Simpler free-energy functional of the Debye-Hückel model of fluids and the nonuniqueness of free-energy functionals in the theory of fluids

R. Piron[1,*] and T. Blenski[2]

[1]CEA, DAM, DIF, F-91297 Arpajon, France
[2]Laboratoire "Interactions, Dynamiques et Lasers", UMR 9222, CEA-CNRS-Université Paris-Saclay, Centre d'Études de Saclay, F-91191 Gif-sur-Yvette Cedex, France

(Received 18 October 2018; published 28 May 2019)

In previous publications [Piron and Blenski, Phys. Rev. E **94**, 062128 (2016); Blenski and Piron, High Energy Density Phys. **24**, 28 (2017)], the authors have proposed Debye-Hückel-approximate free-energy functionals of the pair distribution functions for one-component fluids and two-component plasmas. These functionals yield the corresponding Debye-Hückel integral equations when they are minimized with respect to the pair distribution functions, lead to correct thermodynamic relations, and fulfill the virial theorem. In the present paper, we update our results by providing simpler functionals that have the same properties. We relate these functionals to the approaches of Lado [Phys. Rev. A **8**, 2548 (1973)] and of Olivares and McQuarrie [J. Chem. Phys. **65**, 3604 (1976)]. We also discuss briefly the nonuniqueness issue that is raised by these results.

DOI: 10.1103/PhysRevE.99.052134

I. INTRODUCTION

Models of atoms in plasmas [1–6] should in principle account for ion and electron correlations and their impact on the atomic structure and dynamics. Attempts to account for such effects are an active field of research [7–16]. In this kind of self-consistent models, ions are viewed as classical particles interacting through an effective pair interaction potential that depends on the electronic structure. In some approaches [11,16], the free energy is built from several contributions, including the classical-ion free energy, viewed as a functional of the ion-ion pair correlation function.

A broader interest in variational formulations of approximate theories based on a free-energy functional of the pair distribution function is also well identified in the literature, as, for instance, in Sec. 4.6 of Ref. [17]. Variational formulations of this kind are used as a theoretical tool in a number of works [18–20].

Free-energy functionals of the pair distribution function were proposed in the framework of the hypernetted chain (HNC) model by Morita and Hiroike [21], and also by Lado [22,23]. In the case of the Debye-Hückel (DH) model [24], same kind of functionals were proposed in Refs. [25,26].

Although it is only valid in the low-coupling limit, the DH model qualitatively accounts for the screening of interaction potentials and the decay of correlation functions, both in the framework of simple and multicomponent fluids. Moreover, in the case of long-range attractive interaction potentials, the DH model allows to circumvent the "classical catastrophe" of collapsing particles, which gives it a particular role in the physics of electron-ion plasmas and electrolytes. The DH model is still the object of theoretical studies. For instance, quite recently, it was shown that the energy and virial routes to the compressibility factor are equivalent in the DH model [27].

In the case of approximate models such as HNC, nonlinear DH, and DH, one can derive the integral equation from the classical density functional theory (DFT) of inhomogeneous systems, using a suitable approximation for the intrinsic free energy, and then applying the Percus trick [28]. This "trick" consists in fixing the external potential of the inhomogeneous system to the interaction potential of the homogeneous fluid of interest. The density then gives the pair distribution function. Such derivations are given in Appendix, with references. However, even if it is an efficient way of deriving the model integral equations, this method does not provide a route to the free energy of the model. The reason is that, in the Percus trick, one considers a deviation from the reference state of an homogeneous fluid of interacting particles. Thus, one can only evaluate the free-energy difference with respect to this reference state, which, in the Percus trick framework, corresponds to the excess chemical potential (see, for instance, Eq. (4.3.21) of Ref. [29]). In other words, this method can be viewed as a charging method in which the interaction potential of an additional, fixed particle of the homogeneous fluid is gradually switched on.

Thus, one needs to construct the free energy, starting from the approximate pair distribution function, or, equivalently, from the integral equation. This can be performed using the Debye-Kirkwood charging method [30]. This method uses an exact relation between the excess free energy and the pair distribution function. In this charging method, the interaction potential of *all pairs of particles* is gradually switched on. This charging process is therefore different from that described in previous paragraph. This point is discussed in the literature, as, for example, in the paragraph between Eqs. (8) and (11) of Ref. [31]. In the Debye-Kirkwood charging method, the reference can be a system of noninteracting particles. This method then gives access to the excess free energy.

In Ref. [22], Lado derives a HNC correction to the free energy of a reference system, using the Debye-Kirkwood charging relation. If one assumes a noninteracting reference

---

[*] Corresponding author: robin.piron@cea.fr

system, then his result can be viewed as an HNC excess-free-energy functional of the pair distribution function. The same expression was also previously derived by Morita and Hiroike [21]. It can be shown that this free energy leads to correct thermodynamics and fulfills the virial theorem. In addition to giving the equilibrium free energy, this free-energy functional yields the HNC integral equation when it is minimized with respect to the pair distribution function (it is a generating functional). This functional interpretation was already pointed out in Refs. [21,22].

In Ref. [25], our derivation of a Debye-Hückel (DH) excess-free-energy functional was based on the same starting point as Ref. [22]. In the present work, we follow even more closely the derivation of Ref. [22], and show that we can obtain a different free-energy functional. The latter has the same thermodynamical properties while having a simpler expression. It is also more similar to the expression of [22] for the HNC free energy. This expression can be recovered from the method described by Olivares and McQuarrie in Ref. [32]. However, their method is focused on the construction of generating functionals and does not in itself provide systematically a free-energy functional.

In this paper, starting from a short summary of Lado's derivation, we derive this alternative DH free-energy functional in the one-component and multi-component cases. Each time, we show that it leads to the same thermodynamics as our previously-proposed functionals. We also discuss how the methods of Refs. [22,32] complement each other. Finally, we address briefly the nonuniqueness issue which is raised by the present work.

II. KEY STEPS OF LADO'S CALCULATION

The derivation of the HNC free energy given in Ref. [22], as well as ours in Ref. [25], starts from the charging relation,

$$\frac{A_{\text{eq}}^{\xi}(\varrho,T)}{V}=\frac{\varrho^2}{2}\int_0^{\xi}d\xi'\int d^3r\left\{h_{\text{eq}}^{\xi'}(r)u(r)\right\},\tag{1}$$

where A_{eq}^{ξ}/V is the equilibrium renormalized excess free energy per unit volume [33] of the simple fluid having interparticle interaction potential $\xi u(r)$. $h_{\text{eq}}^{\xi}(r)+1$ is the equilibrium pair distribution function [$h_{\text{eq}}^{\xi}(r)$ is called the equilibrium correlation function]. This charging relation is fulfilled for the exact equilibrium quantities. In the present context, we require it to hold for the approximate equilibrium quantities, stemming from an approximate model such as HNC or DH. The approximate equilibrium pair distribution function is such that the following closure relation holds:

