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Numerical Simulations of Screened Coulomb Systems. A Comparison Between Hyperspherical and Periodic Boundary Conditions

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Numerical simulations or Coulomb systems can be performed in various geometries, for instance in a cube with periodic boundary conditions ($\mathscr{C}^3$) or on the surface of a hypersphere ($\mathscr{S}^3$). We show how to extend these methods of simulations to the case of screened (Yukawa) potentials. We make a detailed comparison between the properties of Yukawa systems in these two geometries and derive the correct configurational energies of some models such as the Yukawa restricted primitive model and the Yukawa one component plasma.

KEY WORDS: Yukawa potential; strongly coupled plasmas; colloids; numerical simulations.

I. INTRODUCTION

The numerical simulation of a fluid phase can be performed either in a cubic simulation box with periodic boundary conditions or on the surface of a four dimensional (4D) sphere, a hypersphere for short. We shall denote $\mathscr{C}^3$ the cube of side L, and $\mathscr{S}^3$ the hypersphere of center O and radius R (equation: $x^2+y^2+z^2+t^2=R^2$). In $\mathscr{C}^3$ we employ periodic boundary conditions. $\mathscr{S}^3$ is a 3D non-Euclidean closed space of $\mathbb{R}^4$ of positive curvature which is homogeneous and isotropic albeit finite. By contrast $\mathscr{C}^3$ is an homogeneous but anisotropic space.

In the case of Coulomb fluids (i.e., systems of charges, dipoles, etc.) it is widely admitted that the pair potentials which must be used in a simulation

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are those which are solution of the basics electrostatics in the considered geometry. For instance, in $\mathscr{C}^3$, the potential of a charge (plus a neutralizing background) should be the Ewald potential.[1–3] Poisson's equation can also be solved in $\mathscr{S}^3$ which allows to perform simulations of Coulomb fluids (and others) in this geometry too.[4–6]

In a recent paper[7] one of us have given a detailed comparison between the electrostatics in $\mathscr{C}^3$ and $\mathscr{S}^3$ and derived the correct configurational energies of two important cases of Coulomb systems, the restricted primitive model (RPM) of electrolytes and the one component plasma (OCP). In the present paper we extend this analysis to the case of screened Coulomb systems (i.e., Yukawa systems). Recently, many models involving Yukawa interactions have been applied for instance to study thermodynamic and structural properties of dusty plasmas[8–11] and spectroscopic properties of dense plasmas.[12, 13] These studies have been performed by means of numerical simulations in $\mathscr{C}^3$. The application of the hypersphere method to Yukawa systems was motivated by an extension of these studies to a wider range of physical parameters in order to use them in a new theoretical model for the equation of state of Deuterium.[14] The validity of the hypersphere method was corroborated in a recent Monte Carlo (MC) study of the OCP.[15]

The paper is organized as follows. In Section 2 we discuss briefly some peculiar points concerning the electrostatics of Yukawa systems in the ordinary space $\mathbb{R}^3$. We also discuss the Hamiltonians of the Yukawa RPM (YRPM) and the Yukawa OCP (YOCP) as well as lower bounds on their configurational energies. In Sections 3 and 4 we discuss the same points than in Section 2 but in the cases of spaces $\mathscr{C}^3$ and $\mathscr{S}^3$ respectively.

II. YUKAWA SYSTEMS IN $\mathbb{R}^3$

A. Point-Charges

The Green's function $\mathscr{G}(\mathbf{r}, \mathbf{r}_0)$ of the Helmholtz equation in $\mathbb{R}^3$ with boundaries at infinity

$$(\Delta_r - \alpha^2)\, \mathscr{G}(\mathbf{r}, \mathbf{r}_0) = -4\pi\delta(\mathbf{r} - \mathbf{r}_0) \tag{2.1}$$

the solution of which reads[16]

$$\mathscr{G}(\mathbf{r}, \mathbf{r}_0) = \frac{\exp(-\alpha\, \|\mathbf{r} - \mathbf{r}_0\|)}{\|\mathbf{r} - \mathbf{r}_0\|} \tag{2.2}$$

can be seen as the screened potential at point $\mathbf{r}$ of a unit point charge located at $\mathbf{r}_0$. Henceforth we shall note $\varphi^{\mathbb{R}^3}(\mathbf{r}-\mathbf{r}_0) \equiv \mathcal{G}(\mathbf{r}, \mathbf{r}_0)$. An important property of $\varphi^{\mathbb{R}^3}$ is that its Fourier transform is non-singular and positive:

$$\tilde{\varphi}^{\mathbb{R}^3}(\mathbf{k}) = \int d^3\mathbf{r}\, \varphi^{\mathbb{R}^3}(\mathbf{r}) \exp(-i\mathbf{r} \cdot \mathbf{k}) = \frac{4\pi}{\mathbf{k}^2 + \alpha^2} \tag{2.3}$$

Yukawa potentials may be seen as effective potentials acting between a subset of charged species of a Coulomb system while the other species are represented by a polarizable background of dielectric constant $\varepsilon(\mathbf{k})$. The effect of the background is taken into account in the frame of the linear response theory. The choice

$$\varepsilon(\mathbf{k}) = 1 + \alpha^2/\mathbf{k}^2 \tag{2.4}$$

leads to the Yukawa form (2.2) of the screened potentials. In the case of a plasma, the electrons constitute the uniform background and the simple form (2.4) of the dielectric constant can be obtained within the linearized Debye–Hückel or Thomas–Fermi approximations.[17] In the former case the approximation is valid at low densities and high temperatures and, in the latter, it applies to a cold and dense quantum gas of electrons. As already mentioned, Yukawa potentials can be used to simulate plasmas,[12, 13, 18, 19] dusty plasmas[8, 11] but also colloids as well.[20, 21] The physics of the model is partially contained in the dependance of the screening parameter α upon the density ρ and temperature T.

The electrostatics built from Yukawa charges differ by many respects to the usual electrostatics. It has been discussed to some extent by Rosenfeld.[22] We resume and complete now his results and give shorter proofs when possible.

B. Distribution of Yukawa Charges

We look at solutions of

$$(\Delta_r - \alpha^2)\, \varphi_n^{\mathbb{R}^3}(\mathbf{r}) = -4\pi n(\mathbf{r}) \tag{2.5}$$

for simple distributions of Yukawa charges $n(\mathbf{r})$ of $\mathbb{R}^3$. The solution of Eq. (2.5) is:[16]

$$\varphi_n^{\mathbb{R}^3}(\mathbf{r}) = \int d^3\mathbf{r}'\, n(\mathbf{r}')\, \mathcal{G}(\mathbf{r}, \mathbf{r}') \tag{2.6}$$

1. Uniform Background. In the case of a uniform background $n(\mathbf{r}) \equiv n_b$ ($\forall \mathbf{r} \in \mathbb{R}^3$), the regular solution of Eq. (2.5) is

$$\varphi_b^{\mathbb{R}^3} = n_b \tilde{\varphi}^{\mathbb{R}^3}(\mathbf{k} = \mathbf{0}) = \frac{4\pi n_b}{\alpha^2} \tag{2.7}$$

Note that, in the coulombic case ($\alpha = 0$), there is no regular solution.

Let us consider now the more complicated case where $n(\mathbf{r}) \equiv 0$ in a region $\mathscr{D}$ of $\mathbb{R}^3$. We denote by $\mathscr{S}(O, a)$ a sphere of center O and radius a included in $\mathscr{D}$, and we define the spherical average of $\varphi_n^{\mathbb{R}^3}$ as

$$\langle \varphi_n^{\mathbb{R}^3} \rangle (a) = \int_{S(O, a)} \frac{d\Omega(\mathbf{a})}{4\pi} \varphi_n^{\mathbb{R}^3}(\mathbf{a}) \tag{2.8}$$

where $\mathbf{a}$ is a vector of the sphere $S(O, a)$ and $d\Omega(\mathbf{a})$ is the solid angle about vector $\mathbf{a}$. $\langle \varphi_n^{\mathbb{R}^3} \rangle (a)$ is a function of the sole radius a, the expression of which is derived in the Appendix and reads

$$\langle \varphi_n^{\mathbb{R}^3} \rangle (a) = \frac{\sinh(\alpha a)}{\alpha a} \varphi_n^{\mathbb{R}^3}(O) \tag{2.9}$$

In the case $\alpha = 0$, we recover a well known property of Coulomb potentials, i.e., $\langle \varphi_n^{\mathbb{R}^3} \rangle (a) = \varphi_n^{\mathbb{R}^3}(O)$.[23]

2. Spherical Surfacic Distributions of Charges. Many results concerning spherical distribution of Yukawa charges can be deduced from Eq. (2.9). Another useful relation is the expression of the Green function $\mathscr{G}(\mathbf{r}, \mathbf{r}')$ of Helmholtz equation in spherical coordinates[16]

$$\mathscr{G}(\mathbf{r}, \mathbf{r}') = \frac{1}{\sqrt{rr'}} \sum_{l=0}^{\infty} (2l+1)\, I_{l+1/2}(\alpha r_<)\, K_{l+1/2}(\alpha r_>)\, P_l(\mathbf{r} \cdot \mathbf{r}'/rr') \tag{2.10}$$

where $r_< = \inf(r, r')$ and $r_> = \sup(r, r')$. In Eq. (2.10) $I_{l+1/2}$ and $K_{l+1/2}$ are Hyperbolic Bessel functions and the P_l's, Legendre polynomials.[16]

Let us consider a sphere of center O, radius a with a charge q uniformly distributed over its surface. The potential $\varphi_\sigma^{\mathbb{R}^3}$ of the distribution is given by Eq. (2.6) with $n(\mathbf{r}) \equiv n_\sigma(\mathbf{r}) = q\delta(|\mathbf{r}| - a)/4\pi a^2$. We insert the expansion (2.10) of the Green function in Eq. (2.6) and notes that only the term $l = 0$ survives to the angular integration. Since $I_{1/2}(x) = \sqrt{2}\, \sinh(x)/\sqrt{\pi x}$ and $K_{1/2}(x) = \sqrt{\pi}\, \exp(-x)/\sqrt{2x}$ it yields readily to a result obtained by Rosenfeld in another way:[22, 25]

$$\varphi_\sigma^{\mathbb{R}^3}(r) = q\,\frac{\sinh(\alpha a)}{\alpha a}\,\frac{\exp(-\alpha r)}{r} \qquad \text{for} \quad r \geqslant a$$

$$= q\,\frac{\sinh(\alpha r)}{\alpha r}\,\frac{\exp(-\alpha a)}{a} \qquad \text{for} \quad r \leqslant a \tag{2.11}$$

