r})\delta\rho_{i\alpha}(\mathbf{r})-\mu_e(\mathbf{r})\delta\rho_e(\mathbf{r}) . \qquad (2.35)$$

The terms proportional to $\delta^2\rho_e(\mathbf{r})$ and $\delta\mu_e(\mathbf{r})\delta\rho_e(\mathbf{r})$ have been removed as a consequence of the LRA and we have retained only the $\delta\rho_{i\alpha}(\mathbf{r})$'s as independent variables, which implies $\delta^n\rho_{i\alpha}(\mathbf{r})=0$ $(n>1)$. Finally, the total entropy variation $\Delta S$ in the volume $V$ is computed by the integration of (2.35) over the space variable $\mathbf{r}$ while the following conservation equations are to be used:

$$\int_V d\mathbf{r}\,\delta(\rho_i(\mathbf{r})u(\mathbf{r}))=0 , \qquad (2.36a)$$

$$\int_V d\mathbf{r}\,\delta\rho_e(\mathbf{r})=0,\quad \int_V d\mathbf{r}\,\delta\rho_{i\alpha}(\mathbf{r})=0 . \qquad (2.36b)$$

We thus get

$$\frac{\Delta S}{k_B}=\frac{\beta}{2V}\int_V d\mathbf{r}\,\delta^2(\rho_i(\mathbf{r})u(\mathbf{r})) -\frac{\beta}{2V}\sum_{\mathbf{k}}{}'\sum_{\alpha,\beta=1}^{2}\delta\hat\mu_{i\alpha}(\mathbf{k})\delta\hat\rho_{i\beta}(-\mathbf{k}) . \qquad (2.37)$$

The prime in the summation means that the zero wave vector is left out to take proper account of (2.36b). The conservation equation (2.36a) may be extended up to second order in the form

$$\frac{\beta}{2V}\int_V d\mathbf{r}\,\delta^2(\rho_i(\mathbf{r})u(\mathbf{r}))=-(E_c+E_p) , \qquad (2.38a)$$

$$E_c=\frac{\beta}{2V}\sum_{\mathbf{k}}{}'\sum_{\alpha,\beta=1}^{2} Z_\alpha Z_\beta\frac{4\pi e^2}{k^2}\delta\hat\rho_{i\alpha}(\mathbf{k})\delta\hat\rho_{i\beta}(-\mathbf{k}) , \qquad (2.38b)$$

$$E_p=\frac{\beta}{2V}\sum_{\mathbf{k}}{}'\sum_{\alpha,\beta=1}^{2} Z_\alpha Z_\beta\frac{4\pi e^2}{k^2}\left[\frac{1}{\epsilon(k)}-1\right] \times\delta\hat\rho_{i\alpha}(\mathbf{k})\delta\hat\rho_{i\beta}(-\mathbf{k}) , \qquad (2.38c)$$

which physically means that, due to the density fluctuations, the internal energy of the system is transformed into a Coulombic macroscopic energy $E_c$ and a term $E_p$ which we add to account for the polarization energy of the electron gas taken in the LRA.[28,29] Equation (2.38a) is a direct consequence of the long-range nature of the Coulomb potential. It expresses the fact that the interaction energy between the subsystems cannot be neglected with respect to the internal energy. This is to be contrasted with the neutral systems where the coupling strength (between subsystems) is ensured only through surface bonds so that (2.37) is just restricted to the term involving the chemical potentials.

The final expression for $\Delta S$, deduced from (2.37) and (2.38) with the help of (2.17), reads

$$\frac{\Delta S}{k_B}=-\tfrac{1}{2}\sum_{\mathbf{k}}{}'\sum_{\alpha,\beta=1}^{2}(c_\alpha c_\beta)^{1/2}[Z_\alpha Z_\beta \hat{v}(k)+\beta n_i \mu_{\alpha\beta}]\times\frac{\delta\hat{\rho}_{i\alpha}(\mathbf{k})\delta\hat{\rho}_{i\beta}(-\mathbf{k})}{(N_{i\alpha}N_{i\beta})^{1/2}}\ , \tag{2.39}$$

where

$$\hat{v}(k)=\frac{4\pi\beta e^2 n_i}{k^2\epsilon(k)}\equiv\frac{3\Gamma}{a_i^2}\frac{1}{k^2\epsilon(k)}\ . \tag{2.40}$$

$\hat{v}(k)$ denotes here the dimensionless Coulomb potential.

The formula (2.39) may alternatively be expressed in terms of the derivatives $\tilde{\mu}_{\alpha\beta}$ (Eq. 2.17) while taking account of Eq. (2.20),

$$\frac{\Delta S}{k_B}=-\tfrac{1}{2}\sum_{\mathbf{k}}{}'\sum_{\alpha,\beta=1}^{2}(c_\alpha c_\beta)^{1/2}[Z_\alpha Z_\beta \Delta\hat{v}(k)+\beta n_i \tilde{\mu}_{\alpha\beta}]\times\frac{\delta\hat{\rho}_{i\alpha}(\mathbf{k})\delta_{i\beta}(-\mathbf{k})}{(N_{i\beta}N_{i\beta})^{1/2}}\ , \tag{2.41}$$

with

$$\Delta\hat{v}(k)=\hat{v}(k)-\frac{1}{\bar{Z}^2}\frac{K_0}{K_e}\ . \tag{2.42}$$

The quantity $\Delta\hat{v}(k)$, which acts as an *effective potential* in the coefficient of the quadratic term $\delta\hat{\rho}_{i\alpha}(\mathbf{k})\delta\hat{\rho}_{i\beta}(-\mathbf{k})$, plays a *central role* in the characterization of the PBIM as a well-behaved model with respect to stability criteria and microscopic critical properties of binary ionic mixtures. This point is clarified in Sec. II E. Before that, we wish to establish the expression of the determinant of the fundamental quadratic forms (2.39)–(2.41) which read, respectively,

$$D(k)=D_R+\bar{Z}^2\hat{v}(k)D_I,\quad \tilde{D}(k)=\tilde{D}_R+\bar{Z}^2\Delta\hat{v}(k)\tilde{D}_I\ , \tag{2.43}$$

with

$$D_R=c_1c_2\det|\beta n_i\mu_{\alpha\beta}|\ ,\quad \tilde{D}_R=c_1c_2\det|\beta n_i\tilde{\mu}_{\alpha\beta}|\ , \tag{2.44a}$$

$$D_I=c_1c_2\beta n_i\sum_{\alpha,\beta=1}^{2}\epsilon_{\alpha\beta}z_{\hat{\alpha}}z_{\hat{\beta}}\mu_{\alpha\beta}\ ,$$

$$\tilde{D}_I=c_1c_2\beta n_i\sum_{\alpha,\beta=1}^{2}\epsilon_{\alpha\beta}z_{\hat{\alpha}}z_{\hat{\beta}}\tilde{\mu}_{\alpha\beta}\ , \tag{2.44b}$$

where the notations $\epsilon_{\alpha\beta}$ and $\hat{\alpha}$ (or $\hat{\beta}$) have been previously defined in Sec. II A.

