Free-energy functional of the Debye-Hückel model of simple 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

The Debye-Hückel approximation to the free energy of a simple fluid is written as a functional of the pair correlation function. This functional can be seen as the Debye-Hückel equivalent to the functional derived in the hypernetted chain framework by Morita and Hiroike, as well as by Lado. It allows one to obtain the Debye-Hückel integral equation through a minimization with respect to the pair correlation function, leads to the correct form of the internal energy, and fulfills the virial theorem.

I. INTRODUCTION

The Debye-Hückel (DH) model originated in the physics of electrolytes [1], that is, fluids of charged particles interacting through a Coulomb potential. It is the linearized version of the classical Hartree-like mean-field model, which is often called the nonlinear Debye-Hückel (NLDH) model or Poisson-Boltzmann model in the context of electrolytes. These two models can be extended to arbitrary interaction potentials, leading respectively to the DH and NLDH models of classical fluids, with the corresponding integral equations.

Although it is based on very strong assumptions, the DH model gives physical insight into the screening of interaction potentials and the decay of correlation functions, both in the framework of simple and multicomponent fluids. The DH model is valid in the low-coupling limit, that is, in the limit of small interactions compared to the kinetic energy of the particles. More sophisticated models of classical fluids exist, as for instance the hypernetted chain (HNC) [2] or Percus-Yevick [3] models, which account for part of the correlations. However, some theoretical studies also proceed by introducing corrections, using the low-coupling DH limit as a starting point (see Refs. [4,5]). It was also recently shown that in the DH model, the energy and virial routes are thermodynamically consistent for any potential [6]. For these reasons, the DH model is of permanent theoretical interest.

Moreover, in a number of applications, modified versions of the DH model are used, as for example in the physics of electrolytes [7,8] or in plasma physics [9,10]. The DH model therefore also has some practical interest.

In the case of a long-range attractive potential, the linearization performed in the DH model allows one to circumvent the classical catastrophe of collapsing particles. To some extent, this explains why this model is so common in plasma physics as well as in the physics of electrolytes.

Apart from the historical derivation as a linearized mean-field theory of a charged-particle mixture [1], the DH model of simple fluids can be obtained from the so-called Percus trick [11] or from a diagrammatic analysis [4,5,12].

In the research on variational models of atoms in plasmas, there is a serious need to account for ion and electron correlations and their impact on the atomic structure and dynamics [13–24]. In this framework, it is also useful to have a variational derivation of simple fluid models, using expressions of the free energy as a functional of the ion-ion pair correlation function. Such a variational expression can be used in a more general theory that also includes the ion electronic structure.

A free-energy functional is available in the HNC theory [25,26]. However, in the well-known DH theory, an expression of the free energy as a functional of the pair correlation function has not been yet proposed. The purpose of this paper is to present a brief derivation of such an expression, which can be seen as the DH equivalent to the HNC free-energy functional of Morita and Hiroike [25], also derived by Lado [26].

II. DEBYE-HÜCKEL INTEGRAL EQUATION

The DH integral equation for a homogeneous simple fluid with the given pair potential $u(r)$ writes (see, for example, Ref. [11], Eq. 6.5):

$$h(r) = -\beta u(r) - \varrho\beta \int d^3r' \{h(r')u(|\mathbf{r} - \mathbf{r}'|)\}, \quad (1)$$

where ϱ is the particle density of the fluid, β the inverse temperature, and $h(r) = g(r) - 1$, $g(r)$ being the usual pair distribution function.

For some particular pair potentials such as the bare Coulomb $(1/r)$ or Yukawa $(e^{-\alpha r}/r)$ potentials, this equation can be recast as a differential equation (Poisson equation in the Coulomb case, Helmholtz equation in the Yukawa case). In a diagrammatic analysis, Eq. (1) corresponds to the sum of all u-bond chain diagrams. Equation (1) can also be seen as a Ornstein-Zernicke relation with the simplest closure $c(r) = -\beta u(r)$, where $c(r)$ is the direct correlation function.