For $r \geqslant a$, $\varphi_\sigma^{\mathbb{R}^3}(r)$ is equal to the potential of a point charge at the center of the sphere with an effective charge

$$q_\sigma(\alpha) = q\,\frac{\sinh \alpha a}{\alpha a} \tag{2.12}$$

The self-energy of the charge distribution is

$$\mathscr{E}_\sigma^{\mathbb{R}^3} = \frac{1}{2}\int d^3\mathbf{r}\; n_\sigma(\mathbf{r})\; \varphi_\sigma^{\mathbb{R}^3}(r) = \frac{1}{2}\, q q_\sigma(\alpha)\,\frac{\exp(-\alpha a)}{a} \tag{2.13}$$

Finally, let us consider two charged spheres of radii a_i $(i = 1, 2)$ and respective charges q_1 and q_2 located at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ such that they do not overlap (i.e., $|\mathbf{r}_1 - \mathbf{r}_2| \geqslant (a_1 + a_2)$). Their mutual interaction energy is given by

$$\Phi_{12,\sigma}^{\mathbb{R}^3}(r_{12}) = \int d^3\mathbf{r}\; n_{\sigma,1}(\mathbf{r} - \mathbf{r}_1)\; \varphi_{\sigma,2}^{\mathbb{R}^3}(\mathbf{r} - \mathbf{r}_2)$$

$$= q_1 \langle \varphi_{\sigma,2}(\mathbf{r} - \mathbf{r}_2) \rangle (a_1)$$

$$= q_{1,\sigma}(\alpha)\; q_{2,\sigma}(\alpha)\,\frac{\exp(-\alpha r_{12})}{r_{12}} \tag{2.14}$$

3. Spherical Volumic Distributions of Charges. Let us consider now a sphere of center O, radius a with a charge q uniformly distributed over its volume. The potential $\varphi_\rho^{\mathbb{R}^3}$ of the distribution can be obtained by integration of $\varphi_\sigma^{\mathbb{R}^3}$. One finds[22]

$$\varphi_\rho^{\mathbb{R}^3}(r) = \frac{3q}{\alpha^2 a^3}\left[1 - (1 + \alpha a)\exp(-\alpha a)\,\frac{\sinh \alpha r}{\alpha r}\right] \qquad \text{for} \quad r \leqslant a$$

$$= \frac{3q}{\alpha^2 a^3}\,\frac{\alpha a \cosh(\alpha a) - \sinh(\alpha a)}{\alpha}\,\frac{\exp(-\alpha r)}{r} \qquad \text{for} \quad r \geqslant a \tag{2.15}$$

For $r \geqslant a$, $\varphi_{\rho}^{\mathbb{R}^3}(r)$ is equal to the potential of a point charge at the center of the sphere with an effective charge

$$q_{\rho}(\alpha) = 3q \frac{\alpha a \cosh(\alpha a) - \sinh(\alpha a)}{(\alpha a)^3} \tag{2.16}$$

The self-energy of the charge distribution reads

$$\mathscr{E}_{\rho}^{\mathbb{R}^3} = \frac{1}{2} \int d^3\mathbf{r}\, n_{\rho}(\mathbf{r})\, \varphi_{\rho}^{\mathbb{R}^3}(r) = \frac{1}{2} \frac{3q}{\alpha^2 a^3} [q - (1 + \alpha a) \exp(-\alpha a)\, q_{\rho}(\alpha)] \tag{2.17}$$

and the interaction energy of two non overlaping spheres has the following expression

$$\Phi_{12,\rho}^{\mathbb{R}^3}(r_{12}) = q_{\rho,1}(\alpha)\, q_{\rho,2}(\alpha) \frac{\exp(-\alpha r_{12})}{r_{12}} \tag{2.18}$$

C. YPRM

The YRPM is an equimolar mixture of $N_+ = N/2$ hard spheres of radius a bearing a charge q at their centers, and $N_- = N_+$ spheres of the same diameter but with an opposite charge $-q$. The phase diagram of the model has been explored recently.[20, 21] The electrostatic energy of the YRPM reads

$$V_{\text{YRPM}}^{\mathbb{R}^3} = \tfrac{1}{2} \sum_{i \neq j} q_i q_j \varphi^{\mathbb{R}^3}(r_{ij}) \tag{2.19}$$

Since configurations with overlaps of spheres do not contribute to the partition function we take advantage of the results of Section IIB2 and replace the point charges by spherical surfacic distributions $\sigma_{\pm}$ giving rise to the same potentials. It follows from Eq. (2.12) that it can be achieved with the choice

$$q_{\pm} = 4\pi\sigma_{\pm} a^2 \frac{\sinh \alpha a}{\alpha a} \tag{2.20}$$

The Yukawa energy $\mathscr{W}$ of these N spheres is finite and positive as a consequence of the positivity of $\tilde{\varphi}^{\mathbb{R}^3}(\mathbf{k})$. Indeed, in Fourier space

$$\mathscr{W} = \frac{1}{2} \frac{1}{(2\pi)^3} \int d^3\mathbf{k}\, |\tilde{n}_T(\mathbf{k})|^2\, \tilde{\varphi}^{\mathbb{R}^3}(\mathbf{k}) \tag{2.21}$$

where $\tilde{n}_T(\mathbf{k})$ denotes the Fourier transform of the total density of charges

$$n_T(\mathbf{r}) = \sum_{i=1}^{N} \sigma_i \delta(a - \|\mathbf{r} - \mathbf{r}_i\|) \tag{2.22}$$

Therefore, from the inequality

$$\mathscr{W} = V_{\mathbf{YRPM}}^{\mathbb{R}^3} + N\mathscr{E}_{\sigma}^{\mathbb{R}^3} \geqslant 0 \tag{2.23}$$

one infers an extensive lower bound for $V_{\mathbf{YRPM}}^{\mathbb{R}^3}$, i.e.

$$\begin{aligned} V_{\mathbf{YRPM}}^{\mathbb{R}^3}(1,..., N) &\geqslant N\mathscr{B}_{\mathbf{YRPM}}^{\mathbb{R}^3} \\ \mathscr{B}_{\mathbf{YRPM}}^{\mathbb{R}^3} &= -\mathscr{E}_{\sigma}^{\mathbb{R}^3} = -\frac{q^2}{2} \frac{\exp(-\alpha a)}{a} \frac{\alpha a}{\sinh \alpha a} \end{aligned} \tag{2.24}$$

a new result to our knowledge. Of course, in the limiting case $\alpha = 0$, one recovers the Onsager's bound $\mathscr{B}_{\mathbf{RPM}}^{\mathbb{R}^3} = -q^2/2a$ of the RPM.[24]

D. YOCP

We deal now with a system of N identical point Yukawa charges q immersed in a uniform neutralizing background of density $n = N/\Omega$, where Ω denotes the volume of the system. The configurational energy of the model is

$$\begin{aligned} V_{\mathbf{OCP}}^{\mathbb{R}^3} = &\frac{q^2}{2} \sum_{i \neq j} \varphi^{\mathbb{R}^3}(r_{ij}) - nq^2 \sum_{i=1}^{N} \int_{\Omega} d^3\mathbf{r}\, \varphi^{\mathbb{R}^3}(\|\mathbf{r} - \mathbf{r}_i\|) \\ &+ \frac{q^2}{2} \int_{\Omega^2} d^3\mathbf{r}\, d^3\mathbf{r}'\, \varphi^{\mathbb{R}^3}(\|\mathbf{r} - \mathbf{r}')\|) + N\mathscr{A}^{\mathbb{R}^3} \end{aligned} \tag{2.25}$$

where the additive constant $\mathscr{A}^{\mathbb{R}^3}$ was included in Eq. (2.25) to fit with the expressions obtained in the frame of a linear response theory treatment of the electron gas, i.e.,[8, 18]

$$\mathscr{A}^{\mathbb{R}^3} = \frac{q^2}{2} \lim_{r \to 0} \left(\varphi^{\mathbb{R}^3}(r) - \frac{1}{r} \right) = -\frac{q^2 \alpha}{2} \tag{2.26}$$

and thus the zero of energy of the YOCP is defined with respect to the (infinite) self-energy of a Coulomb charge q rather than that (also infinite) of a Yukawa charge.[22, 25] The thermodynamic and structural properties of the YOCP depend on the sole dimensionless parameters $\alpha^* = \alpha a_i$ and $\Gamma = \beta q^2/a_i$ ($\beta = 1/kT$, k Boltzmann constant) where a_i is the ionic radius defined by $4\pi n a_i^3/3=1$. Rosenfeld has shown the existence of an extensive lower bound for $\beta V_{\text{YOCP}}^{\mathbb{R}^3}$ which reads[22]

$$\beta V_{\text{YOCP}}^{\mathbb{R}^3} \geqslant N \mathscr{B}_{\text{YOCP}}^{\mathbb{R}^3}$$

$$\mathscr{B}_{\text{YOCP}}^{\mathbb{R}^3} = \frac{\Gamma(1+\alpha^*)\,\alpha^* \exp(-\alpha^*)}{\exp(\alpha^*)(\alpha^*-1)+\exp(-\alpha^*)(\alpha^*+1)} - \frac{3}{2\alpha^{*2}} - \frac{\Gamma\alpha^*}{2} \tag{2.27}$$

As, in the limit $\alpha^* \to 0$

$$\mathscr{B}_{\text{YOCP}}^{\mathbb{R}^3} \sim -\frac{9\Gamma}{10} - \frac{18\Gamma}{175}\alpha^{*2} + \cdots \tag{2.28}$$

one recovers the Lieb–Narnhofer bound $\mathscr{B}_{\text{OCP}}^{\mathbb{R}^3} = -9\Gamma/10$ of the OCP for $\alpha^*=0$.[26]