The determinants in (2.44a) and (2.44b) split into a regular component $D_R$ or $\tilde{D}_R$ quadratic in the $\mu_{\alpha\beta}$ (or the $\tilde{\mu}_{\alpha\beta}$) and an interactive component $D_I$ or $\tilde{D}_I$ linear in the $\mu_{\alpha\beta}$ (or the $\tilde{\mu}_{\alpha\beta}$). With the help of the thermodynamic relationships displayed in Sec. II C, these components may also be written as (see Appendix B)

$$\begin{aligned}D_R&=c_1c_2\frac{K_0}{K_i}\beta\left(\frac{\partial^2 g_i}{\partial c_1^2}\right)_{T,p_i}\\&\equiv c_1c_2\bar{Z}(z_1z_2)^2\frac{K_0}{K_i}\beta\left(\frac{\partial\mu_{c_0}}{\partial c_0}\right)_{T,p_i}\ ,\end{aligned} \tag{2.45a}$$

$$\begin{aligned}\tilde{D}_R&=c_1c_2\frac{K_0}{K}\beta\left(\frac{\partial^2 g}{\partial c_1^2}\right)_{T,p}\\&\equiv c_1c_2\bar{Z}(z_1z_2)^2\frac{K_0}{K}\beta\left(\frac{\partial\mu_{c_0}}{\partial c_0}\right)_{T,p}\ ,\end{aligned} \tag{2.45b}$$

$$\begin{aligned}D_I&=c_1c_2\left[\beta\left(\frac{\partial^2 g_i}{\partial c_1^2}\right)_{T,p_i}+\delta'^2\frac{K_0}{K_i}\right]\\&\equiv c_1c_2\bar{Z}(z_1z_2)^2\beta\left(\frac{\partial\mu_{c_0}}{\partial c_0}\right)_{T,n_e}\ ,\end{aligned} \tag{2.46a}$$

$$\tilde{D}_I=c_1c_2\left[\beta\left(\frac{\partial^2 g}{\partial c_1^2}\right)_{T,p}+\tilde{\delta}'^2\frac{K_0}{K}\right]\equiv D_I\ . \tag{2.46b}$$

The equivalence between $D_I$ and $\tilde{D}_I$ is easily demonstrated from the definitions (2.44b) and the relation (2.20). It does not hold for the regular components linked together under the form

$$D_R=\tilde{D}_R-\frac{K_0}{K_e}\tilde{D}_I=\frac{K_0}{K_i}\tilde{D}_I-c_1c_2\tilde{\delta}'^2\left(\frac{K_0}{K}\right)^2\ , \tag{2.47}$$

a relation which is directly deduced from (2.16a) and (2.16b) [or from the complete equivalence between $D(k)$ and $\tilde{D}(k)$]. It must be noted that the derivative of $\tilde{\mu}_{c_0}$ contained both in the regular component $\tilde{D}_R$ and in the interactive one $\tilde{D}_I$ is taken at fixed temperature and fixed *pressure* in the first case, and at fixed temperature and fixed *electronic density* in the second one.

Finally, it is also useful to recover the above expressions for the limiting case of one single ionic component plasma (OCP). Due to the logarithmic term contained in the ideal part of the chemical potentials, we obtain

$$\lim_{c_\alpha\to 1}c_1c_2\beta\left(\frac{\partial^2 g_i}{\partial c_1^2}\right)_{T,p_i}=\lim_{c_\alpha\to 1}c_1c_2\beta\left(\frac{\partial^2 g}{\partial c_1^2}\right)_{T,p}=1\quad(\alpha=1,2)\ , \tag{2.48}$$

$$\lim_{c_\alpha\to 1}D_R=\frac{K_0}{K_i},\quad \lim_{c_\alpha\to 1}\tilde{D}_R=\frac{K_0}{K}\quad(\alpha=1,2)\ , \tag{2.49a}$$

and

$$\lim_{c_\alpha\to 1}D_I\equiv\lim_{c_\alpha\to 1}\tilde{D}_I=1\quad(\alpha=1,2)\ . \tag{2.49b}$$

### E. Summary: The PBIM model

A coherent approach for the polarized binary ionic mixture taken as an effective two-component system requires us to supplement the superposition approximation scheme with an internal consistency requirement over the electron-gas dielectric function $\epsilon(k)$, considered in the form

$$\epsilon(k)=\frac{k^2+k_{\mathrm{TF}}^2 g(x)}{k^2} . \tag{2.50}$$

$k_{\mathrm{TF}}=(6\pi n_e e^2/E_F)^{1/2}$ denotes the Thomas-Fermi wave vector and the function $g(x)$ depends only on the dimensionless variable $x=k/2k_F$.

The aforementioned internal consistency is secured through the well-known compressibility sum rule[20,21]

$$\underset{k\to 0}{\epsilon(k)}=1+\frac{4\pi n_e^2 e^2 K_e}{k^2} , \tag{2.51}$$

which implies

$$\lim_{x\to 0} g(x)=\tfrac{2}{3} n_e E_F K_e , \tag{2.52}$$

and then

$$\lim_{k\to 0} \bar{Z}^{2}\hat{v}(k)=\frac{K_0}{K_e} , \tag{2.53}$$

so we get from (2.42)

$$\lim_{k\to 0} \Delta\hat{v}(k)=0 \quad (\sim -k^2) \quad (\text{PBIM}) . \tag{2.54}$$

It is also straightforward to check out that the long-wavelength components in the entropy variation (2.41) have exactly the required neutral-like form of a two-component mixture owing to the presence of the $\tilde{\mu}_{\alpha\beta}$ for the *whole system* in the coefficient of the quadratic term $\delta\hat{\rho}_{i\alpha}(\mathbf{k})\delta\hat{\rho}_{i\beta}(-\mathbf{k})$. This convinces us to adopt the definition of the *coherent* PBIM model as a polarized binary ionic mixture where the electron gas is taken in the LRA in addition to the electronic compressibility sum rule requirement. On the other hand, the BIM model with $\epsilon(k)=1$ for all $k$ is entirely governed by the Coulomb potential $\hat{v}_c(k)=4\pi\beta e^2 n_i/k^2$, so that

$$\underset{k\to 0}{\hat{v}(k)}\sim \underset{k\to 0}{\hat{v}_c(k)}\to\infty \quad (\sim k^{-2}) \quad (\text{BIM}) . \tag{2.55}$$