The Fourier transform $\mathcal{F}_\mathbf{k}$ of a function $\mathcal{F}(\mathbf{r})$ is defined as:

$$\mathcal{F}_\mathbf{k} = \int d^3r \{\mathcal{F}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}\}. \quad (2)$$

For a potential that has a Fourier transform, Eq. (1) can be rewritten in the Fourier space as the algebraic relation:

$$h_k = -\beta u_k - \varrho\beta h_k u_k, \quad (3)$$

*Corresponding author: robin.piron@cea.fr

which has the direct formal solution:

$$h_{\mathrm{eq},k} = -\beta u_{s,k}; \quad u_{s,k} \equiv \frac{u_k}{1 + \varrho\beta u_k}. \quad (4)$$

Here, $h_{\mathrm{eq},k}$ denotes the DH equilibrium correlation function and $u_{s,k}$ denotes the screened potential, both in the Fourier space.

For any long-range potential (i.e., Coulombic at infinity), $\lim_{k\to 0} u_k \sim k^{-2}$, which implies $u_{k=0} = -\varrho^{-1}$. This is the case in any model that can be written as an Ornstein-Zernicke equation with a direct correlation function that includes the interaction potential.

In the following, the pair potential $u(r)$ will be replaced by $u^\xi(r) \equiv \xi u(r)$, ξ being a charge parameter, and the corresponding ξ indices will label h_{eq}^ξ, u^ξ, and u_s^ξ.

III. EXPRESSION OF THE FREE-ENERGY FUNCTIONAL

We consider a system that is immersed in a rigid, homogeneous, neutralizing background. Such a background does not impact on the equations of motion or on the DH integral equation. It, however, leads to renormalized energies by accounting for the contribution:

$$\frac{E_{bg}}{V} = -\frac{\varrho^2}{2} \int d^3r \{u^\xi(r)\}, \quad (5)$$

which cancels the divergences of energies in case of a long-range potential. In case of a short-range potential, one can disregard any background by removing this contribution. In the following, we will address the configurational part of the renormalized free energy and give its expression as a functional of the pair correlation function.

In the particular case of the bare Coulomb potential: $u^\xi(r) \equiv \xi/r$, it is easy to check that if one minimizes with respect to $h(r)$ the following functional $A^\xi\{\varrho,\beta,h(r)\}$:

$$\frac{A^\xi}{V} = \frac{2\varrho^2}{3\beta} \int d^3r \left\{ h(r) \left(\frac{h(r)}{2} + \frac{\beta\xi}{r} \right. \right.$$
$$\left. \left. + \frac{\varrho\beta\xi}{2} \int d^3r' \left\{ \frac{h(r')}{|\mathbf{r} - \mathbf{r}'|} \right\} \right) \right\} \quad (6)$$

one gets Eq. (1). This functional also yields all the well-known equilibrium results for the renormalized configurational internal energy U_{eq}^ξ, free energy A_{eq}^ξ, and pressure P_{eq}^ξ (see, for example, Ref. [27], Sec. 78), namely:

$$\frac{U_{\mathrm{eq}}^\xi}{V} = \frac{\partial}{\partial\beta}\left(\frac{\beta A_{\mathrm{eq}}^\xi}{V}\right) = \frac{\partial}{\partial\beta}\left(\frac{\beta A^\xi}{V}\right)\bigg|_{\mathrm{eq}} = -\frac{\xi\varrho}{2}\sqrt{4\pi\varrho\beta\xi} \quad (7)$$

$$\frac{A_{\mathrm{eq}}^\xi}{V} = \frac{2}{3}\frac{U_{\mathrm{eq}}^\xi}{V} \quad (8)$$

$$P_{\mathrm{eq}}^\xi = \varrho^2\frac{\partial}{\partial\varrho}\left(\frac{A_{\mathrm{eq}}^\xi}{\varrho V}\right) = \varrho^2\frac{\partial}{\partial\varrho}\left(\frac{A^\xi}{\varrho V}\right)\bigg|_{\mathrm{eq}} = \frac{1}{3}\frac{U_{\mathrm{eq}}^\xi}{V}, \quad (9)$$

where $|_{\mathrm{eq}}$ means that the functional is taken at the DH equilibrium, that is, for $h(r) = h_{\mathrm{eq}}^\xi(r)$ from Eq. (4). We stress that Eqs. (7), (8), (9) hold for a one-component classical plasma (OCP) with the contribution of the neutralizing background included.