III. YUKAWA SYSTEMS IN $\mathscr{C}^3$

A. Point-Charges

The Green's function $\mathscr{G}^{\mathscr{C}^3}(\mathbf{r}, \mathbf{r}_0)$ of the Helmholtz equation in $\mathscr{C}^3$

$$(\Delta_r - \alpha^2)\, \mathscr{G}^{\mathscr{C}^3}(\mathbf{r}, \mathbf{r}_0) = -4\pi \delta^{\mathscr{C}^3}(\mathbf{r}-\mathbf{r}_0) \qquad (\forall \mathbf{r}, \mathbf{r}_0 \in \mathscr{C}^3) \tag{3.1}$$

can be obtained by expanding both $\mathscr{G}^{\mathscr{C}^3}$ and the Dirac mass $\delta^{\mathscr{C}^3}$ on the eigenfunctions $\exp(i\mathbf{k}\cdot\mathbf{r})$ ($\mathbf{k}=2\pi\mathbf{n}/L$, $\mathbf{n}\in\mathbb{Z}^3$) of the Laplacian, with the result[8, 18, 19]

$$\mathscr{G}^{\mathscr{C}^3}(\mathbf{r}, \mathbf{r}_0) = \frac{1}{L^3} \sum_k \frac{4\pi}{\mathbf{k}^2+\alpha^2} \exp(i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_0)) \tag{3.2}$$

$\mathscr{G}^{\mathscr{C}^3}(\mathbf{r}, \mathbf{r}_0)$ can be seen as the screened potential at point $\mathbf{r}$ of a unit point charge located at $\mathbf{r}_0 \in \mathscr{C}^3$. Henceforth we shall note $\varphi^{\mathscr{C}^3}(\mathbf{r}-\mathbf{r}_0) \equiv \mathscr{G}^{\mathscr{C}^3}(\mathbf{r}, \mathbf{r}_0)$. Contrary to the Laplace–Poisson equation the solutions of the Helmholtz Eq. (3.1) are not defined up to an additive constant (the regular solution of the homogeneous Helmholtz equation is unique). Note the property

$$\int_{\mathscr{C}^3} d^3\mathbf{r}\, \varphi^{\mathscr{C}^3}(\mathbf{r}) = \frac{4\pi}{\alpha^2} \tag{3.3}$$

It follows from Eq. (3.2) that the Fourier component $\tilde{\varphi}_{\mathbf{k}}$ of $\varphi^{\mathscr{C}^3}$ defined as

$$\tilde{\varphi}_{\mathbf{k}} = \int_{\mathscr{C}^3} d^3\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r})\, \varphi^{\mathscr{C}^3}(\mathbf{r}) \tag{3.4}$$

coincides with the Fourier transform $\tilde{\varphi}^{\mathbb{R}^3}(\mathbf{k})$ of the Yukawa potential (cf. Eq. (2.3)) in $\mathbb{R}^3$. It follows from this remark that

$$\begin{aligned}\tilde{\varphi}_{\mathbf{k}} &= \int_{\mathbb{R}^3} d^3\mathbf{r}\, \frac{\exp(-\alpha r)}{r} \exp(-i\mathbf{k}\cdot\mathbf{r}) \\ &= \sum_{\mathbf{n}\in\mathbb{Z}^3} \int_{\mathscr{C}^3(\mathbf{n})} d^3\mathbf{r}\, \frac{\exp(-\alpha r)}{r} \exp(-i\mathbf{k}\cdot\mathbf{r}) \\ &= \int_{\mathscr{C}^3} \sum_{\mathbf{n}\in\mathbb{Z}^3} \frac{\exp(-\alpha\, \|\mathbf{r}+L\mathbf{n}\|)}{\|\mathbf{r}+L\mathbf{n}\|)} \exp(-i\mathbf{k}\cdot\mathbf{r}) \end{aligned} \tag{3.5}$$

where we have divided $\mathbb{R}^3$ into cubic cells $\mathscr{C}^3(\mathbf{n})$ of center $L\mathbf{n}$ ($\mathbf{n}\in\mathbb{Z}^3$) and side L and performed a trivial change of variables. Equation (3.5) gives us an alternative expression of $\varphi^{\mathscr{C}^3}$ as the sum of the Yukawa potentials created by an infinite cubic array of unit point Yukawa charges, i.e.,

$$\varphi^{\mathscr{C}^3}(\mathbf{r}) = \sum_{\mathbf{n}\in\mathbb{Z}^3} \varphi^{\mathbb{R}^3}(\mathbf{r}+L\mathbf{n}) \tag{3.6}$$

For $r \leqslant L/2$ we can easily compute the spherical average of $\varphi^{\mathscr{C}^3}(\mathbf{r})$ from Eq. (3.6):

$$\begin{aligned}\langle \varphi^{\mathscr{C}^3}(\mathbf{r})\rangle(r) &= \left\langle \sum_{\mathbf{n}\in\mathbb{Z}^3} \varphi^{\mathbb{R}^3}(\mathbf{r}+L\mathbf{n}) \right\rangle (r) \\ &= \varphi^{\mathbb{R}^3}(\mathbf{r}) + \sum_{\mathbf{n}\neq\mathbf{0}} \langle \varphi^{\mathbb{R}^3}(\mathbf{r}+L\mathbf{n})\rangle(r) \end{aligned} \tag{3.7}$$

The spherical averages in the r.h.s. of Eq. (3.7) can be evaluated with the help of Eq. (2.9) since, for $\mathbf{n}\neq\mathbf{0}$ and $r \leqslant L/2$, the source points are outside the sphere $S(O, r)$, which yields

$$\langle \varphi^{\mathscr{C}^3}(\mathbf{r})\rangle(r) = \frac{\exp(-\alpha r)}{r} + \frac{\xi}{L} \frac{\sinh(\alpha r)}{\alpha r} \tag{3.8}$$

where

$$\frac{\xi}{L} = \sum_{\mathbf{n}\neq\mathbf{0}} \frac{\exp(-\alpha L\, \|\mathbf{n}\|)}{L\, \|\mathbf{n}\|} \tag{3.9}$$

is equal to the energy of a unit point charge in the center of $\mathscr{C}^3$ within the potential created by its periodical images.

A third expression for $\varphi^{\mathscr{C}^3}(\mathbf{r})$ can be obtained by noting that the equation satisfied by $\varphi^{\mathscr{C}^3}(\mathbf{r})$ can also be seen as an ordinary Helmholtz equation in a cube of $\mathbb{R}^3$ with Neumann boundary conditions. Indeed, as a consequence of the periodicity, the normal derivative $\partial_n \varphi^{\mathscr{C}3}$ vanishes on the surface of the cube. $\varphi^{\mathscr{C}3}(\mathbf{r})$ can thus be written as the sum of a particular solution of Eq. (3.1) (with $\mathbf{r}_0 = \mathbf{0}$) and the solution of the associated homogeneous Helmholtz equation, i.e.,

$$\varphi^{\mathscr{C}3}(\mathbf{r}) = \frac{\exp(-\alpha r)}{r} + \delta\varphi^{\mathscr{C}3}(\mathbf{r}) \qquad (\forall \mathbf{r} \in \mathscr{C}^3) \tag{3.10}$$

where $\delta\varphi^{\mathscr{C}3}(\mathbf{r})$ is solution of

$$[\Delta_r - \alpha^2]\, \delta\varphi^{\mathscr{C}3}(\mathbf{r}) = 0 \qquad (\forall \mathbf{r} \in \mathscr{C}^3) \tag{3.11}$$

Equation (3.11) must be supplemented by specifying the (homogeneous) boundary conditions ($\partial_n \delta\varphi^{\mathscr{C}3} = -\partial_n[\exp(-\alpha r)/r]$ on the surface of the cube). Equation (3.10) furnishes another starting point to obtain the spherical average of $\varphi^{\mathscr{C}3}$. Since $\delta\varphi^{\mathscr{C}3}(\mathbf{r})$ satisfies the homogeneous Helmholtz equation (3.11), Eq. (2.9) can be employed which yields readily

$$\langle \varphi^{\mathscr{C}3}(\mathbf{r}) \rangle (r) = \frac{\exp(-\alpha r)}{r} + \delta\varphi^{\mathscr{C}3}(\mathbf{0})\, \frac{\sinh(\alpha r)}{\alpha r} \tag{3.12}$$

Of course Eqs. (3.8) and (3.12) coincide, which implies that $\delta\varphi^{\mathscr{C}3}(\mathbf{0}) \equiv \xi/L$. Finally it follows trivially from Eqs. (3.10) and (3.12) that

$$\delta\varphi^{\mathscr{C}3}(\mathbf{0}) = \xi/L = \lim_{r \to 0} \left(\varphi^{\mathscr{C}3}(\mathbf{r}) - \frac{\exp(-\alpha r)}{r} \right) \tag{3.13}$$

B. Distribution of Yukawa Charges

We look at periodical solutions of

$$(\Delta_{\mathbf{r}} - \alpha^2)\, \varphi_n^{\mathbb{R}^3}(\mathbf{r}) = -4\pi n(\mathbf{r}) \qquad (\mathbf{r} \in \mathscr{C}^3) \tag{3.14}$$

for simple distributions of Yukawa charges $n^{\mathscr{C}3}(\mathbf{r})$ in space $\mathscr{C}^3$.

