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Free-energy functional of the Debye–Hückel model of two-component plasmas

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ABSTRACT

We present a generalization of the Debye–Hückel free-energy-density functional of simple fluids to the case of two-component systems with arbitrary interaction potentials. It allows one to obtain the two-component Debye–Hückel integral equations through its minimization with respect to the pair correlation functions, leads to the correct form of the internal energy density, and fulfills the virial theorem. It is based on our previous idea, proposed for the one-component Debye–Hückel approach, which was published recently in Ref. [1]. We use the Debye–Kirkwood charging method in the same way as in Ref. [1], in order to build an expression of the free-energy density functional. Main properties of the two-component Debye–Hückel free energy are presented and discussed, including the virial theorem in the case of long-range interaction potentials.

1. Introduction

The Debye–Hückel (DH) model was introduced in the theory of electrolytes [2]. It is the linearized version of the Non-Linear Debye–Hückel (NLDH) or Poisson-Boltzmann model. Both the DH and NLDH models can be in principle extended to arbitrary interaction potentials, with many applications in the physics of classical fluids, charged or not.

An important feature of the one-component DH model is the mean-field screening of the interaction potential, that results in the decay of the correlation function, even when the interaction potential has a Coulomb tail. This property is preserved in the two-component DH theory of plasma or charged mixtures. In general the DH model is valid in the low-coupling limit, i.e. when the interaction energy is small compared to the kinetic energy of particles. The DH theory is a relatively simple mean-field approach to classical fluids in comparison to the Hyper-Netted Chain (HNC) [3] or Percus–Yevick [4] models, which account for part of the correlations. However, several more involved theoretical studies also proceed by introducing corrections, using the low-coupling DH limit as a starting point (see, for instance, [5,6]). Recently it was also shown that, in the DH model, the energy and virial ”routes” are thermodynamically consistent, for any potential [7]. For these reasons, the two-component DH model can be of interest not only for the plasma physics community (see, for instance, [8,9]) but also in the physics of electrolytes (see, for example [10,11]). 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 commonly used in plasma physics as well as in the physics of electrolytes.

Our interest in the DH models stems from our research on density effects in the equation of state and in radiative properties of dense plasmas. We aim to describe these effects using approximate but fully variational models of atoms in plasmas. The ion and free electron correlations and their impact on the atomic structure and dynamics should thus be taken into account while preserving the variational character of the approach. Up to now the most used models are still essentially based on the ion-in-cell picture [12–14]. Some progress towards a variational formulation of quantum atom-in-plasma models was achieved [15–22]. However, it relies on a very simple hypothesis on ion-ion correlations. Attempts to include ion correlations into atom-in-plasma models were also proposed (see, for instance, [23–26]), but do not stem from a fully variational derivation.

The DH model is a natural candidate tool in order to include plasma ions and electron effects for relatively weakly coupled plasma. The results presented in this paper extend the variational free-energy density formula presented in [1] to the two-component case. The present DH theory can also be useful to construct

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variational approaches to models of two-component fluids using expressions of the free-energy density as a functional of the pair correlation functions. In the atom-in-plasma models such a variational expression can be used in a more general theory that also includes the ion electronic structure.

A two-component free-energy density functional is available in the HNC theory [27,28]. However, as it was the case in the well-known one-component DH theory, an expression of the free-energy density as a functional of the pair correlation functions has not been yet proposed. The purpose of this paper is to present a brief derivation of such an expression in the DH approximation, which can be seen as the DH equivalent to the HNC free-energy density functional of Lado [27] (see also [28]).

2. Debye–Hückel integral equations of a two-component fluid

Let us consider a two-component homogeneous fluid at equilibrium, at a temperature $T = 1/(k_B\beta)$. In the case of plasmas or charged liquids the fluid neutrality results in the charge balance $\sum_j \varrho_j z_j = 0$ where ϱ_j is the average particle density and z_j the charge of the j specie, respectively. The particles interact through potentials $u_{ij}(r)$. Using the so called "Percus trick" (see [29,30]) we obtain the following identity :

$$\frac{\varrho^{(1:j)}\{\{\varphi_n(r') = u_{in}(r')\};r\}}{\varrho_j} = g_{ij}(r) \tag{1}$$

where the $g_{ij}(r)$ are the pair distribution functions of the homogeneous fluid, for the species i and j, and $\varrho^{(1:\,j)}(r)$ is the j-specie 1-body reduced density matrix for a non-homogeneous fluid, with an external potential $\varphi_n(r')$ acting on each specie n.