$$\begin{aligned}\ln\left(h_{\text{eq}}^{\xi}(r)+1\right)=&-\beta\xi u(r)+h_{\text{eq}}^{\xi}(r)-c\left\{h_{\text{eq}}^{\xi}(r');r\right\}\\&-b_{\text{approx}}\left\{h_{\text{eq}}^{\xi}(r');r\right\},\end{aligned}\tag{2}$$

with $b_{\text{approx}}\{h^{\xi}(r');r\}$ denoting the approximate bridge function corresponding to the chosen model. $c\{h(r');r\}$ is the direct correlation function, which we regard as a functional of $h(r)$ defined through the Ornstein-Zernike (OZ) relation,

$$h(r)=c(r)+\varrho\int d^3r'\{h(r')c(|\mathbf{r}-\mathbf{r}'|)\}.\tag{3}$$

Performing the derivative with respect to ξ of the equilibrium relation Eq. (2), we obtain easily

$$\begin{aligned}&h_{\text{eq}}^{\xi}(r)\beta u(r)\\&\quad=\frac{\partial}{\partial\xi}\left(\frac{\left[h_{\text{eq}}^{\xi}(r)\right]^2}{2}-\left[h_{\text{eq}}^{\xi}(r)+1\right]c\left\{h_{\text{eq}}^{\xi}(r');r\right\}-\beta\xi u(r)\right)\\&\qquad+c\left\{h_{\text{eq}}^{\xi}(r');r\right\}\frac{\partial h_{\text{eq}}^{\xi}(r)}{\partial\xi}-\left[h_{\text{eq}}^{\xi}(r)+1\right]\frac{\partial}{\partial\xi}b\left\{h_{\text{eq}}^{\xi}(r');r\right\}.\end{aligned}\tag{4}$$

Using again Eq. (2) in the first term of the latter equation's right-hand side, we get

$$\begin{aligned}&h_{\text{eq}}^{\xi}(r)\beta u(r)\\&\quad=\frac{\partial}{\partial\xi}\Bigg(\frac{\left[h_{\text{eq}}^{\xi}(r)\right]^2}{2}+h_{\text{eq}}^{\xi}(r)\beta\xi u(r)-\left[h_{\text{eq}}^{\xi}(r)+1\right]\\&\qquad\times\left[h_{\text{eq}}^{\xi}(r)-\ln\left(h_{\text{eq}}^{\xi}(r)+1\right)-b\left\{h_{\text{eq}}^{\xi}(r');r\right\}\right]\Bigg)\\&\qquad+c\left\{h_{\text{eq}}^{\xi}(r');r\right\}\frac{\partial h_{\text{eq}}^{\xi}(r)}{\partial\xi}-\left[h_{\text{eq}}^{\xi}(r)+1\right]\frac{\partial}{\partial\xi}b\left\{h_{\text{eq}}^{\xi}(r');r\right\}.\end{aligned}\tag{5}$$

Using this equation in the charging relation, Eq. (1), the first term is straightforwardly integrated over the charging parameter ξ. For the purpose of integrating the second term, we switch to the Fourier space and use the OZ relation (i.e., the definition of $c\{h^{\xi}(r');r\}$) to show that

$$\begin{aligned}&\int d^3r\left\{c\{h^{\xi}(r');r\}\frac{\partial h^{\xi}(r)}{\partial\xi}\right\}\\&\quad=\frac{\partial}{\partial\xi}\frac{1}{\varrho^2}\int\frac{d^3k}{(2\pi)^3}\left\{\varrho h_k^{\xi}-\ln\left(1+\varrho h_k^{\xi}\right)\right\}.\end{aligned}\tag{6}$$

Here, we used the following definition of the Fourier transform of a function $f(r)$:

$$\int d^3r\{f(r)e^{i\mathbf{k}.\mathbf{r}}\}.\tag{7}$$

In the case of the HNC model, which is considered in Lado's paper, the bridge function is disregarded: $b\{h(r');r\}=0$. Taking $\xi=1$, this leads to the approximate free energy:

$$\begin{aligned}\frac{A_{\text{eq}}^{\text{HNC}}(\varrho,T)}{V}=&\frac{\varrho^2}{2\beta}\int d^3r\left\{\frac{[h_{\text{eq}}(r)]^2}{2}+h_{\text{eq}}(r)\beta u(r)\right.\\&\left.-[h_{\text{eq}}(r)+1][h_{\text{eq}}(r)-\ln(h_{\text{eq}}(r)+1)]\right\}\\&+\frac{1}{2\beta}\int\frac{d^3k}{(2\pi)^3}\{\varrho h_{\text{eq},k}-\ln(1+\varrho h_{\text{eq},k})\}.\end{aligned}\tag{8}$$

This expression can be viewed as the HNC-equilibrium value of a functional of $h(r)$: $A_{\text{eq}}^{\text{HNC}}(\varrho,T)=A^{\text{HNC}}\{h(r);\varrho,T\}|_{\text{eq}}$. That is, $A^{\text{HNC}}\{h(r);\varrho,T\}$ is defined from the right-hand side of Eq. (8), treating $h_{\text{eq}}(r)$ as a variable. Moreover, it can be checked *a posteriori* that minimization of A^{HNC} with respect to $h(r)$ yields the HNC closure, i.e., Eq. (2) with $b\{h(r');r\}=0$.

Taking the problem from the other side, one can first search for the functionals of $h(r)$ that yields the OZ equation with a chosen closure relation, here: the HNC closure. Such a systematic approach is exposed in Ref. [32]. Once these are found, one can then pick among them a functional that fulfills the charging relation. We will further comment on this point in Sec. IV.

III. ALTERNATIVE DEBYE-HÜCKEL FREE-ENERGY FUNCTIONAL

The DH integral equation for a simple fluid is

$$h^{\xi}_{\mathrm{eq}}(r)=-\beta\xi u(r)-\varrho\beta\xi\int d^3r'\left\{h^{\xi}_{\mathrm{eq}}(r')u(|\mathbf{r}-\mathbf{r}'|)\right\}. \quad (9)$$

This is equivalent to the OZ relation, Eq. (3), with the closure

$$c\left\{h^{\xi}_{\mathrm{eq}}(r');r\right\}=-\beta\xi u(r). \quad (10)$$

From Eq. (2), one can thus write the corresponding bridge function as

$$b\left\{h^{\xi}_{\mathrm{eq}}(r');r\right\}=h^{\xi}_{\mathrm{eq}}(r)-\ln\left(h^{\xi}_{\mathrm{eq}}(r)+1\right). \quad (11)$$

It turns out that the last term in Eq. (5) can then be readily rewritten as

$$\left[h^{\xi}_{\mathrm{eq}}(r)+1\right]\frac{\partial}{\partial\xi}b\left\{h^{\xi}_{\mathrm{eq}}(r');r\right\}=\frac{1}{2}\frac{\partial\left[h^{\xi}_{\mathrm{eq}}(r)\right]^2}{\partial\xi} \quad (12)$$

We end up with

$$\frac{A^{\mathrm{DH}}_{\mathrm{eq}}(\varrho,T)}{V}=\frac{\varrho^2}{2\beta}\int d^3r\{h_{\mathrm{eq}}(r)\beta u(r)\}$$
$$+\frac{1}{2\beta}\int\frac{d^3k}{(2\pi)^3}\{\varrho h_{\mathrm{eq},k}-\ln(1+\varrho h_{\mathrm{eq},k})\} \quad (13)$$
$$=\left.\frac{A^{\mathrm{DH}}\{h(r);\varrho,T\}}{V}\right|_{\mathrm{eq}}. \quad (14)$$

Like in the previous section, $A^{\mathrm{DH}}\{h(r);\varrho,T\}$ is defined from the right-hand side of Eq. (13), treating $h_{\mathrm{eq}}(r)$ as a variable. Here again, one can readily check that minimization of A^{DH} with respect to $h(r)$ yields the DH closure, Eq. (10).