A slightly different functional can be guessed as well in the Yukawa-OCP case: $u^\xi(r) = \xi \exp(-\alpha r)/r$.

The present derivation aims at giving a general form of the free-energy functional for a simple fluid with any pair potential $u(r)$. As in Ref. [26], we use Debye's charging method and build an expression of the renormalized configurational free-energy functional $A^\xi\{\varrho,\beta,u(r),h(r)\}$ from the equilibrium relation:

$$\frac{A_{\mathrm{eq}}^\xi\{\varrho,\beta,u(r)\}}{V} = \frac{\varrho^2}{2}\int_0^\xi\frac{d\xi'}{\xi'}\int d^3r\{h_{\mathrm{eq}}^{\xi'}(r)u^{\xi'}(r)\}. \quad (10)$$

In the case of the exact equilibrium, Eq. (10) is an exact relation. We consider the case of $|_{\mathrm{eq}}$ denoting the DH equilibrium, with $h(r) = h_{\mathrm{eq}}^\xi(r)$ from Eq. (4), and require Eq. (10) to hold.

Let us assume that the free-energy functional $A^\xi\{\varrho,\beta,u(r),h(r)\}$ can be written in the form that follows:

$$\frac{A^\xi}{V} = \int \frac{d^3k}{(2\pi)^3}\left\{ f_k^\xi h_k \left(\frac{h_k}{2} + \beta u_k^\xi + \frac{\varrho\beta}{2}h_k u_k^\xi \right) \right\}, \quad (11)$$

where $f_k^\xi \equiv f(\varrho,\beta,k,\xi,u_k)$ is independent of h_k. Minimization of A^ξ with respect to $h(r)$ then lead to Eq. (3), i.e., to the DH equation.

Differentiating with respect to ξ, we obtain:

$$\frac{\xi}{V}\frac{\partial A_{\mathrm{eq}}^\xi}{\partial\xi} = \frac{\xi}{V}\frac{\partial A^\xi}{\partial\xi}\bigg|_{\mathrm{eq}} \quad (12)$$

$$= \int \frac{d^3k}{(2\pi)^3}\left\{ \xi\frac{\partial f_k^\xi}{\partial\xi}h_k\left(\frac{h_k}{2} + \beta u_k^\xi + \frac{\varrho\beta}{2}h_k u_k^\xi\right) \right.$$
$$\left. + f_k^\xi h_k\left(\beta\xi\frac{\partial u_k^\xi}{\partial\xi} + \frac{\varrho\beta}{2}h_k\xi\frac{\partial u_k^\xi}{\partial\xi}\right) \right\}\bigg|_{\mathrm{eq}}. \quad (13)$$

Using $u_k^\xi = \xi u_k$, and substituting the formal equilibrium solution of Eq. (4), we get:

$$\frac{\xi}{V}\frac{\partial A_{\mathrm{eq}}^\xi}{\partial\xi} = \frac{-\beta^2}{2}\int\frac{d^3k}{(2\pi)^3}\left\{ \frac{\partial}{\partial\xi}\left(\xi f_k^\xi\right)u_{s,k}^\xi u_k^\xi + f_k^\xi u_{s,k}^{\xi\,2} \right\}. \quad (14)$$

On the other hand, from Eqs. (10) and (4) we can write:

$$\frac{\xi}{V}\frac{\partial A_{\mathrm{eq}}^\xi}{\partial\xi} = \frac{-\beta\varrho^2}{2}\int\frac{d^3k}{(2\pi)^3}\{u_{s,k}^\xi u_k^\xi\}. \quad (15)$$

A sufficient condition to fulfill Eq. (10) [or equivalently Eq. (15)], is the equation:

$$\frac{\partial}{\partial\xi}\left(\xi f_k^\xi\right) + \frac{\xi f_k^\xi}{\xi + \varrho\beta u_k\xi^2} = \frac{\varrho^2}{\beta}. \quad (16)$$

This equation can also be obtained starting from an exact relation other than Eq. (10) (see Appendix A). This relation involves the functional derivative of the free energy with respect to u_k^ξ, instead of an integral over a charging parameter.