The DH model is obtained from the static linear response of the density to the external potential:

$$\begin{aligned}\varrho^{(1:j)}\{u_{in}(r'');r\} &\approx \varrho_j \\ &+ \sum_n \int d^3r' \left\{ \frac{\delta\varrho^{(1:j)}\{\{\varphi_n(r'')\};r\}}{\delta\varphi_n(r')}\bigg|_{\{\varphi_n(r')=0\}} u_{in}(r') \right\}\end{aligned} \tag{2}$$

The functional derivatives of the density are (Yvon equations):

$$\begin{aligned}\frac{1}{\beta}\frac{\delta\varrho^{(1:j)}(\mathbf{r})}{\delta\varphi_j(\mathbf{r}')} =& -\varrho^{(2:j)}(\mathbf{r},\mathbf{r}') + \varrho^{(1:j)}(\mathbf{r})\varrho^{(1:j)}(\mathbf{r}') \\ & -\varrho^{(1:j)}(\mathbf{r}')\delta_3(\mathbf{r}-\mathbf{r}')\end{aligned} \tag{3}$$

$$\frac{1}{\beta}\frac{\delta\varrho^{(1:j)}(\mathbf{r})}{\delta\varphi_{n\neq j}(\mathbf{r}')} = -\varrho^{(1:j,1:n)}(\mathbf{r},\mathbf{r}') + \varrho^{(1:j)}(\mathbf{r})\varrho^{(1:n)}(\mathbf{r}') \tag{4}$$

From the above equations and the definition (see, for instance, [30]) of the correlation functions $h_{ij}(r) + 1 = g_{ij}(r)$ one obtains the equations of the Debye–Hückel model:

$$h_{ij}(r) = -\beta u_{ij}(r) - \beta\sum_n \varrho_n \int d^3r'\{u_{in}(r')h_{in}(|\mathbf{r}-\mathbf{r}'|)\} \tag{5}$$

For the purpose of future considerations it is useful to write the DH equations in the following symmetrical form:

$$h_{11}(r) = -\beta u_{11}(r) - \beta\int d^3r'\{\varrho_1 u_{11}(r')h_{11}(|\mathbf{r}-\mathbf{r}'|) - \varrho_2 u_{12}(r')h_{12}(|\mathbf{r}-\mathbf{r}'|)\} \tag{6}$$

$$h_{22}(r) = -\beta u_{22}(r) - \beta\int d^3r'\{\varrho_2 u_{22}(r')h_{22}(|\mathbf{r}-\mathbf{r}'|) - \varrho_1 u_{12}(r')h_{12}(|\mathbf{r}-\mathbf{r}'|)\} \tag{7}$$

$$\begin{aligned}h_{12}(r) = -\beta u_{12}(r) - \frac{\beta}{2}\int d^3r'\{&u_{12}(|\mathbf{r}-\mathbf{r}'|)(\varrho_1 h_{11}(r') + \varrho_2 h_{22}(r')) \\ &+ h_{12}(|\mathbf{r}-\mathbf{r}'|)(\varrho_1 u_{11}(r') + \varrho_2 u_{22}(r'))\}\end{aligned} \tag{8}$$

We define the Fourier transform $\mathcal{F}_\mathbf{k}$ of a function $\mathcal{F}(\mathbf{r})$ as $\mathcal{F}_\mathbf{k} = \int d^3r\{\mathcal{F}(\mathbf{r})e^{i\mathbf{k}.\mathbf{r}}\}$. The DH equations have a simple form in the Fourier space:

$$h_{11;k} + \varrho_1 h_{11;k}\,\beta u_{11;k} + \varrho_2 h_{12;k}\,\beta u_{12;k} = -\beta u_{11;k} \tag{9}$$

$$h_{22;k} + \varrho_1 h_{12;k}\,\beta u_{12;k} + \varrho_2 h_{22;k}\,\beta u_{22;k} = -\beta u_{22;k} \tag{10}$$

$$h_{12;k} + \varrho_1 h_{11;k}\,\beta u_{12;k} + \varrho_2 h_{12;k}\,\beta u_{22;k} = -\beta u_{12;k} \tag{11}$$