In Ref. [32], the mean spherical model, which is closely related to the DH model, is addressed in order to find a generating functional of the direct correlation function $c(r)$. However, one can also use the results of Ref. [32] to obtain the functional of Eq. (13). This is discussed in the next section.

The most direct way of checking the thermodynamical relations obtained using Eq. (13) is to compare the equilibrium value of A^{DH} with that of our previous expression, given in Eq. (19) of Ref. [25]. Let us first recall this expression:

$$\frac{A^{\mathrm{DH}\prime}\{h(r);\varrho,T\}}{V}=\frac{\varrho}{\beta}\int\frac{d^3k}{(2\pi)^3}\left\{\left(1+\frac{1}{\varrho\beta u_k}\right)\right.$$
$$\times\left(1-\frac{\ln(1+\varrho\beta u_k)}{\varrho\beta u_k}\right)$$
$$\left.\times h_k\left(\frac{h_k}{2}+\beta u_k+\frac{\varrho\beta}{2}h_k u_k\right)\right\}. \quad (15)$$

Inserting the DH equilibrium value of h_k,

$$h_{\mathrm{eq},k}=\frac{-\beta u_k}{1+\varrho\beta u_k}, \quad (16)$$

we get after a few simplifications

$$\frac{A^{\mathrm{DH}\prime}\{h_{\mathrm{eq}}(r);\varrho,T\}}{V}=\frac{1}{2\beta}\int\frac{d^3k}{(2\pi)^3}\{-\varrho\beta u_k+\ln(1+\varrho\beta u_k)\}. \quad (17)$$

Furthermore, it can be easily checked that inserting Eq. (16) into Eq. (13) leads to the same expression as Eq. (17).

This identity, in the sense of thermodynamical functions, of both free-energy functionals, when taken at the DH equilibrium, immediately yields the identity of all thermodynamical functions, i.e., derivatives of the equilibrium free energy with respect to the thermodynamic parameters ϱ, T, and also with respect to $u(r)$ [34].

Moreover, it is worth noting that the expression for the internal energy can be obtained more easily from Eq. (13) than from Eq. (15):

$$\frac{U^{\mathrm{DH}}_{\mathrm{eq}}(\varrho,T)}{V}=\frac{\partial}{\partial\beta}\left.\left(\frac{\beta A^{\mathrm{DH}}\{h(r);\varrho,T\}}{V}\right)\right|_{\mathrm{eq}}, \quad (18)$$

$$\frac{\partial}{\partial\beta}\left(\frac{\beta A^{\mathrm{DH}}\{h(r);\varrho,T\}}{V}\right)=\frac{\varrho^2}{2}\int d^3r\{h(r)u(r)\}. \quad (19)$$

It is also easier to show that the virial theorem is fulfilled:

$$P^{\mathrm{DH}}_{\mathrm{eq}}(\varrho,T)=\varrho^2\frac{\partial}{\partial\varrho}\left.\left(\frac{A^{\mathrm{DH}}\{h(r);\varrho,T\}}{\varrho V}\right)\right|_{\mathrm{eq}}, \quad (20)$$

$$\varrho^2\frac{\partial}{\partial\varrho}\left(\frac{A^{\mathrm{DH}}\{h(r);\varrho,T\}}{\varrho V}\right)=\frac{\varrho^2}{2}\int\frac{d^3k}{(2\pi)^3}\{h_k u_k\}$$
$$+\frac{1}{2\beta}\int\frac{d^3k}{(2\pi)^3}\{\ln(1+\varrho h_k)-c_k\{h(r)\}\}, \quad (21)$$

$$P^{\mathrm{DH}}_{\mathrm{eq}}=\frac{U^{\mathrm{DH}}_{\mathrm{eq}}}{V}+\frac{1}{2\beta}\int\frac{d^3k}{(2\pi)^3}\{\varrho\beta u_k-\ln(1+\varrho\beta u_k)\} \quad (22)$$

$$=P^{\mathrm{DH}}_{\mathrm{virial}}, \quad (23)$$

where the expression for $P^{\mathrm{DH}}_{\mathrm{virial}}$ can be checked in Ref. [25], Eq. (16).

As is discussed in Ref. [25], the thermodynamical consistency of the obtained free-energy functional is deeply related to the fact that we required Eq. (1) to hold at equilibrium.

Although the functional of Eq. (13) leads to the same thermodynamics as that of Eq. (15), they still differ as functionals. Among the differences between the two is that the functional of Eq. (13) has the following derivative:

$$\frac{\delta}{\delta u(r)}\frac{A^{\mathrm{DH}}}{V}=\frac{\varrho^2}{2}h(r), \quad (24)$$

whatever $h(r)$ is considered, whereas this relation is only fulfilled at equilibrium with the functional of Eq. (15).

As is noted in Appendix B of Ref. [20], having Eq. (24) to be fulfilled at equilibrium is essential to the thermodynamic consistency of the free-energy functional. This equation indeed follows from the charging relation. However, fulfilling Eq. (24) for all $h(r)$ is a sufficient, but not a necessary, condition for A^{DH} to be a free-energy functional.

IV. RELATION TO THE OLIVARES-MCQUARRIE APPROACH

In Ref. [32], Olivares and McQuarrie propose a somehow systematic method to find generating functionals for the integral-equation models based on the OZ relation. The final purpose of this approach is thus to find functionals $\mathcal{F}\{h(r)\}$ such that the integral equation of the model is equivalent to

$$\frac{\delta\mathcal{F}\{h(r)\}}{\delta h(r)}=0. \tag{25}$$

They choose to first search for a functional $\mathcal{C}\{h(r)\}$ such that the OZ relation is equivalent to

$$\frac{\delta\mathcal{C}\{h(r)\}}{\delta h(r)}=-\varrho^2c(r), \tag{26}$$

that is

$$\frac{\delta\mathcal{C}\{h(r)\}}{\delta h_k}=\frac{-\varrho^2h_k}{1+\varrho h_k}. \tag{27}$$

This leads to

$$\mathcal{C}\{h(r)\}=\mathcal{C}^*+\int\frac{d^3k}{(2\pi)^3}\{\varrho h_k-\ln(1+\varrho h_k)\}, \tag{28}$$