A solution to the differential Eq. (16) for ξf_k^ξ can be obtained, for instance, by the standard method of solving the homogeneous version of the equation and then applying the method of variation of the constant. It can also be searched in the form of a series. This leads to the following expression

for f_k^ξ:

$$f_k^\xi = \frac{\varrho^2}{\beta} F(\varrho\beta u_k^\xi), \tag{17}$$

where the function F is defined as:

$$F(x) = \left(1 + \frac{1}{x}\right)\left(1 - \frac{\ln(1+x)}{x}\right). \tag{18}$$

As can be seen in Eq. (17), the only dependence of f_k^ξ on k and ξ is via the potential u_k^ξ.

Finally, the DH free-energy functional reads:

$$\frac{A^\xi}{V} = \frac{\varrho^2}{\beta} \int \frac{d^3k}{(2\pi)^3} \left\{ \left(1 + \frac{1}{\varrho\beta u_k^\xi}\right)\left(1 - \frac{\ln\left(1 + \varrho\beta u_k^\xi\right)}{\varrho\beta u_k^\xi}\right) \right.$$
$$\left. \times h_k \left(\frac{h_k}{2} + \beta u_k^\xi + \frac{\varrho\beta}{2} h_k u_k^\xi\right) \right\}, \tag{19}$$

which is the main result of the present paper.

It is worth noting that Eq. (19), taken for the bare Coulomb potential does not lead to the functional of Eq. (6). A comment on that point is given in Appendix B.

IV. INTERNAL ENERGY, PRESSURE, AND VIRIAL THEOREM

We first consider the renormalized configurational internal energy, as defined by the thermodynamics:

$$\frac{U_{eq}^\xi}{V} = \frac{\partial}{\partial\beta}\left(\frac{\beta A_{eq}^\xi}{V}\right) = \frac{\partial}{\partial\beta}\left(\frac{\beta A^\xi}{V}\right)\bigg|_{eq}. \tag{20}$$

As can be seen in Eq. (19), $\beta A^\xi / V$ is a functional of $h(r)$, ϱ, and of the product $\beta\xi u(r)$. As a consequence, we can write:

$$\frac{\partial}{\partial\beta}\left(\frac{\beta A^\xi}{V}\right) = \xi \frac{\partial}{\partial\xi}\left(\frac{A^\xi}{V}\right). \tag{21}$$

We then have, in virtue of Eq. (10):

$$\frac{U_{eq}^\xi}{V} = \xi \frac{\partial}{\partial\xi}\left(\frac{A^\xi}{V}\right)\bigg|_{eq} = \frac{\varrho^2}{2} \int d^3r \{h_{eq}^\xi(r) u^\xi(r)\}, \tag{22}$$

which corresponds to the exact expression of the internal energy, with $h_{eq}^\xi(r)$ taken to be the DH approximation to the equilibrium correlation function.

The result Eq. (22) can also be obtained in a more pedestrian way, by making the explicit differentiation of the free-energy expression Eq. (19) and then substituting $h_{eq,k}^\xi$. We do not reproduce this calculation here.