1. Uniform Background. The potential $\varphi_b^{\mathscr{C}3}$ of a uniform background $n^{\mathscr{C}3}(\mathbf{r}) \equiv n_b$ ($\forall \mathbf{r} \in \mathscr{C}^3$) is well defined—contrary to the pure Coulombic case—and still obviously given by $\varphi_b^{\mathscr{C}3} = 4\pi n_b/\alpha^2$. Let us define a pseudo-charge q of $\mathscr{C}^3$ as the association of a point charge q and a neutralizing uniform background of total charge $-q$.[4, 7] The potential $\bar{\varphi}^{\mathscr{C}3}$ of a unit pseudo-charge reads

$$\bar{\varphi}^{\mathscr{C}3}(\mathbf{r}) = \varphi^{\mathscr{C}3}(\mathbf{r}) + \varphi_b^{\mathscr{C}3} = \frac{4\pi}{L^3} \sum_{\mathbf{k}\neq\mathbf{0}} \frac{1}{\mathbf{k}^2+\alpha^2} \exp(i\mathbf{r}\cdot\mathbf{k}) \tag{3.15}$$

since the term $\mathbf{k}=\mathbf{0}$ of the expansion (3.2) of $\varphi^{\mathscr{C}3}(\mathbf{r})$ has been killed by the background contribution. This potential $\bar{\varphi}^{\mathscr{C}3}$ will enter the definition of the hamiltonian of the YOCP (see below). In the limit $\alpha \to 0$, $\bar{\varphi}^{\mathscr{C}3}$ tends to the well known Ewald potential $\psi_{Ew}(\mathbf{r})$—i.e., the potential of a true charge plus its neutralizing background in $\mathscr{C}^3$ [1, 2, 7]—although each of the terms $\varphi^{\mathscr{C}3}$ and $\varphi_b^{\mathscr{C}3}$ diverge in this limit. It follows from the results of the previous section that the spherical average of $\bar{\varphi}^{\mathscr{C}3}$ can be written, for $r \leqslant L/2$, as

$$\begin{aligned}\langle \bar{\varphi}^{\mathscr{C}3} \rangle(r) &= \langle \varphi^{\mathscr{C}3} \rangle(r) - \frac{4\pi}{\alpha^2 L^3} \\ &= \frac{\exp(-\alpha r)}{r} + \frac{4\pi}{\alpha^2 L^3}\left[\frac{\sinh(\alpha r)}{\alpha r} - 1\right] + \frac{\sinh(\alpha r)}{\alpha r}\frac{\bar{\xi}}{L}\end{aligned} \tag{3.16}$$

where

$$\begin{aligned}\frac{\bar{\xi}}{L} &= \lim_{r\to 0}\,[\bar{\varphi}^{\mathscr{C}3}(\mathbf{r}) - \exp(-\alpha r)/r] = \frac{1}{L}\sum_{\mathbf{n}\neq\mathbf{0}} \frac{\exp(-\alpha L\,\|\mathbf{n}\|)}{\|\mathbf{n}\|} - \frac{4\pi}{\alpha^2 L^3} \\ &= \frac{\xi}{L} - \frac{4\pi}{\alpha^2 L^3}\end{aligned} \tag{3.17}$$

The constant $\bar{\xi}/L$ can thus be interpreted as twice the Madelung energy of a simple cubic lattice of unit Yukawa charges immerged in a neutralizing background. In the limit $\alpha \to 0$, $\bar{\varphi}^{\mathscr{C}3} \to \psi_{Ew}$ and therefore $\bar{\xi}$ tends to twice the Madelung constant of a simple cubic Wigner lattice of unit charges and unit spacing $L=1$, i.e., $\xi_{Ew} = \lim_{r\to 0}[\psi_{Ew}(\mathbf{r}) - 1/r] = -2,837297479....$[1, 2] Note that, in the limit $\alpha \to 0$, the constant ξ diverges as $\sim 4\pi/(\alpha L)^2$ as a consequence of Eq. (3.17).

As pointed out by one of us, the sphericalised potential $\langle \bar{\varphi}^{\mathscr{C}3} \rangle(r)$ of Eq. (3.16) can be used instead of the exact $\bar{\varphi}^{\mathscr{C}3}(\mathbf{r})$ in MC simulations of the YOCP in cubic geometries with good practical results.[12, 13, 19]

2. Spherical Surfacic Distributions of Charges. Let us consider a sphere $\mathscr{S}(O, a)$ of radius $a \leqslant L/2$ located at the center of the cube with a total (screened) charge q uniformly distributed over its surface.

We denote by $\sigma = q/(4\pi a^2)$ the surfacic distribution of charge. The potential $\varphi_\sigma^{\mathscr{C}3}$ of this distribution of charges is given by

$$\varphi_\sigma^{\mathscr{C}3}(\mathbf{r}) = q \int_{\mathscr{S}(O,\, a)} \frac{d\Omega(\mathbf{a})}{4\pi}\, \varphi^{\mathscr{C}3}(\mathbf{r}-\mathbf{a}) \tag{3.18}$$

Inserting the expression (3.10) of $\varphi^{\mathscr{C}3}$ in the above equation yields

$$\begin{aligned} \varphi_\sigma^{\mathscr{C}3}(\mathbf{r}) &= \varphi_\sigma^{\mathbb{R}^3}(\mathbf{r}) + q \int_{\mathscr{S}(O,\, a)} \frac{d\Omega(\mathbf{a})}{4\pi}\, \delta\varphi(\mathbf{r}-\mathbf{a}) \\ &= \varphi_\sigma^{\mathbb{R}^3}(\mathbf{r}) + q\, \frac{\sinh(\alpha a)}{\alpha a}\, \delta\varphi(\mathbf{r}) \end{aligned} \tag{3.19}$$

where, once again, we have employed Eq. (2.9). It follows from Eqs. (2.11) and (3.10) that Eq. (3.19) can be rewritten as

$$\begin{aligned} \varphi^{\mathscr{C}3}(\mathbf{r}) &= q_\sigma(\alpha)\, \varphi^{\mathscr{C}3}(\mathbf{r}) && \text{for} \quad r \geqslant a \\ &= q_\sigma(\alpha)\, \delta\varphi^{\mathscr{C}3}(\mathbf{r}) + q\, \frac{\sinh(\alpha r)}{\alpha r}\, \frac{\exp(-\alpha a)}{\alpha a} && \text{for} \quad r \leqslant a \end{aligned} \tag{3.20}$$

where the renormalized charge $q_\sigma(\alpha)$ has been defined at Eq. (2.12). The above result (3.20) is in fact trivial and reflects merely the fact that $\varphi_\sigma^{\mathscr{C}3}(\mathbf{r})$ can be seen as the potential of an infinite cubic array of charged Yukawa spheres. Mathematically, it is a consequence of the absolute convergence (for $r \neq 0$) of the series (3.6) which gives the potential $\varphi^{\mathscr{C}3}(\mathbf{r})$. A direct calculation of the self-energy yields

$$\begin{aligned} \mathscr{E}_\sigma^{\mathscr{C}3} &= \frac{1}{2} \int_{\mathscr{C}3} d^3\mathbf{r}\, n_\sigma(\mathbf{r})\, \varphi_\sigma^{\mathscr{C}3}(\mathbf{r}) \\ &= \frac{q q_\sigma(\alpha)}{2} \int_{\mathscr{S}(O,\, a)} \frac{d\Omega(\mathbf{a})}{4\pi} \left[\frac{\exp(-\alpha a)}{\alpha a} + \delta\varphi^{\mathscr{C}3}(\mathbf{a}) \right] \\ &= \mathscr{E}_\sigma^{\mathbb{R}^3} + \frac{q_\sigma(\alpha)^2}{2}\, \delta\varphi^{\mathscr{C}3}(\mathbf{0}) \end{aligned} \tag{3.21}$$

Since, from the discussion of Section IIIA, $q_\sigma(\alpha)^2\, \delta\varphi^{\mathscr{C}3}(\mathbf{0})$ is equal to the interaction energy of the sphere with its periodical images the result (3.21) is once again trivial.

Similarly the interaction energy of two non-overlaying spheres of $\mathscr{C}^3$ is given of course by

$$\Phi_{12,\,\sigma}^{\mathscr{C}3} = q_{1,\,\sigma}(\alpha)\, q_{2,\,\sigma}(\alpha)\, \varphi^{\mathscr{C}3}(\mathbf{r}_{12}) \qquad \text{for} \quad r_{12} \geqslant 2a \tag{3.22}$$

3. Spherical Volumic Distributions of Charges. We just quote the results in the case of spheres of radius a with a uniform charge density $\rho = 3q/(4\pi a^3)$. With obvious notations one finds

$$\varphi^{\mathscr{C}^3}(\mathbf{r}) = q_\rho(\alpha)\,\varphi^{\mathscr{C}^3}(\mathbf{r}) \qquad \text{for} \quad r \geqslant a \tag{3.23a}$$

$$\mathscr{E}_\rho^{\mathscr{C}^3} = \mathscr{E}_\rho^{\mathbb{R}^3} + \frac{q_\rho(\alpha)^2}{2}\,\delta\varphi^{\mathscr{C}^3}(\mathbf{0}) \tag{3.23b}$$

$$\Phi_{12,\rho}^{\mathscr{C}^3} = q_{1,\rho}(\alpha)\,q_{2,\rho}(\alpha)\,\varphi^{\mathscr{C}^3}(\mathbf{r}_{12}) \qquad \text{for} \quad r_{12} \geqslant a_1 + a_2 \tag{3.23c}$$

where the renormalized charge $q_\rho(\alpha)$ has been defined at Eq. (2.16). It is not difficult to show that, in the case of charges of the same sign

$$(\forall \mathbf{r} \in \mathscr{C}^3) \qquad \Phi_{12,\rho}^{\mathscr{C}^3}(\mathbf{r}) \leqslant q_{1,\rho}^{\mathscr{C}^3}(\alpha)\,q_{2,\rho}^{\mathscr{C}^3}(\alpha)\,\varphi^{\mathscr{C}^3}(\mathbf{r}) \tag{3.24}$$

the equality being satisfied only for $r \geqslant a_1 + a_2$.

C. YRPM

The electrostatic configurational energy of the YRPM in $\mathscr{C}^3$ is given by[20, 21]

$$V_{\mathrm{YRPM}}^{\mathscr{C}^3}(1, 2..., N) = \frac{1}{2}\sum_{i \neq j} q_i q_j \varphi^{\mathscr{C}^3}(\mathbf{r}_{ij}) + \frac{N}{2} q^2\,\delta\varphi^{\mathscr{C}^3}(\mathbf{0}) \tag{3.25}$$

$V_{\mathrm{YRPM}}^{\mathscr{C}^3}$ includes the pair interactions as well as the N individual energies $q^2\,\delta\varphi^{\mathscr{C}^3}(\mathbf{0})/2$ of each charge with its periodical images. In Section IIC we have derived an extensive lower bound for the energy of the YRPM in $\mathbb{R}^3$. Since the YRPM in $\mathscr{C}^3$ can be seen as an infinite system made of periodic images of the basic cubic cell $\mathscr{C}^3$, it may seem obvious a priori that the bound (2.24) is still valid in $\mathscr{C}^3$. However, in this picture, the configurational energy $V_{\mathrm{YRPM}}^{\mathscr{C}^3}$ represents the energy of a subsystem of the infinite—periodic—system and this hasty conclusion could be dubious. A direct check is worthwhile. As in Section IIC we spread the charges uniformly on the surfaces of the spheres leaving unchanged the pair potentials (c.f. Section IIIB2). The energy $\mathscr{W}^{\mathscr{C}^3}$ of the total charge distribution is positive and can be written

$$\mathscr{W}^{\mathscr{C}^3} = \tfrac{1}{2}\sum_{i \neq j} q_i q_j \varphi^{\mathscr{C}^3}(\mathbf{r}_{ij}) + N\mathscr{E}_\sigma^{\mathscr{C}^3} \geqslant 0 \tag{3.26}$$

Combining Eqs. (3.25) and (3.26) and making use of identity (3.21) one finds that for non overlaping configurations of spheres

$$\begin{aligned} V^{\mathscr{C}3}_{\mathbf{YRPM}}(1, 2..., N) &\geqslant \frac{N}{2} q^2\, \delta\varphi^{\mathscr{C}3}(\mathbf{0}) - N\mathscr{E}^{\mathscr{C}3}_{\sigma} \\ &\geqslant -N\mathscr{E}^{\mathbb{R}^3}_{\sigma} = N\mathscr{B}^{\mathbb{R}^3}_{\mathbf{YRPM}} \end{aligned} \tag{3.27}$$

where we have used Eq. (3.21). The bound (2.24) for the YRPM in $\mathbb{R}^3$ still holds in $\mathscr{C}^3$.