The striking discrepancy between (2.54) and (2.55) is explained by the behavior of the screened Coulomb potential at the origin,

$$\lim_{k\to 0}\lim_{r_s\to 0}\hat{v}(k)=\hat{v}_c(k)=\frac{4\pi\beta e^2 n_i}{k^2} \quad (\text{BIM}) , \tag{2.56a}$$

$$\lim_{r_s\to 0}\lim_{k\to 0}\hat{v}(k)=\frac{4\pi\beta e^2 n_i}{k_{\mathrm{TF}}^2 g(0)} \quad (\text{PBIM}) . \tag{2.56b}$$

The first limit diverges as $k^{-2}$ while the second diverges as $k_{\mathrm{TF}}^2\sim r_s^{-1}$. Then for a *finite value* of $r_s$ the screened Coulomb potential is finite at $k\to 0$ while the Coulomb potential is not.

This peculiar feature explains the internal deficiency of the BIM model with the thermodynamic quantities taken at finite $r_s$ value for the electron gas, while the ionic ones are computed at $r_s=0$ through $\hat{v}_c(k)$. This remark leads us to expect the PBIM to be able to display a more consistent framework than the BIM one, as far as the investigation of stability criteria and critical demixing properties of binary ionic mixtures are concerned.

## III. STABILITY CONDITIONS IN THE THEORY OF THERMODYNAMIC FLUCTUATIONS

### A. General

The stability conditions of the system are readily deduced from the entropy variations (2.39) or (2.41) which must fulfill a definite and negative quadratic form in order to prevent the enhancement of ionic density fluctuations. The required conditions are more readily derived while first reexpressing $\Delta S$ in the charge number density fluctuation

$$\delta\rho_{i0}(\mathbf{r})=\sum_{\alpha=1} Z_\alpha\delta\rho_{i\alpha}(\mathbf{r})$$

[see Eq. (2.34b)] and the charge number concentration

$$\delta c_0(\mathbf{r})=\delta(Z_1\rho_{i1}(\mathbf{r})/\rho_{i0}(\mathbf{r}))$$

taken as independent. Details are given in Appendix C. We get

$$\frac{\Delta S}{k_B}=-\frac{1}{2N_i}\sum_{\mathbf{k}}{}' \left\{ \left[\frac{K_0}{K_i}+\bar{Z}^{2}\hat{v}(k)\right]\frac{\delta\rho_{i0}(\mathbf{k})\delta\hat{\rho}_{i0}(-\mathbf{k})}{\bar{Z}^2}-\frac{n_e}{Z_1Z_2}\frac{K_0}{K_i}\delta'[\delta\hat{\rho}_{i0}(\mathbf{k})\delta\hat{c}_0(-\mathbf{k})+\delta\hat{\rho}_{i0}(-\mathbf{k})\delta\hat{c}_0(\mathbf{k})] \right.$$
$$\left. +\frac{n_e^2\bar{Z}^2}{(Z_1Z_2)^2}\left[\beta\left[\frac{\partial^2 g_i}{\partial c_1^2}\right]_{T,p_i}+\delta'^2\frac{K_0}{K_i}\right]\delta\hat{c}_0(\mathbf{k})\delta\hat{c}_0(-\mathbf{k}) \right\} , \tag{3.1a}$$

or alternatively,

$$\frac{\Delta S}{k_B}=-\frac{1}{2N_i}\sum_{\mathbf{k}}{}' \left\{ \left[\frac{K_0}{K}+\bar{Z}^{2}\Delta\hat{v}(k)\right]\frac{\delta\hat{\rho}_{i0}(\mathbf{k})\delta\hat{\rho}_{i0}(-\mathbf{k})}{\bar{Z}^2}-\frac{n_e}{Z_1Z_2}\frac{K_0}{K}\tilde{\delta}'[\delta\hat{\rho}_{i0}(\mathbf{k})\delta\hat{c}_0(-\mathbf{k})+\delta\hat{\rho}_{i0}(-\mathbf{k})\delta\hat{c}_0(\mathbf{k})] \right.$$
$$\left. +\frac{n_e^2\bar{Z}^2}{(Z_1Z_2)^2}\left[\beta\left[\frac{\partial^2 g}{\partial c_1^2}\right]_{T,p}+\tilde{\delta}'^2\frac{K_0}{K}\right]\delta\hat{c}_0(\mathbf{k})\delta\hat{c}_0(-\mathbf{k}) \right\} , \tag{3.1b}$$

where the coefficients $\delta'$ and $\tilde{\delta}'$ have been defined in (2.26). Other expressions equivalent to (3.1a) and (3.1b) but involving the expansion coefficients $\delta$ and $\tilde{\delta}$, respectively, can be derived on the same footing, but with the ionic number density $\delta\rho_i(\mathbf{r})=\sum_{\alpha=1}^{2}\delta\rho_{i\alpha}(\mathbf{r})$ and the concentration number fluctuation $\delta c_1(\mathbf{r})=\delta(\rho_{i1}(\mathbf{r})/\rho_i(\mathbf{r}))$ as independent variables (Appendix C).

The stability conditions are mathematically set up when both the coefficient of $|\delta\hat{\rho}_{i0}(\mathbf{k})|^2$ and the determinant of the quadratic form (3.1a) [or (3.1b)] are definite positive quantities. This secures a positive coefficient for $|\delta\hat{c}_0(\mathbf{k})|^2$ too because (3.1a) and (3.1b) are symmetric quadratic forms. Thus we get, respectively,

$$\frac{K_0}{K_i}+\bar{Z}^2\hat{v}(k)\equiv\frac{K_0}{K}+\bar{Z}^2\Delta\hat{v}(k)\geq 0,\quad k \ll a_i^{-1} \tag{3.2}$$

$$D(k)=D_R+\bar{Z}^2\hat{v}(k)D_I\geq 0,\quad k \ll a_i^{-1} \tag{3.3a}$$

or, equivalently,

$$\tilde{D}(k)=\tilde{D}_R+\bar{Z}^2\Delta\hat{v}(k)\tilde{D}_I\geq 0,\quad k \ll a_i^{-1} \tag{3.3b}$$

where the determinants $D(k)$ and $\tilde{D}(k)$ have been previously defined in (2.43)–(2.46).