The virial configurational pressure as a functional of $\varrho, u(r), h(r)$ is:

$$P_v^\xi = -\frac{1}{3}\frac{\varrho^2}{2} \int d^3r \{h(r)\mathbf{r} \cdot \boldsymbol{\nabla_r} u^\xi(r)\}. \tag{23}$$

For a potential that decays as $1/r$ or faster, using the Fourier representation and integrating by part, we can write from Eq. (23):

$$P_v^\xi = \int d^3r \{h(r)u^\xi(r)\} + \frac{1}{3}\frac{\varrho^2}{2} \int \frac{d^3k}{(2\pi)^3}\{h_k \mathbf{k} \cdot \boldsymbol{\nabla_k} u_k^\xi\}. \tag{24}$$

Using Eq. (4), the equilibrium virial pressure becomes:

$$P_{v,eq}^\xi = \frac{U_{eq}^\xi}{V} - \frac{\varrho^2}{2} \int_0^\infty \frac{dk}{(2\pi)^3}\left\{\frac{4\pi}{3}k^3 \frac{\beta u_k^\xi}{1 + \varrho\beta u_k^\xi}\frac{\partial u_k^\xi}{\partial k}\right\}. \tag{25}$$

Finally, we obtain:

$$P_{v,eq}^\xi = \frac{U_{eq}^\xi}{V} + \frac{1}{2\beta}\int \frac{d^3k}{(2\pi)^3}\{\varrho\beta u_k^\xi - \ln\left(1 + \varrho\beta u_k^\xi\right)\}. \tag{26}$$

Then, differentiating with respect to ξ, we get:

$$\xi \frac{\partial P_{v,eq}^\xi}{\partial\xi} = \frac{-\varrho^2\beta}{2}\int \frac{d^3k}{(2\pi)^3}\{(u_{s,k}^\xi)^2\}. \tag{27}$$

We now consider the equilibrium pressure, as it is defined by the thermodynamics:

$$P_{eq}^\xi = \varrho^2 \frac{\partial}{\partial\varrho}\left(\frac{A_{eq}^\xi}{\varrho V}\right). \tag{28}$$

Using Eq. (10), we obtain:

$$P_{eq}^\xi = \varrho^2 \frac{\partial}{\partial\varrho}\left(\frac{-\beta\varrho}{2}\int_0^\xi \frac{d\xi'}{\xi'}\int \frac{d^3k}{(2\pi)^3}\{u_{s,k}^{\xi'}u_k^{\xi'}\}\right). \tag{29}$$

Performing the differentiation with respect to ϱ, we end up with:

$$P_{eq}^\xi = \frac{-\varrho^2\beta}{2}\int_0^\xi \frac{d\xi'}{\xi'}\int \frac{d^3k}{(2\pi)^3}\{(u_{s,k}^{\xi'})^2\}. \tag{30}$$

Finally, using Eq. (27), we have:

$$P_{eq}^\xi = \int_0^\xi \frac{d\xi'}{\xi'}\left\{\xi'\frac{\partial P_{v,eq}^{\xi'}}{\partial\xi'}\right\} = P_{v,eq}^\xi. \tag{31}$$

Thus, using the exact Eq. (10) in order to define the free energy in the approximate DH case ensures that the virial theorem is fulfilled.

Again, the result Eq. (31) can also be obtained in a more pedestrian way, from the explicit differentiation of the free-energy expression of Eq. (19) and the substitution of $h_{eq,k}^\xi$. We do not reproduce this calculation here either.

V. CONCLUSION

Our Eq. (19) is an explicit expression of the renormalized configurational free-energy functional in the Debye-Hückel approximation. This expression allows one to obtain the Debye-Hückel equation from a minimization procedure with respect to the pair correlation function. In the DH case, as in the HNC case of Refs. [25,26], requiring the exact charging relation to hold in the approximate model allows one to define a free-energy functional that yields the correct expression for the internal energy and fulfills the virial theorem. Work is now in progress in order to generalize the present formalism to multicomponent fluids, as it was done in the HNC case [28,29].