D. YOCP

The configurational energy of the YOCP in $\mathscr{C}^3$ has been given by Hubbard and Slattery.[18] It reads

$$V^{\mathscr{C}3}_{\mathbf{YOCP}} = V^{\mathscr{C}3}_{\mathbf{OCP}} + \frac{q^2}{2}\frac{4\pi}{L^3} \sum_{i,\,j}^{N} \sum_{\mathbf{k}\neq\mathbf{0}} \exp[i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_j)](\varepsilon(\mathbf{k})^{-1} - 1)/\mathbf{k}^2 \tag{3.28}$$

where $V^{\mathscr{C}3}_{\mathbf{OCP}}$ is the configurational energy of the OCP and $\varepsilon(\mathbf{k})$ a dielectric constant which takes into account the background charge fluctuations. $V^{\mathscr{S}3}_{\mathbf{OCP}}$ has the following expression[1]

$$\begin{aligned} V^{\mathscr{C}3}_{\mathbf{OCP}} &= N\mathscr{A}^{\mathscr{C}3}_{\mathbf{OCP}} + \frac{q^2}{2} \sum_{i\neq j}^{N} \psi_{Ew}(\mathbf{r}_{ij}) \\ \mathscr{A}^{\mathscr{C}3}_{\mathbf{OCP}} &= \frac{q^2}{2L}\, \xi_{Ew} \end{aligned} \tag{3.29}$$

where $\psi_{Ew} \equiv \bar{\varphi}^{\mathscr{C}3}$ $(\alpha = 0)$ is the Ewald potential and ξ_{Ew} the Madelung constant of the OCP (c.f. Section IIIB1).

If the dielectric constant $\varepsilon(\mathbf{k})$ is given by Eq. (2.4) we recover Yukawa interactions. With the notations of Sections IIIA and IIIB1) $V^{\mathscr{C}3}_{\mathbf{YOCP}}$ can be rewritten either as

$$\begin{aligned} V^{\mathscr{C}3}_{\mathbf{YOCP}} &= N\mathscr{A}^{\mathscr{C}3}_{\mathbf{YOCP}} + \frac{q^2}{2} \sum_{i\neq j}^{N} \bar{\varphi}^{\mathscr{C}3}(\mathbf{r}_{ij}) \\ \mathscr{A}^{\mathscr{C}3}_{\mathbf{YOCP}} &= \mathscr{A}^{\mathscr{C}3}_{\mathbf{OCP}} + \delta\mathscr{A}^{\mathscr{C}3}_{\mathbf{YOCP}} \end{aligned} \tag{3.30}$$

or

$$
\begin{aligned}
V^{\mathscr{C}^3}_{\text{YOCP}} &= N\bar{\mathscr{A}}^{\mathscr{C}^3}_{\text{YOCP}} - \frac{N}{2} n \frac{4\pi q^2}{\alpha^2} + \frac{q^2}{2} \sum_{i \neq j}^{N} \varphi^{\mathscr{C}^3}(\mathbf{r}_{ij}) \\
\bar{\mathscr{A}}^{\mathscr{C}^3}_{\text{YOCP}} &= \mathscr{A}^{\mathscr{C}^3}_{\text{YOCP}} + \frac{1}{2} \frac{4\pi q^2}{\alpha^2 L^3}
\end{aligned}
\tag{3.31}
$$

where $n = N/L^3$ denotes the number density of ions. The additional constant $\delta\mathscr{A}^{\mathscr{C}^3}_{\text{YOCP}}$ in Eq. (3.30) originates from the terms $i = j$ in the r.h.s. of Eq. (3.28), i.e.,

$$
\begin{aligned}
\delta\mathscr{A}^{\mathscr{C}^3}_{\text{YOCP}} &= \frac{q^2}{2} \frac{4\pi}{L^3} \sum_{\mathbf{k} \neq \mathbf{0}} \left[\frac{1}{\varepsilon(\mathbf{k})} - 1 \right] \Big/ \mathbf{k}^2 \\
&= \frac{q^2}{2L} \lim_{r \to 0} \left[\bar{\varphi}^{\mathscr{C}^3}(\mathbf{r}) - \psi_{Ew}(\mathbf{r}) \right] = \frac{q^2}{2L} \left[-\xi_{Ew} + \bar{\xi} \right] - \frac{q^2 \alpha}{2}
\end{aligned}
\tag{3.32}
$$

where the Madelung constants $\bar{\xi}$ and ξ_{Ew} have been defined in Section IIIB1. Note that in the limit $\alpha \to 0$, $\bar{\xi} \to \xi_{Ew}$ and thus $\delta\mathscr{A}^{\mathscr{C}^3}_{\text{YOCP}} \to 0$, as it should. Moreover in the limits $\alpha \to \infty$, L fixed or alternatively $L \to \infty$, α fixed one has $\beta\delta\mathscr{A}^{\mathscr{L}^3}_{\text{YOCP}} \sim -\alpha^* \Gamma/2$. It follows from Eqs. (3.30), (3.32), and (3.17) that

$$
\bar{\mathscr{A}}^{\mathscr{C}^3}_{\text{YOCP}} = \frac{q^2}{2} \left(\delta\varphi^{\mathscr{C}^3}(\mathbf{0}) - \alpha \right) \tag{3.33}
$$

We want to show now that the lower bound on $V^{\mathbb{R}^3}_{\text{YOCP}}$ derived by Rosenfeld[22] remains valid for $V^{\mathscr{C}^3}_{\text{YOCP}}$. In order to do so, we replace each point charge q by a sphere of radius a with a charge q^0_ρ uniformly distributed over its volume. The value of q^0 is chosen such that the effective charge q^0_ρ associated with it is equal to q (c.f. Eq. (2.16)). q being fixed, q^0 is therefore a function of a. Moreover we associate to these spheres a uniform background of charge density $-Nq^0/L^3$. The, electrostatic energy of these N spheres in their background is well defined (i.e., non-diverging), positive and can be written

$$
\mathscr{W} = N\mathscr{E}^{\mathscr{C}^3}_{\rho} + \frac{1}{2} \sum_{i \neq j} \Phi^{\mathscr{C}^3}_{ij,\rho} - \frac{N}{2} n \frac{4\pi q_0^2}{\alpha^2} \geqslant 0 \tag{3.34}
$$

where the expressions of the self-energy $\mathscr{E}^{\mathscr{C}^3}_{\rho}$ and the pair-interactions $\Phi^{\mathscr{C}^3}_{ij,\rho}$ have been given in Section IIIB3. Adding and subtracting $\mathscr{W}$ in the r.h.s of Eq. (3.31) yields

$$
\begin{aligned}
V^{\mathscr{C}^3}_{\text{YOCP}} &= \frac{1}{2} Nq^2(\delta\varphi^{\mathscr{C}^3}(\mathbf{0}) - \alpha) - \frac{N}{2} n \frac{4\pi[q^2 - q_0^2]}{\alpha^2} \\
&\quad + \frac{1}{2} \sum_{i \neq j}^{N} (q^2 \varphi^{\mathscr{C}^3}((\mathbf{r}_{ij}) - \Phi^{\mathscr{C}^3}_{ij, \rho}) + \mathscr{W} - N\mathscr{E}^{\mathscr{C}^3}_{\rho} \\
&\geqslant \frac{1}{2} Nq^2(\delta\varphi^{\mathscr{C}^3}(\mathbf{0}) - \alpha) - N\left(\mathscr{E}^{\mathscr{C}^3}_{\rho} + \frac{1}{2} n \frac{4\pi}{\alpha^2} [q^2 - q_0^2]\right)
\end{aligned} \tag{3.35}
$$

where we have made use of the inequalities (3.24) and (3.34). Since the self-energy $\mathscr{E}^{\mathscr{C}^3}_{\rho}$ is simply related to that in $\mathbb{R}^3$ (c.f. Eq. (3.23b) we obtain finally

$$
\begin{aligned}
&\beta V^{\mathscr{C}^3}_{\text{YOCP}} \geqslant N\mathscr{B}^{\mathscr{C}^3}_{\text{YOCP}}(a) \\
&\beta^{-1}\mathscr{B}^{\mathscr{C}^3}_{\text{YOCP}}(a) = -\frac{q^2\alpha}{2} - \mathscr{E}^{\mathbb{R}^3}_{\rho}(a) - \frac{1}{2} n \frac{4\pi}{\alpha^2} [q^2 - q_0^2(a)]
\end{aligned} \tag{3.36}
$$

The result for $\mathscr{B}^{\mathscr{C}^3}_{\text{YOCP}}(a)$ is identical to that obtained by Rosenfeld in $\mathbb{R}^3$.[22] The best bound is obtained by maximizing $\mathscr{B}^{\mathscr{C}^3}_{\text{YOCP}}(a) \equiv \mathscr{B}^{\mathbb{R}^3}_{\text{YOCP}}(a)$ with respect to the diameter a. One finds that a must be chosen equal to the ionic radius. Therefore

$$
\beta V^{\mathscr{C}^3}_{\text{YOCP}} \geqslant N\mathscr{B}^{\mathbb{R}^3}_{\text{YOCP}} \tag{3.37}
$$

where $\mathscr{B}^{\mathbb{R}^3}_{\text{YOCP}}$ is given by Eq. (2.27). Note that the result (3.37), as in the case of the YRPM, although physically reasonable, is not trivial.