$\mathcal{C}^*$ being a constant with respect to $h(r)$. Then, a functional $\mathcal{F}\{h(r)\}$ can be formed in the following way:

$$\mathcal{F}\{h(r)\}=\mathcal{F}^*+\alpha^*(\mathcal{C}\{h(r)\}+\mathcal{A}\{h(r)\}), \tag{29}$$

where $\mathcal{F}^*$, α^* are constants with respect to $h(r)$, and where $\mathcal{A}\{h(r)\}$ is such that the closure relation is equivalent to

$$\frac{\delta\mathcal{A}\{h(r)\}}{\delta h(r)}=+\varrho^2c(r). \tag{30}$$

If the closure relation has the form $c(r)=\psi(h(r);r)$, then this amounts to requiring

$$\frac{\delta\mathcal{A}\{h(r)\}}{\delta h(r)}=\varrho^2\psi(h(r);r), \tag{31}$$

which leads to

$$\mathcal{A}\{h(r)\}=\mathcal{A}^*+\varrho^2\int_0^1dt\int d^3r\{h(r)\psi(th(r);r)\}, \tag{32}$$

where $\mathcal{A}^*$ is constant with respect to $h(r)$. In view of Eq. (29), we can choose to set $\mathcal{C}^*=\mathcal{A}^*=0$ and keep only $\mathcal{F}^*$ without loss of generality.

We can go a step further than Olivares and McQuarrie toward free-energy functionals by requiring the charging relation to hold at equilibrium. Let us assume a closure relation of the form: $c(r)=-\beta u(r)+\psi'(h(r);r)$, where $\psi'(h(r);r)$ does not depend on $u(r)$. If one writes the functional $\mathcal{F}^\xi$ related to a system with interaction potential $\xi u(r)$, then one has

$$\begin{aligned}\mathcal{F}^\xi\{h(r)\}=\mathcal{F}^{*\xi}+\alpha^{*\xi}\bigg(&\int\frac{d^3k}{(2\pi)^3}\{\varrho h_k-\ln(1+\varrho h_k)\}\\&-\varrho^2\beta\int d^3r\{h(r)\xi u(r)\}\\&+\varrho^2\int d^3r\bigg\{h(r)\int_0^1dt\{\psi(th(r);r)\}\bigg\}\bigg).\end{aligned} \tag{33}$$

On the other hand, we can recast the charging relation for the renormalized excess free energy, Eq. (1), as

$$\frac{\partial}{\partial\xi}\left(\frac{A^\xi\{h_{\mathrm{eq}}^\xi(r);\varrho,T\}}{V}\right)=\frac{\varrho^2}{2}\int d^3r\{h_{\mathrm{eq}}^\xi(r)u(r)\}, \tag{34}$$

with the condition that $A_{\mathrm{eq}}^\xi(\varrho,T)/V=0$ if $\xi=0$. Differentiating the equilibrium value of $\mathcal{F}^\xi$ with respect to ξ, we get

$$\begin{aligned}\frac{\partial\mathcal{F}^\xi\{h_{\mathrm{eq}}^\xi(r)\}}{\partial\xi}&=\frac{\partial\mathcal{F}^\xi\{h(r)\}}{\partial\xi}\bigg|_{h_{\mathrm{eq}}^\xi(r)}\\&=-\alpha^{*\xi}\varrho^2\beta\int d^3r\{h_{\mathrm{eq}}^\xi(r)u(r)\}+\frac{\partial\mathcal{F}^{*\xi}}{\partial\xi}\\&\quad+\frac{\partial\alpha^{*\xi}}{\partial\xi}\bigg(\int\frac{d^3k}{(2\pi)^3}\{\varrho h_k-\ln(1+\varrho h_k)\}\\&\quad-\varrho^2\beta\int d^3r\{h(r)\xi u(r)\}\\&\quad+\varrho^2\int d^3r\bigg\{h(r)\int_0^1dt\{\psi(th(r);r)\}\bigg\}\bigg).\end{aligned} \tag{35, 36}$$

Thus, the choice $\alpha^{*\xi}=-1/(2\beta)$, $\mathcal{F}^{*\xi}=0$ is sufficient to fulfill Eq. (34). This choice leads to the functional of Eq. (13) in the DH case, and to Lado's functional of Eq. (8) in the HNC case. However, in view of Eq. (36), this choice is sufficient but not necessary. Finding another set of $\alpha^{*\xi}$, $\mathcal{F}^{*\xi}$ which fulfills Eq. (34) is probably possible but may be cumbersome. However, this is mostly a matter of formulation of the problem.

Let us now consider a slightly different formulation in the DH case. If one addresses the same problem of finding a functional $\mathcal{F}$ such that the DH equation is equivalent to Eq. (25), but without separating explicitly the OZ relation through the functional $\mathcal{C}$, then one can search for

$$\frac{\delta\mathcal{F}\{h(r)\}}{\delta h_k}=\gamma_k^*(h_k+\beta u_k+\varrho\beta h_ku_k), \tag{37}$$

with γ_k^* independent of h_k. This leads to

$$\mathcal{F}\{h(r)\} = \mathcal{F}^* + \int \frac{d^3k}{(2\pi)^3}\left\{\gamma_k^* h_k\left(\frac{h_k}{2} + \beta u_k + \frac{\varrho\beta}{2}h_k u_k\right)\right\}, \tag{38}$$

which corresponds to the form that we postulate in Eq. (11) of Ref. [25]. Then, requiring the charging relation to hold at equilibrium leads to our previous result, recalled in Eq. (15).

V. EXTENSION TO MULTICOMPONENT FLUIDS

In Ref. [32] the authors extend to multicomponent fluids the formalism that we use in previous section. We can then use their approach to extend our free-energy expression of Eq. (13) to multicomponent fluids. For that purpose, we define the matrices of functions:

$$\bar{\bar{f}}(r) = \begin{bmatrix} \varrho_1 f_{11}(r) & \sqrt{\varrho_1\varrho_2} f_{12}(r) & \cdots \\ \sqrt{\varrho_1\varrho_2} f_{12}(r) & \varrho_2 f_{22}(r) & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix}, \tag{39}$$

where f can be the correlation function, the interaction potential, or the direct correlation function. The indices label the various species of the multicomponent system. The multicomponent OZ relation is

$$h_{ij}(r) = c_{ij}(r) + \sum_\ell \varrho_\ell \int d^3r'\{h_{i\ell}(r')c_{\ell j}(|\mathbf{r} - \mathbf{r}'|)\}. \tag{40}$$

Using the matrices defined in Eq. (39), in the Fourier space, the OZ relation can be written as

$$\bar{\bar{c}}_k = (\mathbb{I} + \bar{\bar{h}}_k)^{-1}\bar{\bar{h}}_k. \tag{41}$$

The functional $\mathcal{C}$ such that

$$\frac{\delta\mathcal{C}\{\bar{\bar{h}}(r)\}}{\delta\bar{\bar{h}}_k} = -(\mathbb{I} + \bar{\bar{h}}_k)^{-1}\bar{\bar{h}}_k \tag{42}$$

is given in Ref. [32] as

$$\mathcal{C}\{\bar{\bar{h}}(r)\} = \int \frac{d^3k}{(2\pi)^3}\{\ln(\det(\mathbb{I} + \bar{\bar{h}}_k)) - \mathrm{Tr}(\bar{\bar{h}}_k)\}, \tag{43}$$

where we have set the constant $\mathcal{C}^*$ to zero.