APPENDIX A: ANOTHER DERIVATION OF EQ. (16)

Instead of requiring Eq. (10) as a charging relation, we could have required, equivalently, the relation that follows (see, for instance, Ref. [30]):

$$\frac{1}{V}\frac{\delta A_{\mathrm{eq}}\{\varrho,\beta,u_k^\xi\}}{\delta u_k^\xi} = \frac{\varrho^2}{2}h_{\mathrm{eq},k}^\xi \qquad (A1)$$

This relation only has a meaning when the equilibrium free energy A_{eq} is considered to be a functional of an arbitrary potential. It has the same origin as Eq. (10), and is exact in the case of the exact equilibrium. Equation (A1) is in fact equivalent to Eq. (10) as soon as a functional dependency of an arbitrary interaction potential $u^\xi(r)$ is considered. In that case, the equilibrium configurational free energy A_{eq}, with its functional dependency on the interaction potential, can be written:

$$\frac{A_{\mathrm{eq}}\{\varrho,\beta,u^\xi(r)\}}{V} = \int_0^\xi d\xi' \int d^3r \left\{ \frac{\delta A_{\mathrm{eq}}}{\delta u^{\xi'}(r)}\frac{du^{\xi'}(r)}{d\xi'} \right\}. \quad (A2)$$

From the definition of the charge parameter: $u^\xi(r) = \xi u(r)$, and the charging relation of Eq. (10), we can directly identify the functional derivative:

$$\frac{1}{V}\frac{\delta A_{\mathrm{eq}}\{\varrho,\beta,u^{\xi'}(r')\}}{\delta u^\xi(r)} = \frac{\varrho^2}{2}h_{\mathrm{eq}}^\xi(r). \qquad (A3)$$

The latter relation becomes Eq. (A1) in the Fourier space. This stresses the particular role of Eq. (A1) in all theories that rely on an arbitrary interaction potential.

Using the postulated form of the functional Eq. (11) with $f_k^\xi \equiv f(\varrho,\beta,u_k^\xi)$, we can write:

$$\frac{1}{V}\frac{\delta A_{\mathrm{eq}}}{\delta u_k^\xi} = \frac{1}{V}\frac{\delta A}{\delta u_k^\xi}\bigg|_{\mathrm{eq}} \qquad (A4)$$

$$= \frac{\partial f(\varrho,\beta,u)}{\partial u}\bigg|_{u_k^\xi} h_{\mathrm{eq},k}^\xi \left(\frac{h_k}{2} + \beta u_k^\xi + \frac{\varrho\beta}{2}h_k u_k^\xi \right)\bigg|_{\mathrm{eq}}$$

$$+ f(\varrho,\beta,u_k^\xi)h_{\mathrm{eq},k}^\xi \left(\beta + \frac{\varrho\beta}{2}h_{\mathrm{eq},k}^\xi \right) \qquad (A5)$$

$$= \frac{\partial f(\varrho,\beta,u)}{\partial u}\bigg|_{u_k^\xi} h_{\mathrm{eq},k}^\xi \frac{\beta}{2}u_k^\xi$$

$$+ f(\varrho,\beta,u_k^\xi)h_{\mathrm{eq},k}^\xi \left(\beta + \frac{\varrho\beta}{2}h_{\mathrm{eq},k}^\xi \right). \qquad (A6)$$

Using that $u_k^\xi = \xi u_k$, we have:

$$u_k^\xi \frac{\partial f(\varrho,\beta,u)}{\partial u}\bigg|_{u_k^\xi} = \xi \frac{\partial f(\varrho,\beta,u_k^\xi)}{\partial \xi} = \xi \frac{\partial f_k^\xi}{\partial \xi}. \qquad (A7)$$

Substituting the above relation in Eq. (A6), we get:

$$\frac{1}{V}\frac{\delta A_{\mathrm{eq}}}{\delta u_k^\xi} = \xi \frac{\partial f_k^\xi}{\partial \xi}\frac{\beta}{2}h_{\mathrm{eq},k}^\xi + f_k^\xi h_{\mathrm{eq},k}^\xi \left(\beta + \frac{\varrho\beta}{2}h_{\mathrm{eq},k}^\xi \right) \quad (A8)$$

$$= \frac{\beta}{2}h_{\mathrm{eq},k}^\xi \left(\frac{\partial}{\partial \xi}\left(\xi f_k^\xi \right) + f_k^\xi \left(1 + \varrho h_{\mathrm{eq},k}^\xi \right) \right) \qquad (A9)$$

$$= \frac{\beta}{2}h_{\mathrm{eq},k}^\xi \left(\frac{\partial}{\partial \xi}\left(\xi f_k^\xi \right) + \frac{f_k^\xi}{1 + \varrho\beta u_k^\xi} \right). \qquad (A10)$$

Finally, requiring that Eq. (A1) is fulfilled leads to the Eq. (16).