Regardless of the appearance of the potential $\hat{v}(k)$ in the preceding inequalities, and owing to the presence of the inverse compressibility and the Gibbs free-energy derivatives on the left-hand side (lhs), respectively, we refer to the former [Eq. (3.2)] as the mechanical stability condition (MSC) and to the latter [Eqs. (3.3a) and (3.3b)] as the interdiffusion stability condition (ISC). With the limits (2.49a) and (2.49b), they reduce to the MSC alone in the case of a single ionic component plasma.

### B. Stability conditions in the PBIM

Applying the long-wavelength sum rule (2.54) to the MSC and the ISC leads to

$$\frac{K_0}{K_i}+\bar{Z}^2\underset{k\to 0}{\hat{v}(k)}\equiv\frac{K_0}{K}\geq 0\quad(\text{MSC, PBIM})\,, \tag{3.4a}$$

$$\tilde{D}_R=c_1c_2\frac{K_0}{K}\beta\left[\frac{\partial^2 g}{\partial c_1^2}\right]_{T,p}\geq 0\Longrightarrow\beta\left[\frac{\partial^2 g}{\partial c_1^2}\right]_{T,p}\geq 0\quad(\text{ISC, PBIM})\,. \tag{3.4b}$$

The stability conditions of the PBIM are thus *exactly the same* as in a neutral mixture, which means that the Gibbs free energy $g(T,p,c_1)$ of the *whole system* must be a concave function of the concentration $c_1$ (at constant temperature $T$ and constant expression $p$) in order to prevent the enhancement of the interdiffusion phenomenon associated to the critical phase separation. The *total* compressibility $K$ must remain positive to secure the mechanical stability.

It should be noted that the ISC in the PBIM is directly related to the sign of the regular component $\tilde{D}_R$ appearing in the definition of $\tilde{D}(k)$ [Eq. (2.43)]. With the help of the equality (2.15b), it may be alternatively expressed in the following forms:

$$\beta\left[\frac{\partial\tilde{\mu}_c}{\partial c_1}\right]_{T,p}\geq 0\quad\text{or}\quad\beta\left[\frac{\partial\tilde{\mu}_{c_0}}{\partial c_0}\right]_{T,p}\geq 0\quad(\text{ISC, PBIM})\,. \tag{3.5}$$

### C. Stability conditions in the BIM

Equations (3.2) and (3.3) are now governed by the divergence of the Coulomb potential $\hat{v}_c(k)$ at $k\to 0$, so that

$$\frac{K_0}{K_i}+\bar{Z}^2\underset{k\to 0}{\hat{v}_c(k)}\geq 0\quad(\text{MSC, BIM})\,, \tag{3.6a}$$

$$D_R+\bar{Z}^2\underset{k\to 0}{\hat{v}_c(k)}D_I\geq 0\quad(\text{ISC, BIM})\,. \tag{3.6b}$$

Clearly the MSC (3.6a) is always satisfied irrespective of the sign of the ionic compressibility $K_i$ which, as is well known, becomes effectively negative in the BIM (Ref. 6) just as in the OCP (Ref. 30) for $\Gamma'\gtrsim 3$. This result is explained by the emergence of an induced macroscopic electric field arising from the ionic density fluctuations, preventing the latter from building up indefinitely. As shown by Lieb and Narnhofer,[31] for the classical OCP, the existence of negative (ionic) compressibility and pressure does not entail fundamental difficulties.

It is very instructive to contrast the corresponding MSC inequalities (3.4a) and (3.6a) in the PBIM and the BIM, respectively. We note first that the finite term $\bar{Z}^2\hat{v}(k=0)$, which gives rise to the inverse electronic compressibility in the former model [see Eq. (2.53)], is replaced by an infinite quantity $\bar{Z}^2\hat{v}_c(k\to 0)$ in the latter, owing to the inversion in the limits (2.56a) and (2.56b). Thus $\bar{Z}^2\hat{v}_c(k\to 0)$ may be seen as an "infinite equivalent inverse electronic compressibility" which acts at the *microscopic level* in the BIM and ensures that the MSC will be fulfilled once for ever. Moreover, although it follows from our numerical results in the $H^+$-$He^{2+}$, displayed in Sec. III of the following paper, that *the ionic compressibility $K_i$ can also turn negative* in the PBIM, the total compressibility $K$ has to remain positive in order to secure the mechanical stability condition (3.4a). This is to be contrasted with the BIM, where the existence of a definite and positive compressibility $K$ *for the whole system* does not follow from a thermodynamic criterion but has to be physically imposed through a restrictive choice for the parameters $r_s$ and $\Gamma$, so that the positive inverse electronic compressibility $K_e^{-1}$ (or pressure) compensates at least the negative ionic one within the previously defined superposition approximation scheme.

The interdiffusion stability condition (3.6b) in the BIM is related to the sign of the interactive component $D_I$ while it depends on $\tilde{D}_R$ in the BIM [Eq. (3.4b)]. Consequently, it reads

$$D_I=\tilde{D}_I=c_1c_2\left[\beta\left[\frac{\partial^2 g}{\partial c_1^2}\right]_{T,p}+\tilde{\delta}'^2\frac{K_0}{K}\right]\geq 0\quad(\text{ISC, BIM})\,, \tag{3.7}$$

or alternatively [see Eq. (2.46a)],

$$\beta\left[\frac{\partial\mu_{c_0}}{\partial c_0}\right]_{T,n_e}\geq 0 \quad (\text{ISC, BIM})\ . \tag{3.8}$$

The inequality (3.7) no longer has the usual neutral-like form (3.4b) owing to the presence of the definite positive term $\tilde{\delta}'^2(K_0/K)$ which ensures that the BIM can sustain nonexploding ionic density fluctuations even in the vicinity of the spinodal decomposition curve $(\partial^2 g/\partial c_1^2)_{T,p}=0$. This follows directly from the general property that the interdiffusion stability criterion $(\partial^2 g/\partial c_1^2)_{T,p}\geq 0$ breaks down *before* the mechanical one[1] $K\geq 0$. Moreover, it can be further stated that ISC in the BIM is *always* fulfilled, exactly as the MSC, which means that $\tilde{D}_I$ is a *strictly definite positive quantity.* This assumption is obviously true in the one single-component limit where $\tilde{D}_I$ reduces to unity [Eq. (2.49b)]. Thus hypothesizing a change in sign for $\tilde{D}_I$ in some intermediate concentration range would imply that the system remains fully stable or fully instable, the lhs of (3.6b) varying discontinuously from $+\infty$ to $-\infty$. This unphysical and novel feature is a by-product of the Coulomb term and can be explained by the appearance of an infinite electrostatic energy if undamped ionic density fluctuations are allowed to build up in the system. The preceding argument may be indirectly checked out against the known properties of the BIM equation of state. In the case of weakly asymmetric mixtures, HTV (Ref. 6) have shown that the excess internal energy $u_i^{\text{exc}}$ or excess Helmholtz free energy $f_i^{\text{exc}}$ is remarkably linear in the concentration $c_1$, when it is computed at constant $\Gamma'$ (i.e., at constant temperature and constant electronic density),

$$f_{\text{BIM}}^{\text{exc}}(\Gamma')\approx c_1 f_{\text{OCP}}^{\text{exc}}(\Gamma' Z_1^{5/3})+c_2 f_{\text{OCP}}^{\text{exc}}(\Gamma' Z_2^{5/3})\ . \tag{3.9}$$

$f_{\text{OCP}}^{\text{exc}}$ denotes here the Helmholtz free energy of the OCP.