The multicomponent DH closure relation is

$$c_{ij}(r) = -\beta u_{ij}(r). \tag{44}$$

The functional $\mathcal{A}$ such that

$$\frac{\delta\mathcal{A}\{\bar{\bar{h}}(r)\}}{\delta\bar{\bar{h}}_{ij}(r)} = -\beta\bar{\bar{u}}_{ij}(r) \tag{45}$$

can be written as

$$\mathcal{A}\{\bar{\bar{h}}(r)\} = -\beta\int d^3r\left\{\sum_{i,j}\bar{\bar{h}}_{ij}(r)\bar{\bar{u}}_{ij}(r)\right\}, \tag{46}$$

where we have set the constant $\mathcal{A}^*$ to zero. Again, a generating functional for the DH integral equation can be constructed as

$$\mathcal{F}\{\bar{\bar{h}}(r)\} = \mathcal{F}^* + \alpha^*(\mathcal{C}\{\bar{\bar{h}}(r)\} + \mathcal{A}\{\bar{\bar{h}}(r)\}). \tag{47}$$

In the multicomponent case, the charging relation reads

$$\frac{\partial}{\partial\xi}\left(\frac{A^\xi\{\bar{\bar{h}}^\xi_{\text{eq}}(r); T\}}{V}\right) = \frac{1}{2}\int d^3r\left\{\sum_{i,j}\bar{\bar{h}}^\xi_{\text{eq},ij}(r)\bar{\bar{u}}_{ij}(r)\right\}. \tag{48}$$

Like in the one-component case, we can choose $\alpha^{*\xi} = -1/(2\beta)$, $\mathcal{F}^{*\xi} = 0$, which is sufficient to fulfill Eq. (48). Finally, we obtain for the DH free-energy functional

$$\begin{aligned}\frac{A^{\text{DH}}\{\bar{\bar{h}}(r); T\}}{V} = {}& \frac{1}{2\beta}\int \frac{d^3k}{(2\pi)^3}\{\mathrm{Tr}(\bar{\bar{h}}_k) - \ln(\det(\mathbb{I} + \bar{\bar{h}}_k))\}\\ &+ \frac{1}{2}\int d^3r\left\{\sum_{i,j}\bar{\bar{h}}_{ij}(r)\bar{\bar{u}}_{ij}(r)\right\}.\end{aligned} \tag{49}$$

First, one can readily check that in the one-component case, Eq. (49) reduces to Eq. (13). Moreover, it was shown that the functional of Ref. [26] reduces to that of Ref. [25] in the one-component case. Therefore, it is clear that the functional of Eq. (49) is distinct from that of Ref. [26].

However, in the two-component case, one can compare the equilibrium value of the present functional to that of Ref. [26]. For a two-component fluid, the equilibrium correlation functions are given by

$$\varrho_1 h_{\text{eq},11;k} = \frac{1 + \beta\varrho_2 u_{22;k}}{D_k} - 1, \tag{50}$$

$$\varrho_2 h_{\text{eq},22;k} = \frac{1 + \beta\varrho_1 u_{11;k}}{D_k} - 1, \tag{51}$$

$$\sqrt{\varrho_1\varrho_2}\, h_{\text{eq},12;k} = -\frac{\beta\sqrt{\varrho_1\varrho_2}\, u_{12;k}}{D_k}, \tag{52}$$

with

$$D_k = 1 + \beta(\varrho_1 u_{11;k} + \varrho_2 u_{22;k}) + \beta^2\varrho_1\varrho_2\big(u_{11;k}u_{22;k} - u_{12;k}^2\big). \tag{53}$$

Substituting these into Eq. (49), one can check that the equilibrium value of the functional is

$$\begin{aligned}\frac{A^{\text{DH}}\{\bar{\bar{h}}_{\text{eq}}(r); T\}}{V} = {}& \frac{1}{2\beta}\int \frac{d^3k}{(2\pi)^3}\{\ln(D_k) - \varrho_1\beta u_{11;k}\\ &- \varrho_2\beta u_{22;k}\},\end{aligned} \tag{54}$$

which is identical to Eq. (21) of Ref. [26]. Once again, the identity, in the sense of thermodynamical functions, of both free-energy functionals, taken at equilibrium, immediately yields the identity of all thermodynamical functions.

Like in the one-component case, a notable difference between the free-energy functional of Eq. (49) and that of Ref. [26] is the fact that the present functional has the derivative

$$\frac{\delta}{\delta\bar{\bar{u}}(r)}\frac{A^{\text{DH}}}{V} = \frac{1}{2}\bar{\bar{h}}(r) \tag{55}$$

for all $\bar{\bar{h}}(r)$.

VI. DISCUSSION

In Eqs. (13) and (49), we propose two free-energy functionals that are distinct from the functionals of Refs. [25,26], respectively. The former two, however, have the same thermodynamical properties as the latter two and, indeed, are identical to them at the DH equilibrium. They only differ when one considers pair distribution functions (or, equivalently, correlation functions) that are not solutions of the DH equation.

In the present work, we are dealing with the statistical physics of a homogeneous fluid, which can be addressed, for some aspects, using the DFT of a nonhomogeneous system, and then the Percus trick. As is explained in the Appendix, only approximate integral equations for the pair distribution functions and approximate expressions of the chemical potential can be obtained from this approach. The grand potential used in this derivation does not provide us with the free energy of the homogeneous system. To derive the approximate free energy, we need to obtain it from the approximate pair distribution function. We perform such derivation using the Debye-Kirkwood charging method, which is not related to the DFT formalism. Deriving the free energy through this method, it is also possible to obtain the free energy as a generating functional of the approximate integral equation.

As we explain in Sec. IV on the DH case, several generating functionals fulfilling the charging relation at equilibrium can be obtained, through different choices of integration constants. There is no uniqueness of the generating free-energy functional in this context. The various generating free-energy functionals are meaningless when the corresponding, approximate, equilibrium integral equation is not fulfilled (see the Appendix). Somehow, this implies that variational approaches to homogeneous-fluid models proceeding by minimization with respect to the pair distribution function should be considered as practical mathematical formulations, rather than as physically-motivated ways of deriving the integral equations of these models.

Finally, let us mention that for practical approaches in which a classical-fluid free-energy functional is used, choosing a functional that fulfills Eq. (24) for all $h(r)$ [or Eq. (55) for all $\bar{\bar{h}}(r)$] can have a strong practical interest. For instance, the free-energy functional of Eq. (49) was used in Ref. [16] to construct a variational theory of electron-ion plasmas. In this theory, the classical-fluid free energy is added to a contribution stemming from the quantum shell-structure of the ions. The shell-structure is accounted for in the classical-fluid part through self-consistent pair interaction potentials, that have to be determined from the minimization of the total free energy. In such a context, choosing a free-energy functional fulfilling Eq. (55) for all $\bar{\bar{h}}(r)$ allows one to greatly simplify the variational calculation. Constructing the same kind of model with the free-energy functional of Ref. [26] would have yield a much more complicated derivation, leading eventually to the same result for the equilibrium model equations.