IV. YUKAWA SYSTEMS IN $\mathscr{S}^3$

A. Point-Charges

The Green's function $\mathscr{G}^{\mathscr{S}^3}(M, M_0)$ of the Helmholtz equation in $\mathscr{S}^3$ reads

$$
(\Delta^{\mathscr{S}^3}_{M} - \alpha^2)\, \mathscr{G}^{\mathscr{S}^3}(M, M_0) = -4\pi\delta^{\mathscr{S}^3}(M, M_0) \qquad (\forall M, M_0 \in \mathscr{S}^3) \tag{4.1}
$$

To solve (4.1) we expand both the Green function $\mathscr{G}^{\mathscr{S}^3}(M, M_0)$ and the Dirac distribution $\delta^{\mathscr{S}^3}(M, M_0)$ upon the complete, orthogonal basis set of 4D spherical harmonics $Y_{L,m}$.[4, 5, 27–29]

$$
\delta^{\mathscr{S}^3}(M, M_0) = \frac{1}{R^3} \sum_{L=0}^{\infty} \sum_{m} Y^*_{L,m}(M_0)\, Y_{L,m}(M) \tag{4.2}
$$

$$
\mathscr{G}^{\mathscr{S}^3}(M, M_0) = \sum_{L=0}^{\infty} \sum_{m} \mathscr{G}_{L,m}(M_0)\, Y_{L,m}(M) \tag{4.3}
$$

The 4D spherical harmonics $Y_{L,\mathbf{m}}$ identify with the Wigner functions $\mathscr{D}^{L/2}_{m_1,m_2}$ with L integer. $\mathbf{m}=(m_1, m_2)$ and m_i $(i=1, 2)$ takes the $L+1$ values $m_i = -L/2, -L/2+1,..., L/2$. These functions play in $\mathscr{S}^3$ the role devoted to the plane waves in $\mathscr{C}^3$. In particular the $Y_{L,\mathbf{m}}$ are eigenfunctions of the Laplace–Beltrami operator $\Delta^{\mathscr{S}^3}$ with eigenvalues $-L(L+2)/R^2$.[27–29] It follows from this remark that

$$\mathscr{G}_{L,\mathbf{m}}(M_0)=\frac{4\pi}{R}\frac{1}{L(L+2)+\alpha^2R^2}\,Y^*_{L,\mathbf{m}}(M_0) \tag{4.4}$$

which solves Eq. (4.1). Moreover the spherical harmonics satisfy an addition theorem[4, 5, 27–29]

$$\sum_{\mathbf{m}} Y^*_{L,\mathbf{m}}(M_0)\; Y_{L,\mathbf{m}}(M)=\frac{L+1}{2\pi^2}\frac{\sin(L+1)\,\psi_{M,M_0}}{\sin\psi_{M,M_0}} \tag{4.5}$$

$$\psi_{M,M_0}=\arccos\left(\frac{\mathbf{OM}\cdot\mathbf{OM_0}}{R^2}\right) \tag{4.6}$$

from which it follows that

$$\mathscr{G}^{\mathscr{S}^3}(M, M_0)=\frac{2}{\pi R\sin\psi_{M,M_0}}\sum_{L=0}^{\infty}\frac{L+1}{L(L+2)+\alpha^2R^2}\sin(L+1)\,\psi_{M,M_0} \tag{4.7}$$

As a consequence of the isotropy of $\mathscr{S}^3$ the Green function $\mathscr{G}^{\mathscr{S}^3}(M, M_0)$ depends on the sole geodesic distance $x_{M,M_0}=R\psi_{M,M_0}$ between the points M and M_0.

The series (4.7) can be summed with the result

$$\mathscr{G}^{\mathscr{S}^3}(M, M_0)=\frac{1}{R}\frac{\sinh\omega(\pi-\psi_{M,M_0})}{\sin\psi_{M,M_0}\sinh\omega\pi}\qquad\text{for}\quad \alpha R\geqslant 1 \tag{4.8}$$

$$=\frac{1}{R}\frac{\sin\omega(\pi-\psi_{M,M_0})}{\sin\psi_{M,M_0}\sin\omega\pi}\qquad\text{for}\quad \alpha R\leqslant 1 \tag{4.9}$$

with $\omega=\sqrt{|\alpha^2R^2-1|}$. It turns out that the analytical expression of $\mathscr{G}^{\mathscr{S}^3}(M, M_0)$ changes at $\alpha R=1$, an often met curiosity of the Helmholtz equation.[16] $\mathscr{G}^{\mathscr{S}^3}(M, M_0)$ is singular for $M=M_0$. More precisely we note that, at a given $x_{M,M_0}=R\psi_{M,M_0}$ and in the limit $R\to\infty$, or equivalently at a given R and in the limit $\psi_{M,M_0}\to 0$ the Green function $\mathscr{G}^{\mathscr{S}^3}(M, M_0)$ tends to the Euclidean Green function in $\mathbb{R}^3$, i.e., $\mathscr{G}^{\mathscr{S}^3}(M, M_0)\sim \exp(-\alpha x_{M,M_0})/x_{M,M_0}$.

As in the previous sections $\mathscr{G}^{\mathscr{S}^3}(M, M_0)$ identify with the potential at point M of a unit Yukawa point charge located at point M_0. Henceforth we shall note $\varphi^{\mathscr{S}^3}(\psi_{M, M_0}) \equiv \mathscr{G}^{\mathscr{S}^3}(M, M_0)$. Note that the Property (3.3) still holds in $\mathscr{S}^3$; indeed it follows from Eq. (4.7) that

$$\int_{\mathscr{S}^3} d\tau(M)\, \varphi^{\mathscr{S}^3}(M) = \frac{4\pi}{\alpha^2} \tag{4.10}$$

where $d\tau(M)$ is the infinitesimal volume element of $\mathscr{S}^3$.

B. Distribution of Yukawa Charges

We look at solutions of

$$(\Delta_M^{\mathscr{S}^3} - \alpha^2)\, \varphi_n^{\mathscr{S}^3}(M) = -4\pi n(M) \qquad (\forall M \in \mathscr{S}^3) \tag{4.11}$$

for simple distributions of Yukawa charges $n(M)$ on the hypersphere.

1. Uniform Background. Let us first consider a uniform background $n(M) \equiv n_b$ $(\forall M \in \mathscr{S}^3)$. We look at a general solution of Eq. (4.11) with an axial symmetry. i.e., a solution of the type $\varphi_{n_B}^{\mathscr{S}^3}(w)$ where w denotes the colatitude of point M: $w = \arccos(\mathbf{OM} \cdot \mathbf{x}_4/R)$, where $\mathbf{x}_4$ is the fourth vector of an orthonormal basis $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4)$ of $\mathbb{R}^4$. Note that Rw is the geodesic distance between the north pole N of $\mathscr{S}^3$ and the point M.

In spherical coordinates Eq. (4.11) reads[5, 27–29]

$$\left[\frac{1}{R^2 \sin^2 w} \frac{\partial}{\partial w} \sin^2 w \frac{\partial}{\partial w} - \alpha^2\right] \varphi_{n_B}^{\mathscr{S}^3}(w) = -4\pi n_b \tag{4.12}$$

the general solution of which is easily obtained and reads

$$\begin{aligned} \varphi_{n_B}^{\mathscr{S}^3}(w) &= A\, \frac{\sinh \omega w}{\sin w} + B\, \frac{\sinh \omega(\pi - w)}{\sin w} + \frac{4\pi n_b}{\alpha^2} \qquad \text{if} \quad \alpha R \geqslant 1 \\ &= A\, \frac{\sin \omega w}{\sin w} + B\, \frac{\sin \omega(\pi - w)}{\sin w} + \frac{4\pi n_b}{\alpha^2} \qquad \text{if} \quad \alpha R \leqslant 1 \end{aligned} \tag{4.13}$$

A, B are arbitrary constants and ω was defined in Section IVA. The solution $\varphi_{n_B}^{\mathscr{S}^3}(w)$ is singular at $w = 0$ if $B \neq 0$ and at $w = \pi$ if $A \neq 0$. These singularities are a consequence of the singularities at $w = 0$, π of the Laplacian operator in spherical coordinates; they correspond to two Dirac masses at the north and south pole of the sphere. For $n_b = 0$ the singular solution $A=0$, $B\neq 0$ of Eq. (4.13) is solution of the homogeneous Helmholtz equation with a singularity at $w=0$. Therefore it should coincide with the potential of a point charge located at the North pole of the hypersphere. Choosing B in such a way that Eq. (4.10) is satisfied gives indeed again Eq. (4.9). Finally we note that, for $n_B\neq 0$, the regular solution $(A=B=0)$ of Eq. (4.13) is the same constant than in $\mathbb{R}^3$ and $\mathscr{C}^3$.