APPENDIX B: COMMENT ON THE DIFFERENCE BETWEEN EQ. (6) AND EQ. (19)

An extension of the functional of Eq. (6) to a general non-Coulomb potential would not lead to the correct thermodynamical quantities. Moreover, it can be noticed that Eq. (19), taken for the bare Coulomb potential $u_k^\xi = 4\pi\xi/k^2$, does not lead to the same functional as Eq. (6). Both of them however give the same correct equilibrium relations Eqs. (7), (8), (9).

In the general case of an arbitrary interaction potential, we apply the reasoning of Appendix A and end up with Eq. (16).

Now consider that u_k is not belonging to the general class of all interaction potentials, but rather to a given subclass of functions $\bar{u}_k(\{x_i\})$, which depend on a limited number of parameters $\{x_i\}$. Then, the equilibrium free energy A_{eq} becomes a function of the $\{x_i\}$ instead of a functional of $u(r)$ (or u_k):

$$A_{\mathrm{eq}}(\varrho,\beta,\{x_i\}) \equiv A_{\mathrm{eq}}\{\varrho,\beta,\bar{u}_k(\{x_i\})\}. \qquad (B1)$$

Equation (A1) becomes meaningless and we have instead analogous equations that involve the derivatives with respect to the $\{x_i\}$.

As in Eq. (11), we assume the following form for the free-energy functional $A\{\varrho,\beta,\{x_i\},h_k\}$:

$$\frac{A}{V} = \int \frac{d^3k}{(2\pi)^3}\left\{ f(\varrho,\beta,k,\{x_i\})h_k \right.$$

$$\left. \times \left(\frac{h_k}{2} + \beta\bar{u}_k(\{x_i\}) + \frac{\varrho\beta}{2}h_k\bar{u}_k(\{x_i\}) \right) \right\} \quad (B2)$$

and require for the derivatives:

$$\frac{1}{V}\frac{\partial A_{\mathrm{eq}}(\varrho,\beta,\{x_i\})}{\partial x_i} = \frac{1}{V}\int \frac{d^3k}{(2\pi)^3}\left\{ \frac{\delta A_{\mathrm{eq}}\{\varrho,\beta,u_k\}}{\delta u_k}\bigg|_{\bar{u}_k}\frac{\partial\bar{u}_k}{\partial x_i} \right\} \quad (B3)$$

$$= \frac{\varrho^2}{2}\int \frac{d^3k}{(2\pi)^3}\left\{ h_{\mathrm{eq},k}(\{x_i\})\frac{\partial\bar{u}_k}{\partial x_i} \right\}, \quad (B4)$$

where $h_{\mathrm{eq},k}(\{x_i\})$ is solution of the DH equation for the interaction potential $\bar{u}_k(\{x_i\})$. We thus get a set of equations:

$$\int \frac{d^3k}{(2\pi)^3}\left\{ h_{\mathrm{eq},k}\left(\frac{\partial f}{\partial x_i}\bar{u}_k + f(2 + \varrho h_{\mathrm{eq},k})\frac{\partial\bar{u}_k}{\partial x_i} \right) \right\}$$

$$= \frac{\varrho^2}{\beta}\int \frac{d^3k}{(2\pi)^3}\left\{ h_{\mathrm{eq},k}\frac{\partial\bar{u}_k}{\partial x_i} \right\}. \qquad (B5)$$