VII. CONCLUSION

In the present article, we supplement the results of our previous publications [25,26] by proposing alternative Debye-Hückel free-energy functionals in both the cases of one-component and multicomponent fluids. While resulting in the same thermodynamical relations, these functionals differ for pair distribution functions which do not fulfill the Debye-Hückel equation. We discuss how these functionals can be obtained following the approach of Lado [22] as well as that of Olivares and McQuarrie [32]. We also show that the nonuniqueness issue, which is raised by these results, may be explained through a choice of constants that appear in the method of Olivares and McQuarrie. Finally, we comment briefly on this nonuniqueness issue in the context of the statistical physics of homogeneous fluids.

APPENDIX: DENSITY FUNCTIONAL THEORY AND APPROXIMATE MODELS OF HOMOGENEOUS FLUIDS

We recall here briefly how the classical DFT can be used to derive the integral equations of the HNC, nonlinear DH, and DH approximate models. We also explain how such derivations allow us to calculate the excess chemical potential of the system, but neither the free energy nor the grand potential.

In the density functional theory, the grand potential for a system of particles in an external potential $v_{\text{ext}}(\mathbf{r})$ is viewed as a unique functional of the particle density $n(\mathbf{r})$. We denote this grand-potential functional as $\Omega\{n(\mathbf{r}), v_{\text{ext}}(\mathbf{r}); \mu, T\}$. It is written as

$$\Omega\{n(\mathbf{r}), v_{\text{ext}}(\mathbf{r}); \mu, T\} = F_{\text{id}}\{n(\mathbf{r}); T\} + F_{\text{ex}}\{n(\mathbf{r}); T\} + \int d^3r\{n(\mathbf{r})(v_{\text{ext}}(\mathbf{r}) - \mu)\}, \quad \text{(A1)}$$

where F_{id} is the ideal-gas part of the intrinsic free energy, F_{ex} is the excess free energy, and μ is the chemical potential. The ideal-gas part of the intrinsic free energy is written as

$$F_{\text{id}}\{n(\mathbf{r}); T\} = \frac{1}{\beta}\int d^3r\{n(\mathbf{r})[\ln(n(\mathbf{r})\Lambda^3) - 1]\}, \quad \text{(A2)}$$

where $\Lambda = h/\sqrt{2\pi m k_B T}$ is the classical thermal length.

So as to apply the Percus trick afterwards, we first approximate the excess free energy using a second-order expansion around a homogeneous reference system, of density n_0. $n(\mathbf{r})$ tends to n_0 far from the origin:

$$F_{\text{ex}}\{n(\mathbf{r}); T\} = F_{\text{ex}}\{n_0; T\} + \int d^3r\left\{[n(\mathbf{r}) - n_0]\left.\frac{\delta F_{\text{ex}}}{\delta n(\mathbf{r})}\right|_{n_0}\right\} + \frac{1}{2}\int d^3r d^3r'\left\{[n(\mathbf{r}) - n_0][n(\mathbf{r}') - n_0] \times \left.\frac{\delta^2 F_{\text{ex}}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n_0}\right\}. \quad \text{(A3)}$$

For the total intrinsic free energy F, we have the relation

$$\frac{\delta F}{\delta n(\mathbf{r})} = \frac{\delta}{\delta n(\mathbf{r})}(F_{\text{id}} + F_{\text{ex}}) = \mu - v\{n(\mathbf{r}'); \mathbf{r}\}, \quad \text{(A4)}$$

where $v\{n(\mathbf{r}'); \mathbf{r}\}$ is the external potential such that $n(\mathbf{r}')$ is the equilibrium density. In the case of the homogeneous system of density n_0, we then have

$$\left.\frac{\delta F_{\text{ex}}}{\delta n(\mathbf{r})}\right|_{n_0} = \mu_0 - \frac{1}{\beta}\ln(n_0\Lambda^3), \quad \text{(A5)}$$

μ_0 being the chemical potential of the homogeneous system.

1. HNC model

We define the second-order direct correlation function of the homogeneous system, $c(|\mathbf{r}-\mathbf{r}'|)$, as

$$c(|\mathbf{r}-\mathbf{r}'|) = -\left.\frac{\delta^2\beta F_{\rm ex}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n_0}. \tag{A6}$$

This function fulfills the OZ equation, which relates it to the exact correlation function $h(r)$ (see, for instance, Refs. [28,29]). Here, we will consider the OZ relation as a definition for $c(r)$, holding also with the approximate $h(r)$, as in Eq. (3).

Minimizing Ω with respect to $n(\mathbf{r})$, for a given external potential, we get

$$\ln\left(\frac{n(\mathbf{r})}{n_0}\right) = \beta[\mu-\mu_0-v_{\rm ext}(\mathbf{r})] + n_0\int d^3r'\left\{\left[\frac{n(\mathbf{r}')}{n_0}-1\right]c(|\mathbf{r}-\mathbf{r}'|)\right\}. \tag{A7}$$

One immediately sees that, if $n(\mathbf{r})$ tends to n_0 far from the origin, then we have $\mu=\mu_0$.

Finally, we use the Percus trick, that is we consider the density $n(\mathbf{r})$ around a particle of the homogeneous fluid fixed at the origin. This density is directly related to the pair distribution function of the homogeneous fluid [28]:

$$v_{\rm ext}(\mathbf{r}) \equiv u(r)\,;\ \frac{n(\mathbf{r})}{n_0} = g(r)\,;\ n_0 \equiv \varrho, \tag{A8}$$

where $u(r)$ is the pair interaction potential, and $g(r)=h(r)+1$ is the pair distribution function. We denote by ϱ the particle density of the homogeneous fluid. We get

$$\ln\left(g(r)\right) = -\beta u(r) + \varrho\int d^3r'\{h(r')c(|\mathbf{r}-\mathbf{r}'|)\}, \tag{A9}$$

and, using the OZ relation, we obtain

$$\ln\left(g(r)\right) = -\beta u(r) + h(r) - c(r), \tag{A10}$$

which is the HNC closure. Such a derivation is, for example, given in Refs. [29,35].

Of course, one can formally write the grand potential from Eq. (A1). However, this expression includes the reference excess free energy $F_{\rm ex}\{n_0;T\}$, which is not known *a priori*. One thus needs to relate $F_{\rm ex}\{n_0;T\}$ to the pair distribution function in some way. This is the purpose of paragraph 4 of Ref. [21] and, somehow, of Ref. [22]. The charging relation of Eq. (1), used in these papers, is one of the routes to construct the free energy from the pair distribution function. This relation is rigorously obtained in the case of the exact free energy and pair distribution function. However, as soon as one uses this relation with an approximate pair distribution function, one should check the thermodynamical consistency of the obtained approximate free energy.