As in $\mathscr{S}^3$ we define a pseudo Yukawa charge q as the association of a bare charge q and a uniform neutralizing background of density $n_b=-q/\Lambda$ where $\Lambda=2\pi^2R^3$ is the volume of $\mathscr{S}^3$. The potential $\bar{\varphi}^{\mathscr{C}^3}(w)$ of unit point pseudo-charge located at the north-pole reads

$$\bar{\varphi}^{\mathscr{S}^3}(w)=\varphi^{\mathscr{S}^3}(w)-\frac{4\pi}{\alpha^2\Lambda}=\frac{2}{\pi R\sin w}\sum_{L=1}^{\infty}\frac{L+1}{L(L+2)+\alpha^2R^2}\sin(L+1)\,w \tag{4.14}$$

As in the case of $\mathscr{C}^3$, the contribution of the background kills the term $L=0$ in the expansion of $\varphi^{\mathscr{C}^3}(w)$ upon the eigenfunctions of the Laplace operator. It follows from Eq. (4.10) that the integral of $\bar{\varphi}^{\mathscr{S}^3}$ over $\mathscr{S}^3$ vanishes. In the limit $\alpha\to 0$ the potential $\bar{\varphi}^{\mathscr{S}^3}(w)$ is regular for $w\neq 0$ and one checks that

$$\forall w\in\,]0,\pi]\ \lim_{\alpha\to 0}\bar{\varphi}^{\mathscr{S}^3}(w)\equiv\psi^{\mathscr{S}^3}(w)=\frac{1}{\pi R}\left[(\pi-w)\cot(w)-\frac{1}{2}\right] \tag{4.15}$$

an expression which coincides with the potential $\psi^{\mathscr{S}^3}(w)$ of a coulombic pseudo-charge in $\mathscr{S}^3$.[4, 5, 7]

2. Spherical Surfacic Distributions of Charges. Let us consider a sphere $\mathscr{S}(N,a)$ of radius $a=Rw_0$ located at the north pole N of the hypersphere. It is defined as the set of points M at a geodesic distance $Rw\leqslant a$ from N. It is not a flat object but rather a curved one which can be seen as a contact lense on a 4D eye-ball. The sphere is charged with a charge q uniformly spread over its surface $s(w_0)=4\pi R^2\sin^2 w_0$.[4, 5, 7] The associated density of charge is $n_\sigma(M)=\sigma\delta(Rw-Rw_0)$, $\sigma=q/s(w_0)$ and the potential $\varphi_\sigma^{\mathscr{S}^3}(M)$ reads

$$\varphi_\sigma^{\mathscr{S}^3}(M)=\int_{\mathscr{S}^3}d\tau(M')\,n_\sigma(M')\,\mathscr{G}^{\mathscr{S}^3}(M',M) \tag{4.16}$$

It follow from Eq. (4.10) that

$$\int_{\mathscr{S}^3}d\tau\,\varphi_\sigma^{\mathscr{S}^3}(M)=\frac{4\pi q}{\alpha^2} \tag{4.17}$$

A direct calculation by means of Eq. (4.16) seems difficult and we take advantage of the symmetry property $\varphi_\sigma^{\mathscr{S}^3}(M) \equiv \varphi_\sigma^{\mathscr{S}^3}(w)$ to compute $\varphi_\sigma^{\mathscr{S}^3}(w)$ by making use of the results of Section IVB1. In both regions $0 \leqslant w \leqslant w_0$ and $w_0 \leqslant w \leqslant \pi$ $\varphi_\sigma^{\mathscr{S}^3}(w)$ is a regular solution of the homogeneous Helmholtz equation and we can therefore use Eqs. (4.13) with $n_b \equiv 0$. The constants A and B which enters Eq. (4.13) must be chosen in such a way that $\varphi_\sigma^{\mathscr{S}^3}(w)$ is regular for $w = 0$ and $w = \pi$. In the case $\alpha R \geqslant 1$ we can thus write

$$\begin{aligned} 0 \leqslant w \leqslant w_0 \qquad & \varphi_\sigma^{\mathscr{S}^3}(w) = A_1 \frac{\sinh \omega w}{\sin w} \\ w_0 \leqslant w \leqslant \pi \qquad & \varphi_\sigma^{\mathscr{S}^3}(w) = A_2 \frac{\sinh \omega(\pi - w)}{\sin w} \end{aligned} \tag{4.18}$$

where the constant A_1 and A_2 remain to be specified. In the case $\alpha R \leqslant 1$ we have similar expressions but with, the sinh replaced by sin. The constants A_1 and A_2 are determined unambiguously by Eq. (4.17) and by the condition of continuity of the potential at $w = w_0$ i.e., in the case $\alpha R \geqslant 1$, by the relations

$$4\pi R^3 \int_0^\pi dw \sin^2 w \varphi_\sigma^{\mathscr{S}^3}(w) = \frac{4\pi q}{\alpha^2} \tag{4.19a}$$

$$A_1 \frac{\sinh \omega w_0}{\sin w_0} = A_2 \frac{\sinh \omega(\pi - w_0)}{\sin w_0} \tag{4.19b}$$

In the case $\alpha R \leqslant 1$, relations analogous to Eqs. (4.19) hold but with all the "sinh" replaced by "sin." Solving Eqs. (4.19) for A_1 and A_2 yields, for $\alpha R \geqslant 1$, to the desired result

$$\begin{aligned} 0 \leqslant w \leqslant w_0 \qquad & \varphi_\sigma^{\mathscr{S}^3}(w) = \frac{q}{R} \frac{\sinh \omega(\pi - w_0)}{\omega \sin w_0 \sinh \omega\pi} \frac{\sinh \omega w}{\sin w} \\ w_0 \leqslant w \leqslant \pi \qquad & \varphi_\sigma^{\mathscr{S}^3}(w) = \frac{q}{R} \frac{\sinh \omega w_0}{\omega \sin w_0 \sinh \omega\pi} \frac{\sinh \omega(\pi - w)}{\sin w} \end{aligned} \tag{4.20}$$

For $\alpha R \leqslant 1$ all the sinh entering the above equations must be replaced by sin functions.

As in the case of $\mathbb{R}^3$ and $\mathscr{C}^3$ it is convenient to define renormalized charges $q_\sigma^{\mathscr{S}^3}(\alpha)$ according to the relations

$$q_\sigma^{\mathscr{S}^3}(\alpha) = q \frac{\sin \omega w_0}{\omega \sin w_0} \qquad \alpha R \leqslant 1 = q \frac{\sinh \omega w_0}{\omega \sin w_0} \qquad \alpha R \geqslant 1 \tag{4.21}$$

A direct comparison of Eqs. (4.20) and (4.9) shows that

$$\forall w \in [0, \pi] \qquad \varphi_{\sigma}^{\mathcal{S}^3}(w) \leqslant q_{\sigma}^{\mathcal{S}^3}(\alpha)\, \varphi^{\mathcal{S}^3}(w) \tag{4.22}$$

the equality being satisfied only for $w \geqslant w_0$. It is easy to check that, in the Euclidean limit $R \to \infty$, we have $q_{\sigma}^{\mathcal{S}^3}(\alpha) \to q_{\sigma}(\alpha)$.

The self-energy of the sphere is given by

$$\mathscr{E}_{\sigma}^{\mathcal{S}^3} = \frac{1}{2} \int_{\mathcal{S}^3} d\tau\, n_{\sigma}(M)\, \varphi_{\sigma}^{\mathcal{S}^3}(M) = \frac{1}{2} q q_{\sigma}^{\mathcal{S}^3}(\alpha)\, \varphi_{\sigma}^{\mathcal{S}^3}(w_0) \tag{4.23}$$

and tends to the Euclidean value $\mathscr{E}_{\sigma}^{\mathbb{R}^3}$ for $R \to \infty$. Similarly, one finds that the interaction energy of two non-overlaping charged spheres of center M_1 and M_2 and respective charges (q_1, q_2) and radii (a_1, a_2) is given by

$$\Phi_{12,\sigma}^{\mathcal{S}^3} = q_{1,\sigma}^{\mathcal{S}^3}(\alpha)\, q_{2,\sigma}^{\mathcal{S}^3}(\alpha)\, \varphi^{\mathcal{S}^3}(\psi_{M_1, M_2}) \qquad (R\psi_{M_1 M_2} \geqslant a_1 + a_2) \tag{4.24}$$

Moreover, in the case of spheres bearing charges of the same sign, it follows from (4.22) that

$$\forall w \in [0, \pi] \qquad \Phi_{12,\sigma}^{\mathcal{S}^3}(w) \leqslant q_{1,\sigma}^{\mathcal{S}^3}(\alpha)\, q_{2,\sigma}^{\mathcal{S}^3}(\alpha)\, \varphi^{\mathcal{S}^3}(w) \tag{4.25}$$

3. Spherical Volumic Distributions of Charges. We consider a sphere $S(N, a \equiv Rw_0)$ with its center at the north pole of $\mathcal{S}^3$. Its total charge q is supposed to be distributed over its volume

$$v(Rw_0) = 2\pi R^3 (w_0 - \sin w_0 \cos w_0) \tag{4.26}$$

with a uniform density $\rho = q/v(Rw_0)$. The potential $\varphi_{\rho}^{\mathcal{S}^3}(w)$ of this distribution is determined either by integration of $\varphi_{\sigma}^{\mathcal{S}^3}(w)$ or, directly, following arguments similar to those of Section IVB2. For $\alpha R \geqslant 1$ one finds

$$\begin{aligned}
&0 \leqslant w \leqslant w_0 \varphi_{\rho}^{\mathcal{S}^3}(w) = A_1 \frac{\sinh \omega w}{\sin w} + \frac{4\pi\rho}{\alpha^2} \\
&w_0 \leqslant w \leqslant \pi \varphi_{\rho}^{\mathcal{S}^3}(w) = A_2 \frac{\sinh \omega(\pi - w)}{\sin w} \\
&A_1 = \frac{\sinh \omega(\pi - w_0)}{\sinh \omega w_0} A_2 - \frac{4\pi\rho}{\alpha^2} \frac{\sin w_0}{\sinh \omega w_0} \\
&A_2 = \frac{4\pi\rho}{\alpha^2} \frac{1}{\omega \sinh \omega\pi} [\omega \cosh \omega w_0 \sin w_0 - \sinh \omega w_0 \cos w_0]
\end{aligned} \tag{4.27}$$

In the case $\alpha R \leqslant 1$ all the hyperbolic functions in Eqs. (4.27) must be replaced by their trigonometric counterparts. Note that, of course, the condition (4.17) holds for $\varphi_{\rho}^{\mathscr{S}^3}(w)$. We define a renormalized charge $q_{\rho}^{\mathscr{S}^3}(\alpha)$ according to the relations

$$q_{\rho}^{\mathscr{S}^3}(\alpha) = \frac{4\pi q R}{\alpha^2 \omega v(R w_0)} [\omega \cosh \omega w_0 \sin w_0 - \sinh \omega w_0 \cos w_0] \qquad (\alpha R \leqslant 1)$$
$$= \frac{4\pi q R}{\alpha^2 \omega v(R w_0)} [\omega \cos \omega w_0 \sin w_0 - \sin \omega w_0 \cos w_0] \qquad (\alpha R \geqslant 1) \tag{4.28}$$

which allows to rewrite Eq. (4.27) in a more compact way

$$\forall w \in [0, \pi] \qquad \varphi_{\rho}^{\mathscr{S}^3}(w) \leqslant q_{\rho}^{\mathscr{S}^3}(\alpha)\, \varphi^{\mathscr{S}^3}(w) \tag{4.29}$$

the equality being satisfied only for $w \geqslant w_0$. It is easy to check that, in the Euclidean limit $R \to \infty$, we have $q_{\rho}^{\mathscr{S}^3}(\alpha) \to q_{\rho}(\alpha)$.