The solutions of these equations are:

$$h_{\mathrm{eq},11;k} = -\frac{1}{\varrho_1} + \frac{1}{\varrho_1\beta}\frac{\beta + \beta^2\varrho_2 u_{22;k}}{D_k} \tag{12}$$

$$h_{\mathrm{eq},22;k} = -\frac{1}{\varrho_2} + \frac{1}{\varrho_2\beta}\frac{\beta + \beta^2\varrho_1 u_{11;k}}{D_k} \tag{13}$$

$$h_{\mathrm{eq},12;k} = -\frac{1}{\varrho_1\varrho_2\beta}\frac{\beta^2\varrho_1\varrho_2 u_{12;k}}{D_k} \tag{14}$$

where we have defined:

$$D_k = 1 + \beta(\varrho_1 u_{11;k} + \varrho_2 u_{22;k}) + \beta^2\varrho_1\varrho_2(u_{11;k}u_{22;k} - u_{12;k}^2) \tag{15}$$

3. Expression for a free-energy functional of a two-component fluid

We are looking for a functional of trial correlations functions $h_{ij}(r)$ which, when minimized with respect to these functions, gives the DH equations and, at the DH equilibrium, has the value of the free-energy excess due to the interactions. As in [1,27,31], we use the charging procedure due to Debye and Kirkwood [32]. The charging parameter ξ allows one to switch on the interaction potentials from zero to their actual values $u_{ij}^{\xi}(r) = \xi\, u_{ij}(r)$. For an exact interacting system one gets from the grand canonical statistical sum (see, for instance, [30]) the following exact expression for the free-energy excess per unit volume:

$$\frac{A_{\mathrm{eq}}^{\xi}\{\{\varrho_i\},\beta,\{u_{ij}(r)\}\}}{V} = \int_0^{\xi}\frac{d\xi'}{\xi'}\int d^3r\left\{\frac{1}{2}\sum_{i,j}\varrho_i\varrho_j h_{\mathrm{eq},ij}^{\xi'}(r)u_{ij}^{\xi'}(r)\right\} \tag{16}$$

We require, as in [1,27,31], that in our approximate two-component DH theory, the searched free-energy density functional gives, at the equilibrium, the value of Eq. (16), with DH equilibrium functions $h_{\mathrm{eq},ij}(r)$ (or their equivalent forms in the Fourier space). Moreover, as in [1], we postulate that the searched functional, which depends on arbitrary trial functions $h_{ij;k}$, can be written as follows in the Fourier space:

$$\begin{aligned}&\frac{A\{\{\varrho_i\},\beta,\{u_{ij}(r)\},\{h_{ij}(r)\}\}}{V} \\ &= \int\frac{d^3k}{(2\pi)^3}\left\{\frac{f_k}{2}\left[\varrho_1^2\left(\frac{h_{11;k}^2}{2} + \beta u_{11;k}h_{11;k} + \varrho_1\beta u_{11;k}\frac{h_{11;k}^2}{2} + \varrho_2\beta u_{12;k}h_{11;k}h_{12;k}\right)\right.\right. \\ &\quad + \varrho_2^2\left(\frac{h_{22;k}^2}{2} + \beta u_{22;k}h_{22;k} + \varrho_2\beta u_{22;k}\frac{h_{22;k}^2}{2} + \varrho_1\beta u_{12;k}h_{22;k}h_{12;k}\right) \\ &\quad \left.\left. + 2\varrho_1\varrho_2\left(\frac{h_{12;k}^2}{2} + \beta u_{12;k}h_{12;k} + \frac{h_{12;k}^2}{2}\frac{1}{2}(\varrho_1\beta u_{11;k} + \varrho_2\beta u_{22;k})\right)\right]\right\}\end{aligned} \tag{17}$$

where the function f_k depends on all ϱ_i, $\{u_{ij;k}\}$ and on β, but not on the $\{h_{ij;k}\}$. It is easy to check that the functional derivatives of $A\{\{\varrho_i\}, \beta, \{u_{ij}(r)\}, \{h_{ij}(r)\}\}$ with respect to the $\{h_{ij;k}\}$, at fixed ϱ_i and $\{u_{ij;k}\}$, lead to the DH Eqs. (9)–(11).

We postulate that such a function f_k exists and that the functional of Eq. (17), taken at equilibrium, has the value given in Eq. (16). A