Even if the above, DFT-based approach does not give in itself the grand potential of the system, one can nonetheless evaluate its increment, which corresponds to the excess chemical potential (see, for instance, Ref. [29]):

$$\mu_{\rm ex} = \frac{\varrho}{\beta}\int d^3r\left\{\frac{1}{2}h(r)[h(r)-c(r)]-c(r)\right\}. \tag{A11}$$

The renormalized excess chemical potential is

$$\mu_{\rm ex}^{\rm renorm} = \mu_{\rm ex} - \varrho\int d^3r\{u(r)\} \tag{A12}$$

$$= \frac{\varrho}{\beta}\int d^3r\left\{\frac{1}{2}h(r)[h(r)-c(r)]-c(r)-\beta u(r)\right\}. \tag{A13}$$

It can be checked that this expression can be recovered from Lado's free-energy functional recalled in Eq. (8), by calculating

$$\mu_{\rm ex}^{\rm renorm} = \left.\frac{\partial}{\partial\varrho}\left(\frac{A^{\rm HNC}}{V}\right)\right|_{\rm eq}, \tag{A14}$$

with $|_{\rm eq}$ denoting the HNC equilibrium.

2. Nonlinear DH model

In the nonlinear DH model, like in the HNC model, we use the exact expression for the ideal-gas part of the intrinsic free energy $F_{\rm id}$. However, we treat the excess-free-energy term in the mean-field approximation. In the mean-field approximation, each particle of the homogeneous fluid interacts with the nonhomogeneous average density of the other particles. This amounts to write

$$F_{\rm ex}\{n(\mathbf{r});T\} = F_{\rm ex}\{n_0;T\} + \int d^3r\left\{[n(\mathbf{r})-n_0]\left.\frac{\delta F_{\rm ex}}{\delta n(\mathbf{r})}\right|_{n_0}\right\} + \frac{1}{2}\int d^3r d^3r'\{[n(\mathbf{r})-n_0][n(\mathbf{r}')-n_0] \times u(|\mathbf{r}-\mathbf{r}'|)\}. \tag{A15}$$

First, it is worth noting that, in the mean-field approximation, the $F_{\rm ex}\{n_0;T\}$ term still includes a correlation part, that is, from the homogeneous-fluid point of view, it accounts for two-body correlations in the interactions. For that reason, the problem is of the exact same kind as in the HNC case: We need to obtain the free energy starting from the approximate pair distribution function. At present, we do not know of such a derivation for the nonlinear DH model of homogeneous fluid with arbitrary interaction potential.

It is also worth noting that the mean-field approximation does not require the definition of a direct correlation function through the OZ relation.

As in the HNC case, even if we cannot directly obtain the free energy or the grand potential, we can obtain the integral equation for the pair distribution function from the minimization of Ω and the Percus trick. Minimization of Ω yields

$$\ln\left(\frac{n(\mathbf{r})}{n_0}\right) = \beta(\mu-\mu_0-v_{\rm ext}(\mathbf{r})) - \beta n_0\int d^3r'\left\{\left(\frac{n(\mathbf{r}')}{n_0}-1\right)u(|\mathbf{r}-\mathbf{r}'|)\right\}. \tag{A16}$$

Using the Percus trick, Eq. (A8), we get

$$\ln(g(r)) = -\beta u(r) - \varrho\beta\int d^3r'\{h(r')u(|\mathbf{r}-\mathbf{r}'|)\}, \quad (A17)$$

which is the nonlinear DH integral equation.

We can also obtain the excess chemical potential:

$$\mu_{\mathrm{ex}} = \frac{\varrho}{\beta}\int d^3r\left\{\frac{1}{2}h(r)[\ln(g(r)) + \beta u(r)] - h(r) + \ln(g(r)) + \beta u(r)\right\}. \quad (A18)$$

3. DH model

In the linear DH model, while keeping the mean-field approximation of Eq. (A15) for the excess free energy, we limit ourselves to a second-order expansion of the ideal-gas part of the intrinsic free energy F_{id}:

$$F_{\mathrm{id}}\{n(\mathbf{r});T\} = F_{\mathrm{id}}\{n_0;T\} + \int d^3r\left\{[n(\mathbf{r}) - n_0]\frac{1}{\beta}\ln(n_0\Lambda^3)\right\} + \frac{1}{2}\int d^3r d^3r'\left\{[n(\mathbf{r}) - n_0][n(\mathbf{r}') - n_0] \times \frac{\delta_3(\mathbf{r}-\mathbf{r}')}{\beta n_0}\right\}. \quad (A19)$$

Here, minimization of Ω yields

$$\frac{n(\mathbf{r})}{n_0} - 1 = \beta(\mu - \mu_0 - v_{\mathrm{ext}}(\mathbf{r})) - \beta n_0\int d^3r'\left\{\left(\frac{n(\mathbf{r}')}{n_0} - 1\right)u(|\mathbf{r}-\mathbf{r}'|)\right\}. \quad (A20)$$

Again, using the Percus trick, Eq. (A8), we get

$$h(r) = -\beta u(r) - \varrho\beta\int d^3r'\{h(r')u(|\mathbf{r}-\mathbf{r}'|)\}, \quad (A21)$$

which is the DH integral equation, Eq. (9).

In the latter case, it is the purpose of Refs. [25,26] and of the present paper to obtain a free-energy expression from the DH integral equation, through the Debye-Kirkwood charging method. However, one can note that, in the particular case of the Coulomb interaction, paragraph 78 of Ref. [36] describes another route, which consists in integrating over the inverse temperature β rather than over a charging parameter. These two methods can be shown to be equivalent in the case of an exact system. It is also shown in Ref. [25] that they lead to identical thermodynamics in the DH case.

Finally, we can write the excess chemical potential:

$$\mu_{\mathrm{ex}} = \varrho\int d^3r\{u(r)\} + \frac{\varrho}{2}\int d^3r\{h(r)u(r)\}, \quad (A22)$$

$$\mu_{\mathrm{ex}}^{\mathrm{renorm}} = \frac{\varrho}{2}\int d^3r\{h(r)u(r)\}. \quad (A23)$$

The latter equation is easily recovered from our functional of Eq. (13), in the same way as described in Eq. (A14).