As shown in Appendix D, the excess (nonideal) component of $\tilde{D}_I$ is identically zero when it is computed with the above linear equation of state so that $\tilde{D}_I$ reduces only to its ideal part $\tilde{D}_I^{\text{id}}$ (see also Appendix D for the derivation of $\tilde{D}_I^{\text{id}}$),

$$\tilde{D}_I=\tilde{D}_I^{\text{id}}+\tilde{D}_I^{\text{exc}}\approx\tilde{D}_I^{\text{id}}\equiv\overline{z^2}\ , \tag{3.10}$$

which is obviously positive.

The variables kept constant in the derivative $\partial\mu_{c_0}/\partial c_0$ [Eqs. (3.5) and (3.8)] are $T$ and $p$ in the PBIM and $T$ and $n_e$ in the BIM, respectively. In the high-density limit $r_s\to 0$, the ionic pressure becomes negligible compared to the electronic one ($p_i \ll p_e$). Since $p_e$ is a function of $r_s$ only, the condition of constant pressure is then equivalent to the condition of constant electronic density (or equivalently to the condition of constant parameter $\Gamma'$ at fixed $T$). We thus expect that the ISC inequalities will be identical in the BIM and the PBIM, taken in the high-density limit. Some attention must be paid, however, to the precise definition of the latter. There is no doubt that at constant plasma parameter $\Gamma$ and composition $c_1$ the thermodynamic quantities of the PBIM reduce to that of the BIM for $r_s\to 0$. This holds for the term $\tilde{\delta}'^2(K_0/K)$ entering in the definition (3.7), but it can be shown further that this term remains *finite* in the limit $r_s\to 0$ taken *constant temperature.* The last result, demonstrated in Appendix E, confirms once more the atypical behavior of the ISC in the BIM.

## IV. PROVISIONAL CONCLUSION

We have, as announced in the Introduction, developed the TTF formalism for studying in a coherent scheme demixing phenomena in strongly coupled binary ionic mixtures. Up to now we have put emphasis on the formal technicalities as evidenced in the appendixes. For the first time, a consistent analysis has been produced which agrees with the stability condition requirements and, as detailed in the following paper, ensures that the structure factors will diverge at critical values of the thermodynamic parameters at which the second-order derivative of the Gibbs free energy simultaneously vanishes.

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## APPENDIX A: BASIC THERMODYNAMICAL RELATIONSHIPS

### 1. Derivation of Eq. (2.16a)

We have only to detail the lhs equality in (2.16a). The right-hand side equality is then obtained in the same fashion through a change in the notation, owing to the identity (2.12c). We first write

$$\beta\left[\frac{\partial\mu_{c_0}}{\partial c_0}\right]_{T,p_i}=\beta\left[\frac{\partial\mu_{c_0}}{\partial c_0}\right]_{T,n_e}+\beta\left[\frac{\partial\mu_{c_0}}{\partial n_e}\right]_{T,c_0}\left[\frac{\partial n_e}{\partial c_0}\right]_{T,p_i} \tag{A1}$$

with

$$\beta\left[\frac{\partial\mu_{c_0}}{\partial n_e}\right]_{T,c_0}=\frac{\beta}{n_e^2}\left[\frac{\partial p_i}{\partial c_0}\right]_{T,n_e}\ , \tag{A2}$$

a result which follows directly from the differential (2.12a) when reexpressed in terms of the independent variables $(T,n_e,c_0)$. Moreover,

$$\beta\left[\frac{\partial p_i}{\partial c_0}\right]_{T,n_e}=-\beta\left[\frac{\partial p_i}{\partial n_e}\right]_{T,c_0}\left[\frac{\partial n_e}{\partial c_0}\right]_{T,p_i}\ . \tag{A3}$$

Noting that the derivatives taken at constant $c_0$ are equivalent to the derivatives taken at constant $c_1$ (with $dc_0=z_1z_2dc_1$), one gets with the definition (2.18a) (left equality)

$$\frac{K_0}{K_i}\equiv\bar{Z}\beta\left[\frac{\partial p_i}{\partial n_e}\right]_{T,c_0} \quad (K_0=\beta/n_i)\ .$$

Also, the definition (2.26) reads

$$\delta'=z_1z_2\frac{1}{n_e}\left[\frac{\partial n_e}{\partial c_0}\right]_{T,p_i}\ .$$

Then multiplying each member of the equality (A1) with $\bar{Z}(z_1z_2)^2$ leads to

$$\bar{Z}(z_1z_2)^2\beta\left[\frac{\partial\mu_{c_0}}{\partial c_0}\right]_{T,p_i}=\bar{Z}(z_1z_2)^2\beta\left[\frac{\partial\mu_{c_0}}{\partial c_0}\right]_{T,n_e}-\delta'^2\frac{K_0}{K_i}\ . \tag{A4}$$

The identity (2.16a) (lhs) follows directly from the result (A4) supplemented with (2.15a).

### 2. Derivation of the relations (2.18a) and (2.18b)

We start from the Gibbs-Duhem relationship (2.13a) first reexpressed in terms of $n_{i\alpha}=c_\alpha n_i$ $(\alpha=1,2)$. One thus gets

$$(dp_i)_T=\sum_{\alpha,\beta=1}^{2}\mu_{\alpha\beta}n_{i\alpha}dn_{i\beta}\ , \tag{A5}$$

where the notation (2.17) has been used.

Introducing Eq. (A5) in the definition (2.18a) (lhs) for the inverse compressibility yields

$$\frac{K_0}{K_i}=\beta n_i\sum_{\alpha,\beta=1}^{2}c_\alpha c_\beta\mu_{\alpha\beta}\ . \tag{A6}$$

The relation (2.18b) can be derived similarly with the replacements $K_i\to K$ and $\mu_{\alpha\beta}\to\tilde{\mu}_{\alpha\beta}$.