Consider now a case for which the only parameter of the set $\{x_i\}$ is the charge parameter ξ, such that $\bar{u}_k^\xi \equiv \xi w_k$, with

given w_k. Then Eq. (B4) becomes the charging relation for $A_{\mathrm{eq}}(\varrho,\beta,\xi)$, which resemble Eq. (10), but where A_{eq} is not a functional of the potential w_k. Eq. (B5) becomes:

$$\int \frac{d^3k}{(2\pi)^3} \left\{ h_{\mathrm{eq},k} w_k \left(\xi \frac{\partial f}{\partial \xi} + f(2 + \varrho h_{\mathrm{eq},k}) \right) \right\}$$
$$= \frac{\varrho^2}{\beta} \int \frac{d^3k}{(2\pi)^3} \{h_{\mathrm{eq},k} w_k\}. \tag{B6}$$

We can either require the equality of the integrands, which will lead to Eq. (16) and to the general formula Eq. (19), or we can find some particular $f(\varrho,\beta,k,\xi)$ that will fulfill the equation

for the chosen w_k potential. For example, in the case of the bare Coulomb potential, it can be checked that the choice:

$$f(\varrho,\beta,k,\xi) = \frac{2\varrho^2}{3\beta} \tag{B7}$$

fulfills the Eq. (B6), and leads to the functional of Eq. (6).

If instead of considering a limited number of parameters $\{x_i\}$, we consider the continuum of parameters u_k, Eq. (B5) then becomes the equation for the functional derivative (A1). Then, only the general solution of Eq. (19) remains valid.

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

[2] T. Morita, Theory of classical fluids: Hyper-netted chain approximation, I, Prog. Theor. Phys. **20**, 920 (1958).

[3] J. K. Percus and G. J. Yevick, Analysis of classical statistical mechanics by means of collective coordinates, Phys. Rev. **110**, 1 (1958).

[4] R. Abe, Giant cluster expansion theory and its application to high temperature plasma, Prog. Theor. Phys. **22**, 213 (1959).

[5] H. E. DeWitt, Classical theory of the pair distribution function of plasmas, Phys. Rev. **140**, A466 (1965).

[6] 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).

[7] S. Nordholm, Simple analysis of the thermodynamic properties of the one-component plasma, Chem. Phys. Lett. **105**, 302 (1984).

[8] R. Penfold, S. Nordholm, B. Jönsson, and C. E. Woodward, A simple analysis of ion-ion correlation in polyelectrolyte solutions, J. Chem. Phys. **92**, 1915 (1990).

[9] R. E. Kidder and H. E. DeWitt, Application of a modified Debye-Hückel theory to fully ionized gases, J. Nucl. Energy, Part C: Plasma Phys. **2**, 218 (1961).

[10] P. Vieillefosse, Improved Debye Hückel theory for one- and multicomponent plasmas, J. Phys. **42**, 723 (1981).

[11] J. K. Percus, *The Equilibrium Theory of Classical Fluids* (W. A. Benjamin, New York, 1964), pp. II-33–II-170.

[12] J. E. Mayer, The theory of ionic solutions, J. Chem. Phys. **18**, 1426 (1950).

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

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

[15] 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 Ener. Dens. Phys. **3**, 34 (2007).

[16] R. Piron and T. Blenski, Variational-average-atom-in-quantum-plasmas (VAAQP) 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).

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

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

[19] R. Piron and T. Blenski, Variational Average-Atom in Quantum Plasmas (VAAQP) – Application to radiative properties, High. Ener. Dens. Phys. **9**, 702 (2013).

[20] C. Caizergues, T. Blenski, and R. Piron, Linear response of a variational average atom in plasma: Semi-classical model, High. Ener. Dens. Phys. **12**, 12 (2014).

[21] C. Caizergues, T. Blenski, and R. Piron, Dynamic linear response of atoms in plasmas and photo-absorption cross-section in the dipole approximation, High. Ener. Dens. Phys. **18**, 7 (2016).

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

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

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

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

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

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

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

[29] E. Enciso, F. Lado, M. Lombardero, J. L. F. Abascal, and S. Lago, Extension of the optimized RHNC equation to multicomponent liquids, J. Chem. Phys. **87**, 2249 (1987).

[30] R. Evans, The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids, Adv. Phys. **28**, 143 (1979).