4. Link with the nonuniqueness issue

The DFT derivation of the approximate integral equations can be summarized as follows. We write the grand potential for the nonhomogeneous fluid corresponding to the Percus situation:

$$\Omega\{n_0g(r), u(r); \mu, T\} = F\{n_0;T\} + \Delta F\{n_0g(r), n_0;T\} + \int d^3r\{n_0g(r)[u(r) - \mu]\}, \quad (A24)$$

with a suitable approximation of the ΔF term. Here, Ω is a unique functional of $g(r)$. The approximate integral equation is obtained through

$$g(r) = \underset{g(r)}{\mathrm{Argmin}}\,\Omega\{n_0g(r), u(r); \mu, T\}, \quad (A25)$$

that is

$$\frac{\delta\Omega\{n_0g(r), u(r); \mu, T\}}{\delta g(r)} = 0. \quad (A26)$$

This does not give access to $F\{n_0;T\}$, which is seen here as constant with respect to $g(r)$. Calculating $F\{n_0;T\}$ from the approximate $g(r)$ is the purpose of using the Debye-Kirkwood charging method, and we choose to formulate it such that

$$F\{n_0;T\} = \underset{g(r)}{\mathrm{Min}}\,F'\{n_0, g(r);T\}, \quad (A27)$$

with $F'\{n_0, g(r);T\}$ being minimal for that $g(r)$ which fulfills the approximate integral equation. The approximate integral equation is then given by

$$g(r) = \underset{g(r)}{\mathrm{Argmin}}\,F'\{n_0, g(r);T\}. \quad (A28)$$

Despite the formal similarity with Eq. (A25), this is a different minimization and there is no reason for which F' should be a unique functional of $g(r)$. Indeed, we show in the case of the DH model that it is not.

---

[1] D. A. Liberman, Self-consistent field model for condensed matter, Phys. Rev. B **20**, 4981 (1979).

[2] T. Blenski and B. Cichocki, Variational theory of average-atom and superconfigurations in quantum plasmas, Phys. Rev. E **75**, 056402 (2007).

[3] T. Blenski and B. Cichocki, Variational approach to the average-atom-in-jellium and superconfigurations-in-jellium models with all electrons treated quantum-mechanically, High Energy Density Phys. **3**, 34 (2007).

[4] R. Piron and T. Blenski, Variational-average-atom-in-quantum-plasmas (code and virial theorem: Equation-of-state and shock-Hugoniot calculations for warm dense Al, Fe, Cu, and Pb, Phys. Rev. E **83**, 026403 (2011).

[5] R. Piron and T. Blenski, Variational average-atom in quantum plasmas—Recent progress, virial theorem and applications to the equation-of-state of warm dense Be, High Energy Density Phys. **7**, 346 (2011).

[6] T. Blenski, R. Piron, C. Caizergues, and B. Cichocki, Models of atoms in plasmas based on common formalism for bound and free electrons, High Energy Density Phys. **9**, 687 (2013).

[7] M. W. C. Dharma-wardana and F. Perrot, Density-functional theory of hydrogen plasmas, Phys. Rev. A **26**, 2096 (1982).

[8] F. Perrot and M. W. C. Dharma-wardana, Hydrogen plasmas beyond density-functional theory: Dynamic correlations and the onset of localization, Phys. Rev. A **29**, 1378 (1984).

[9] F. Perrot, Dense simple plasmas as high-temperature liquid simple metals, Phys. Rev. A **42**, 4871 (1990).

[10] F. Perrot, Ion-ion interaction and equation of state of a dense plasma: Application to beryllium, Phys. Rev. E **47**, 570 (1993).

[11] F. Perrot and M. W. C. Dharma-wardana, Equation of state and transport properties of an interacting multispecies plasma: Application to a multiply ionized al plasma, Phys. Rev. E **52**, 5352 (1995).

[12] Dror Ofer, E. Nardi, and Y. Rosenfeld, Interionic correlations in plasmas: Thomas-Fermi hypernetted-chain density-functional theory, Phys. Rev. A **38**, 5801 (1988).

[13] C. E. Starrett and D. Saumon, Fully variational average atom model with ion-ion correlations, Phys. Rev. E **85**, 026403 (2012).

[14] C. E. Starrett and D. Saumon, A variational average atom approach to closing the quantum Ornstein–Zernike relations, High Energy Density Phys. **8**, 101 (2012).

[15] J. Chihara, Average atom model based on quantum hyper-netted chain method, High Energy Density Phys. **19**, 38 (2016).

[16] R. Piron and T. Blenski, Variational average-atom model of electron-ion plasma with correlations and quantum bound electrons, arXiv:1904.13289.

[17] A. Alastuey, Propriétés d'équilibre du plasma classique à une composante en trois et deux dimensions, Ann. Phys. Fr. **11**, 653 (1986).

[18] Y. Rosenfeld, Comments on the mean spherical approximation for hard-core and soft potentials and an application to the one-component plasma, J. Stat. Phys. **37**, 215 (1984).

[19] G. Pastore, O. Akinlade, F. Matthews, and Z. Badirkhan, Optimized random-phase approximations for arbitrary reference systems: Extremum conditions and thermodynamic consistence, Phys. Rev. E **57**, 460 (1998).

[20] R. Fantoni and G. Pastore, Generating functionals, consistency, and uniqueness in the integral equation theory of liquids, J. Chem. Phys. **119**, 3810 (2003).

[21] T. Morita and K. Hiroike, A new approach to the theory of classical fluids, Prog. Theor. Phys. **23**, 1003 (1960).

[22] F. Lado, Perturbation correction for the free energy and structure of simple fluids, Phys. Rev. A **8**, 2548 (1973).

[23] F. Lado, Perturbation correction for the free energy and structure of simple fluid mixtures, J. Chem. Phys. **59**, 4830 (1973).

[24] P. Debye and E. Hückel, Zur Theorie des Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen, Z. Phys. **24**, 185 (1923).

[25] R. Piron and T. Blenski, Free-energy functional of the Debye-Hückel model of simple fluids, Phys. Rev. E **94**, 062128 (2016).

[26] T. Blenski and R. Piron, Free-energy functional of the Debye-Hückel model of two-component plasmas, High Energy Density Phys. **24**, 28 (2017).

[27] A. Santos, R. Fantoni, and A. Giacometti, Thermodynamic consistency of energy and virial routes: An exact proof within the linearized Debye-Hückel theory, J. Chem. Phys. **131**, 181105 (2009).

[28] J. K. Percus, Classical fluids, in *The Equilibrium Theory of Classical Fluids* (Wiley, New York, 1964), pp. II-33–II-170.

[29] J.-P. Hansen and I. R. MacDonald, *Theory of Simple Liquids* (Academic Press, London, 2006).

[30] J. G. Kirkwood, Statistical mechanics of fluid mixtures, J. Chem. Phys. **3**, 300 (1935).

[31] H. E. DeWitt and F. J. Rogers, Helmholtz free energy of electron screened plasmas in the hypernetted-chain approximation, Phys. Lett. A **132**, 273 (1988).

[32] W. Olivares and D. A. McQuarrie, A variational approach to the theory of ionic solutions, J. Chem. Phys. **65**, 3604 (1976).

[33] For the sake of consistency with our previous publications [25,26], and unlike Lado [22], we will work with the renormalized excess free energy per unit volume.

[34] In the latter case, one views any thermodynamic function as a functional of $u(r)$. However, for the sake of conciseness, we did not write explicitly the $u(r)$ dependency of the thermodynamic functions. Any time it is useful we mention in the text whether a function depends or not on $u(r)$.

[35] A. Ayadim, M. Oettel, and S. Amokrane, Optimum free energy in the reference functional approach for the integral equations theory, J. Phys.: Condens. Matter **21**, 115103 (2009).

[36] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, UK, 1959).