### 3. Derivation of the relations (2.21a) and (2.21b)

Considering the chemical potentials $\mu_{i\alpha}$ $(\alpha=1,2)$ as functions of the independent variables $T$, $V$, $N_{i1}$, and $N_{i2}$ yields

$$\begin{aligned}\left[\frac{\partial\mu_{i\alpha}}{\partial N_{i\beta}}\right]_{T,V,N_{i\gamma}}&=\left[\frac{\partial\mu_{i\alpha}}{\partial N_{i\beta}}\right]_{T,p_i,N_{i\gamma}}\\&\quad-\left[\frac{\partial\mu_{i\alpha}}{\partial V}\right]_{T,N_{i\beta},N_{i\gamma}}\left[\frac{\partial V}{\partial N_{i\beta}}\right]_{T,p_i,N_{i\gamma}}\\&\quad(\gamma\neq\beta)\ .\end{aligned} \tag{A7}$$

One also uses

$$\begin{aligned}\left[\frac{\partial\mu_{i\alpha}}{\partial V}\right]_{T,N_{i1},N_{i2}}&=-\left[\frac{\partial p_i}{\partial N_{i\alpha}}\right]_{T,V,N_{i\gamma}}\\&=\left[\frac{\partial p_i}{\partial V}\right]_{T,N_{i\alpha},N_{i\gamma}}\\&\quad\times\left[\frac{\partial V}{\partial N_{i\alpha}}\right]_{T,p_i,N_{i\gamma}}\quad(\gamma\neq\alpha)\ .\end{aligned} \tag{A8}$$

Thus, owing to the definitions (2.22) and the identity

$$K_i=-\frac{1}{V}\left[\frac{\partial V}{\partial p_i}\right]_T\ ,$$

we get

$$\left[\frac{\partial\mu_{i\alpha}}{\partial N_{i\beta}}\right]_{T,V,N_{i\gamma}}=\left[\frac{\partial\mu_{i\alpha}}{\partial N_{i\beta}}\right]_{T,p_i,N_{i\gamma}}+\frac{v_\alpha v_\beta}{VK_i}\quad(\gamma\neq\beta)\ . \tag{A9}$$

Multiplying each member of (A9) with $V$ and changing the set of variables from $(T,V,N_{i\alpha})$ to $(T,n_{i\alpha})$ yields directly the expected result (2.21a). (2.21b) is deduced in a similar manner with the replacements $\mu_{\alpha\beta}\to\tilde{\mu}_{\alpha\beta}$, $K_i\to K$, $p_i\to p$, and $v_\alpha\to\tilde{v}_\alpha$.

## APPENDIX B: DETERMINANT OF THE SECOND DIFFERENTIAL OF ENTROPY

We detail in what follows the derivation of the expressions (2.45a) and (2.46a) for $D_R$ and $D_I$, respectively. A similar derivation holds for $\tilde{D}_R$ and $\tilde{D}_I$ at the expense of a simple change in the notation. Hereafter, the variables taken as constant in the partial derivatives, such as $\partial\mu_{i\alpha}/\partial c_\beta$ $(\alpha,\beta=1$ or $2)$, are assumed to be $T$ and $p_i$.

### 1. Derivation of $D_R$ [Eq. (2.45a)]

With the help of the transformation relations (2.21a), the expression (2.44a) for $D_R$ reads

$$\begin{aligned}D_R=\frac{c_1c_2}{2}\sum_{\alpha,\beta=1}^{2}\epsilon_{\alpha\beta}&\left[\beta c_{\hat{\beta}}\frac{\partial\mu_{i\alpha}}{\partial c_\beta}+\frac{K_0}{K_i}\frac{(n_{i\alpha}v_\alpha)(n_{i\beta}v_\beta)}{c_\alpha c_\beta}\right]\\&\times\left[\beta c_\beta\frac{\partial\mu_{i\hat{\alpha}}}{\partial c_{\hat{\beta}}}+\frac{K_0}{K_i}\frac{(n_{i\hat{\alpha}}v_{\hat{\alpha}})(n_{i\hat{\beta}}v_{\hat{\beta}})}{c_{\hat{\alpha}}c_{\hat{\beta}}}\right]\ .\end{aligned} \tag{B1}$$

Obviously,

$$\frac{\partial\mu_{i\alpha}}{\partial c_\beta}=-\frac{\partial\mu_{i\alpha}}{\partial c_{\hat{\beta}}}\quad(\alpha,\beta=1.2)\ ,$$

so that,

$$D_R=\beta\frac{K_0}{K_i}\sum_{\alpha,\beta=1}^{2}\left[c_\alpha\frac{\partial\mu_{i\alpha}}{\partial c_\alpha}(n_{i\hat{\alpha}}v_{\hat{\alpha}})(n_{i\hat{\beta}}v_{\hat{\beta}})\right]\ . \tag{B2}$$

Using relations (2.14) (left equality) together with the additive properties (2.23b) for the partial ionic volumes, yields straightforwardly

$$D_R=c_1c_2\frac{K_0}{K_i}\frac{\beta}{c_2}\left[\frac{\partial\mu_{i1}}{\partial c_1}\right]_{T,p_i}\equiv c_1c_2\frac{K_0}{K_i}\beta\left[\frac{\partial^2g_i}{\partial c_1^2}\right]_{T,p_i}\ , \tag{B3}$$

which corresponds to (2.45a) (left equality).

### 2. Derivation of $D_I$ [Eq (2.46a)]

We introduce again the basic transformation relation (2.21a) into the expression (2.44b) for $D_I$,

$$D_I=c_1c_2\sum_{\alpha,\beta=1}^{2}\epsilon_{\alpha\beta}z_{\hat{\alpha}}z_{\hat{\beta}}\left[\beta c_{\hat{\beta}}\frac{\partial\mu_{i\alpha}}{\partial c_\beta}+\frac{K_0}{K_i}\frac{(n_{i\alpha}v_\alpha)(n_{i\beta}v_\beta)}{c_\alpha c_\beta}\right] \tag{B4}$$

and then the relations (2.14), (2.23a), and (2.23b) to derive

$$D_I=c_1c_2\left[\frac{K_0}{K_i}n_i^2(z_2v_1-z_1v_2)^2+\frac{\beta}{c_2}\left[\frac{\partial\mu_{i1}}{\partial c_1}\right]_{T,p_i}\right] . \tag{B5}$$

Next, with the help of (2.25) and (2.28), we note that

$$n_i(z_2v_1-z_1v_2)=-(\delta+z_1-z_2)=-\delta' ,$$

so we finally get

$$D_I=c_1c_2\left[\frac{K_0}{K_i}\delta'^2+\beta\left[\frac{\partial^2 g}{\partial c_1^2}\right]_{T,p_i}\right] , \tag{B6}$$

corresponding to (2.46a) (left equality).

## APPENDIX C: EXPRESSION OF OR THE SECOND-ORDER DIFFERENTIAL OF THE ENTROPY IN TERMS OF THE VARIABLES $\delta\hat{\rho}_{i0}(\mathbf{k})$ AND $\delta\hat{c}_0(\mathbf{k})$

For the sake of simplicity we omit in what follows the explicit **k** dependence for the fluctuations $\delta\hat{f}(\mathbf{k})$. Products like $\delta\hat{f}(\mathbf{k})\delta\hat{g}(-\mathbf{k})$ will be noted simply as $\delta\hat{f}\delta\hat{g}$ and assumed to be ordered from left to right. For our purpose we will consider in a first step the transformation $(\delta\hat{\rho}_{i1},\delta\hat{\rho}_{i2})\rightarrow(\delta\hat{\rho}_i,\delta\hat{c}_1)$, and then in a second step the transformation $(\delta\hat{\rho}_i,\delta\hat{c}_1)\rightarrow(\delta\hat{\rho}_{i0},\delta\hat{c}_0)$, in order to derive the expression (3.1a) for $\Delta S$, starting from Eq. (2.39). The transformation (2.41)→(3.1b) is derived in the same way and will not be detailed any further.

The first variables' change quoted above, with $\delta\hat{\rho}_i=\delta\hat{\rho}_{i1}+\delta\hat{\rho}_{i2}$ and $n_i\delta\hat{c}_1=c_2\delta\hat{\rho}_{i1}-c_1\delta\hat{\rho}_{i2}$, reads

$$\delta\hat{\rho}_{i\alpha}=c_\alpha\delta\hat{\rho}_i+n_i\delta\hat{c}_\alpha \quad (\alpha=1,2) \text{ with } \sum_{\alpha=1}^{2}\delta\hat{c}_\alpha=0 ,$$

so we reach

$$\frac{\Delta S}{k_B}=-\frac{1}{2N_i}\sum_{\mathbf{k}}{}'\sum_{\alpha,\beta=1}^{2}\{[Z_\alpha Z_\beta\hat{v}(k)+\beta n_i\mu_{\alpha\beta}](c_\alpha c_\beta\delta\hat{\rho}_i^2)$$
$$+[Z_\alpha Z_\beta\hat{v}(k)+\beta n_i\mu_{\alpha\beta}][n_i^2\delta\hat{c}_\alpha\delta\hat{c}_\beta+n_i(c_\alpha\delta\hat{c}_\beta\delta\hat{\rho}_i+c_\beta\delta\hat{\rho}_i\delta\hat{c}_\alpha)]\} . \tag{C1}$$

We made use of (2.18a) (right equality) to insert $K_0/K_i$ into the term proportional to $\delta\hat{\rho}_i^2$. Then we transform the $\mu_{\alpha\beta}$ in the other terms according to (2.21a). Finally, a straightforward application of the relations (2.14), (2.23a), (2.23b), and (2.25) yields after some algebraic calculation

$$\frac{\Delta S}{k_B}=-\frac{1}{2N_i}\sum_{\mathbf{k}}{}'\left\{\left[\bar{Z}^2\hat{v}(k)+\frac{K_0}{K_i}\right]\delta\hat{\rho}_i^2+\left[\bar{Z}(Z_1-Z_2)\hat{v}(k)-\delta\frac{K_0}{K_i}\right]n_i(\delta\hat{\rho}_i\delta\hat{c}_1+\delta\hat{c}_1\delta\hat{\rho}_i)\right.$$
$$\left.+\left[(Z_1-Z_2)^2\hat{v}(k)+\delta^2\frac{K_0}{K_i}+\beta\left[\frac{\partial^2 g_i}{\partial c_1^2}\right]_{T,p_i}\right]n_i^2\delta\hat{c}_1^2\right\} . \tag{C2}$$

A similar equation can be derived starting from (2.41) with $\hat{v}(k)\rightarrow\Delta\hat{v}(k)$, $K_i\rightarrow K$, $p_i\rightarrow p$, $g_i\rightarrow g$, and $\delta\rightarrow\tilde{\delta}$.

The second variables' change $(\delta\hat{\rho}_{i1},\delta\hat{c}_1)\rightarrow(\delta\hat{\rho}_{i0},\delta\hat{c}_0)$ reads

$$\left.\begin{aligned}\delta\hat{\rho}_{i0}=n_i(Z_1-Z_2)\delta\hat{c}_1+\bar{Z}\,\delta\hat{\rho}_i\\ \delta\hat{c}_0=z_1z_2\,\delta\hat{c}_1\end{aligned}\right\}\Longrightarrow\left\{\begin{aligned}&\bar{Z}\,\delta\hat{\rho}_i=\delta\hat{\rho}_{i0}-n_i\frac{(Z_1-Z_2)}{z_1z_2}\delta\hat{c}_0,\\ &\delta\hat{c}_1=\frac{\delta\hat{c}_0}{z_1z_2},\end{aligned}\right.$$

which implies

$$\frac{\Delta S}{k_B}=\frac{-1}{2N_i}\sum_{\mathbf{k}}{}'\left\{\left[\bar{Z}^2\hat{v}(k)+\frac{K_0}{K_i}\right]\frac{\delta\hat{\rho}_{i0}^2}{\bar{Z}^2}-\frac{K_0}{K_i}(\delta+z_1-z_2)\frac{n_i}{\bar{Z}z_1z_2}(\delta\hat{\rho}_{i0}\delta\hat{c}_0+\delta\hat{c}_0\delta\hat{\rho}_{i0})\right.$$
$$\left.+\left[(\delta+z_1-z_2)^2\frac{K_0}{K_i}+\beta\left[\frac{\partial^2 g_i}{\partial c_1^2}\right]_{T,p_i}\right]\frac{n_i^2\delta\hat{c}_0^2}{(z_1z_2)^2}\right\} . \tag{C3}$$

Identifying $\delta'$ with $(\delta+z_1-z_2)$ [see Eq. (2.28), left equality] and replacing $n_i$ by $n_e/\overline{Z}$, we get the expected result (3.1a). A similar derivation holds for Eq. (3.1b) with $\hat{v}(k)\rightarrow\Delta\hat{v}(k)$, $K_i\rightarrow K$, $p_i\rightarrow p$, $g_i\rightarrow g$, and $\tilde{\delta}\rightarrow\tilde{\delta}'$.

## APPENDIX D: CALCULATION OF $\tilde{D}_I$ IN THE BIM WITH THE HTV's EQUATION OF STATE

We start from the expression (2.46a) (right equality) for $D_I$ or $\tilde{D}_I$, supplemented with the definition (2.12a) for $\mu_{c_0}$, and make the replacement $dc_0=z_1z_2dc_1$. We get

$$D_I=\tilde{D}_I\equiv c_1c_2\frac{\beta}{\overline{Z}}\left[\frac{\partial}{\partial c_1}(Z_2\mu_{i1}-Z_1\mu_{i2})\right]_{T,n_e} . \tag{D1}$$

We will compute (D1) with the help of the following thermodynamical relationship:

$$\mu_{i\alpha}=z_\alpha f_k+(1-c_\alpha)\overline{Z}\left[\frac{\partial}{\partial c_\alpha}\left[\frac{f_i}{\overline{Z}}\right]\right]_{T,n_e}+Z_\alpha\frac{p_i}{n_e} , \tag{D2}$$

relating the chemical potentials $\mu_{i\alpha}$ to the Helmholtz free energy $f_i$ expressed as a function of $T$, $c_1$, and $n_e$.

In the case of the BIM, where $p_i^{\text{exc}}/n_i=\frac{1}{3}u_i^{\text{exc}}$, the excess part of (D2) reduces to

$$\mu_{i\alpha}^{\text{exc}}=z_\alpha(f_i^{\text{exc}}+\tfrac{1}{3}u_i^{\text{exc}})+(1-c_\alpha)\overline{Z}\left[\frac{\partial}{\partial c_\alpha}\left[\frac{f_i^{\text{exc}}}{\overline{Z}}\right]\right]_{T,n_e} . \tag{D3}$$

Obviously the contribution of the first term in the above relation does not contribute to $\tilde{D}_I^{\text{exc}}$, which then simplifies as

$$\tilde{D}_i^{\text{exc}}=\frac{\beta}{\overline{Z}}\left\{\frac{\partial}{\partial c_1}\left[\overline{Z}^2\frac{\partial}{\partial c_1}\left[\frac{f_i^{\text{exc}}}{\overline{Z}}\right]\right]\right\}_{T,n_e} . \tag{D4}$$

Noting finally that the derivatives at constant $T$ and $n_e$ imply also that the parameter $\Gamma'$ be kept constant, it is a straightforward matter to check out that the rhs of (D4) identically vanishes when it is computed with HTV's linear equation of state (3.9).

The ideal part of $\tilde{D}_I$ is derived from (D1), writing[32] $\beta\mu_{i\alpha}=\ln(c_\alpha n_e/\overline{Z})+\varphi_\alpha(T)$. One obtains

$$\tilde{D}_I=1+c_1c_2\frac{(Z_1-Z_2)^2}{\overline{Z}^2}\equiv\overline{z^2} . \tag{D5}$$

## APPENDIX E: CALCULATION OF $\tilde{\delta}'^2(K_0/K)$ IN THE HIGH-DENSITY LIMIT $r_s\rightarrow 0$

The sequel is devoted to the calculation of the $r_s\rightarrow 0$ limit of the basic quantity $\tilde{\delta}'^2(K_0/K)$ contained in the interacting component $\tilde{D}_I$ [Eq. (2.46b)] related to the ISC (3.7) of the BIM. For jellium this limit is equivalent to the ideal Fermi gas, taken as nonrelativistic in what follows. Conversely, the $r_s\rightarrow 0$ limit pertaining to the ionic component can be defined in two distinct ways, whether or not $\Gamma'$ (or $\Gamma$ since $c_1$ is kept fixed) or $T$ is kept constant. The first case corresponds to the "natural" high-density limit of the PBIM, giving rise to the BIM at a given value of the plasma parameter. The second one corresponds to the *correct* high-density limit fulfilling the conditions (3.7) or (3.8).

We reexpress $\tilde{\delta}'$ as

$$\tilde{\delta}'\equiv\frac{1}{n_e}\left[\frac{\partial n_e}{\partial c_1}\right]_{T,p}=-\frac{1}{n_e}\frac{\left[\dfrac{\partial p}{\partial c_1}\right]_{T,n_e}}{\left[\dfrac{\partial p}{\partial n_e}\right]_{T,c_1}} , \tag{E1}$$

so that, with $p=p_e+p_i$,

$$\tilde{\delta}'=-K\left[\frac{\partial p_i}{\partial c_1}\right]_{T,n_e}=-\overline{Z}\frac{K}{K_0}\left[\frac{\partial}{\partial c_1}\left[\frac{\beta p_i}{n_e}\right]\right]_{T,n_e} . \tag{E2}$$

In the $r_s\rightarrow 0$ limit at constant $\Gamma'$, the pressure term $\beta p_i/n_e$ reduces to its BIM value where it depends only on $\Gamma'$ (or $\Gamma$). Thus $\tilde{\delta}'$ behaves like $K/K_0$ and $\tilde{\delta}'^2(K_0/K)$ behaves the same way. However, in the $r_s\rightarrow 0$ limit, $K_i$ becomes negligible compared to $K_e$, which tends towards its ideal expression, so that

$$\frac{K}{K_0}\approx\frac{K_e}{K_0}=\frac{3}{\lambda^2}\frac{r_s}{\overline{Z}\Gamma'} \quad \text{with } \lambda=\left[\frac{9\pi}{4}\right]^{1/3} . \tag{E3}$$

Thus $\tilde{\delta}'^2(K_0/K)$ vanishes with $r_s$ in the limit $r_s\rightarrow 0$ taken at constant $\Gamma'$.

Now we pay attention to the limit $r_s\rightarrow 0$ at constant temperature. This implies that $\Gamma$ or $\Gamma'$ becomes very large, so that we can use the asymptotic Salpeter[33] "ion-sphere" model to compute $p_i$ in (E2) as

$$\frac{\beta p_i}{n_i}=-\frac{A}{3}\Gamma'\overline{Z^{5/3}} \quad \text{with } A=0.9 . \tag{E4}$$

The calculation of $\tilde{\delta}'$ thus leads to

$$\tilde{\delta}'=\frac{A}{\lambda^2}\frac{Z_1Z_2}{\overline{Z}^2}(Z_1^{2/3}-Z_2^{2/3})r_s , \tag{E5}$$

with

$$\lim_{r_s\rightarrow 0}\tilde{\delta}'^2\frac{K_0}{K}=\frac{\beta e^2}{a_0}\frac{A^2}{3\lambda^2}\frac{(Z_1Z_2)^2}{\overline{Z}^3}(Z_1^{2/3}-Z_2^{2/3}) , \tag{E6}$$

which remains finite when $T$ (i.e., $\beta$) is kept constant.

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