The self-energy of the sphere is given by

$$\mathscr{E}_{\rho}^{\mathscr{S}^3} = \frac{1}{2} \frac{4\pi q^2}{\alpha^2 v(R w_0)} + \frac{1}{2} \frac{\omega \sinh \omega(\pi - w_0)}{R \sinh \omega\pi \sinh \omega w_0} [q_{\rho}^{\mathscr{S}^3}(\alpha)]^2$$
$$- \frac{1}{2} \frac{4\pi}{\alpha^2} \frac{q q_{\rho}^{\mathscr{S}^3}(\alpha)}{\alpha^2 v(R w_0)} \frac{\omega \sin w_0}{\sinh \omega w_0} \qquad (\alpha R \geqslant 1)$$
$$= \frac{1}{2} \frac{4\pi q^2}{\alpha^2 v(R w_0)} + \frac{1}{2} \frac{\omega \sin \omega(\pi - w_0)}{R \sin \omega\pi \sin \omega w_0} [q_{\rho}^{\mathscr{S}^3}(\alpha)]^2$$
$$- \frac{1}{2} \frac{4\pi}{\alpha^2} \frac{q q_{\rho}^{\mathscr{S}^3}(\alpha)}{\alpha^2 v(R w_0)} \frac{\omega \sin w_0}{\sin \omega w_0} \qquad (\alpha R \leqslant 1) \tag{4.30}$$

and tends to the Euclidean value $\mathscr{E}_{\rho}^{\mathbb{R}^3}$ for $R \to \infty$. Similarly, one finds that the interaction energy of two non-overlaping charged spheres of center M_1 and M_2 and respective charges (q_1, q_2) and radii (a_1, a_2) is given by

$$\Phi_{12,\rho}^{\mathscr{S}^3} = q_{1,\rho}^{\mathscr{S}^3}(\alpha)\, q_{2,\rho}^{\mathscr{S}^3}(\alpha)\, \varphi^{\mathscr{S}^3}(\psi_{M_1 M_2}) \qquad (R\psi_{M_1 M_2} \geqslant a_1 + a_2) \tag{4.31}$$

Moreover, in the case of spheres hearing charges of the same sign, it follows from (4.29) that

$$\forall w \in [0, \pi] \qquad \Phi_{12,\rho}^{\mathscr{S}^3}(w) \leqslant q_{1,\rho}^{\mathscr{S}^3}(\alpha)\, q_{2,\rho}^{\mathscr{S}^3}(\alpha)\, \varphi^{\mathscr{S}^3}(w) \tag{4.32}$$

C. YRPM

We *define* the electrostatic energy of the YRPM in $\mathscr{S}^3$ as

$$V_{\mathbf{YRPM}}^{\mathscr{S}^3}(1, 2..., N) = \frac{1}{2} \sum_{i \neq j} q_i q_j \varphi^{\mathscr{S}^3}(\psi_{ij}) + N \mathscr{A}_{\mathbf{YRPM}}^{\mathscr{S}^3} \tag{4.33}$$

where $\mathscr{A}_{\mathbf{YRPM}}^{\mathscr{S}^3}$ is a constant which fixes the zero of energy of the system. An interesting problem concerning finite spaces such that $\mathscr{S}^3$ is how to define this zero of energy. In $\mathbb{R}^3$ the usual statement is that the energy of a system of N interacting particles vanishes when the particles are rejected to infinity. Obviously this prescription does not hold in a finite space such as $\mathscr{S}^3$. In space $\mathscr{C}^3$ the same problem holds but can be solved for systems involving long range interactions—such that the YRPM for instance—since the system may be seen as an infinite periodic system of $\mathbb{R}^3$. We shall adopt for the YRPM in $\mathscr{S}^3$ the same heuristic prescription as the one we adopted recently for the RPM.[7] We choose $\mathscr{A}_{\mathbf{YRPM}}^{\mathscr{S}^3}$ in such a way that $V_{\mathbf{YRPM}}^{\mathscr{S}^3}(1, 2..., N)$ as the same lower extensive bound $\mathscr{B}_{\mathbf{YRPM}}^{\mathbb{R}^3}$ than its Euclidean counterpart $V_{\mathbf{YRPM}}^{\mathbb{R}^3}(1, 2..., N)$.

In order to find a lower bound for $V_{\mathbf{YRPM}}^{\mathscr{S}^3}(1, 2..., N) - N\mathscr{A}_{\mathbf{YRPM}}^{\mathscr{S}^3}$ we proceeds as in Sections IIC and IIIC. For configurations where the spheres do not overlap we can replace the point charges $\pm q$ at the centers of the spheres by superficial distributions of charges of density $\sigma_{\pm}$. If $\sigma_{\pm}$ is chosen such that the associated renormalized charges $\pm q_{\sigma}^{\mathscr{S}^3}(\alpha)$ coincide with the point charges $\pm q$, the procedure leaves the pair potentials unchanged. Following the same arguments as those of Sections IIC and IIIC one can then show that

$$V_{\mathbf{YRPM}}^{\mathscr{S}^3}(1, 2..., N) - N\mathscr{A}_{\mathbf{YRPM}}^{\mathscr{S}^3} \geqslant N\mathscr{B}_{\mathbf{YRPM}}^{\mathscr{S}^3} = -N\mathscr{E}_{\sigma}^{\mathscr{S}^3} \tag{4.34}$$

where $\mathscr{E}_{\sigma}^{\mathscr{S}^3}$ has been given at Eq. (4.23). According to the preliminary discussion of this section are thus led to define

$$\mathscr{A}_{\mathbf{YRPM}}^{\mathscr{S}^3} = \mathscr{B}_{\mathbf{YRPM}}^{\mathbb{R}^3} - \mathscr{B}_{\mathbf{YRPM}}^{\mathscr{S}^3} \tag{4.35}$$

In the case $\alpha \neq 0$ $\mathscr{A}_{\mathbf{YRPM}}^{\mathscr{S}^3}$ decays exponentially with system size. Its inclusion in a MC simulation should however leads to better results (i.e., a minimization of finite size effects and a faster convergence towards the thermodynamic limit).

D. YOCP

In order to emphasize once again the formal unity of electrostatics in the two spaces $\mathscr{C}^3$ and $\mathscr{S}^3$, we define the configurational energy $V_{\mathbf{YOCP}}^{\mathscr{S}^3}$ of the YOCP in $\mathscr{S}^3$ by an expression similar to that given in Section IIID for $V_{\mathrm{YOCP}}^{\mathscr{C}^3}$ (cf. Eq. (3.28))

$$V_{\mathrm{YOCP}}^{\mathscr{S}^3} = V_{\mathrm{OCP}}^{\mathscr{S}^3} + \frac{q^2}{2} \frac{4\pi}{R} \sum_{i,j}^{N} \sum_{L=1}^{\infty} \sum_{\mathbf{m}} \left[\frac{1}{\varepsilon(L)} - 1 \right] \frac{1}{L(L+2)} Y_{L,\mathbf{m}}^{*}(M_i)\, Y_{L,\mathbf{m}}(M_j) \tag{4.36}$$

where $V_{\mathrm{OCP}}^{\mathscr{S}^3}$ is the configurational energy of the OCP[7]

$$V_{\mathrm{OCP}}^{\mathscr{S}^3} = N\mathscr{A}_{\mathrm{OCP}}^{\mathscr{S}^3} + \frac{q^2}{2} \sum_{i \neq j}^{N} \psi_{ij}^{\mathscr{S}^3} \tag{4.37}$$

where $\psi_{ij}^{\mathscr{S}^3}$ has been given in Eq. (4.25). In Eq. (4.37) $\mathscr{A}_{\mathrm{OCP}}^{\mathscr{S}^3}$ is a constant which fixes the zero of energy and which can be ascribed a value only by some heuristic prescription. An adequate ansazt (as confirmed recently by extensive MC simulations of the OCP in $\mathscr{S}^3$)[15] is to choose $\mathscr{A}_{\mathrm{OCP}}^{\mathscr{S}^3}$ in such a way that the Lieb–Narnhofer[26] lower bounds on $\beta V_{\mathrm{OCP}}^{\mathscr{S}^3}$ and $\beta V_{\mathrm{OCP}}^{\mathbb{R}^3}$ are identical (and equal to $-9N\Gamma/10$). With this prescription one has[7]

$$\begin{aligned} \beta\mathscr{A}_{\mathrm{OCP}}^{\mathscr{S}^3} &= -\frac{9}{10}\Gamma - \frac{3\Gamma}{4\pi R^*} \\ &\quad + \frac{\Gamma}{2R^* d(R^{*-1})} \left[\frac{3}{2} + \sin^2(R^{*-1}) - \frac{R^{*-1}\sin^2(R^{*-1})}{d(R^{*-1})} \right] \\ &= -\frac{3\Gamma}{4\pi R^*} - \frac{12}{175}\frac{\Gamma}{R^{*2}} + \frac{2}{875}\frac{\Gamma}{R^{*4}} + O(1/R^{*6}) \end{aligned} \tag{4.38}$$

where $d(x) = x - \sin(x)\cos(x)$. In Eq. (4.38) $R^* = R/a^{\mathscr{S}^3}$ is the reduced radius of the hypersphere and $\Gamma = \beta q^2/a^{\mathscr{S}^3}$ the dimensionless coupling parameter of the OCP. In $\mathscr{S}^3$ the ionic radius $a^{\mathscr{S}^3}$ is defined by the relation $nv(a^{\mathscr{S}^3}) = 1$, where $v(a^{\mathscr{S}^3})$ is the volume (4.26) of a sphere of $\mathscr{S}^3$ of radius $a^{\mathscr{S}^3}$. Note that $a^{\mathscr{S}^3}$ and the euclidean ionic radius $a = (3/4\pi n)^{1/3}$, $n = N/\Lambda$, differ by terms bf order R^{*-2}.

We have already pointed out the correspondences $Y_{L,\mathbf{m}}(M) \leftrightarrow \exp(i\mathbf{k}\cdot\mathbf{r})$ and $L(L+2)/R^2 \leftrightarrow \mathbf{k}^2$ which allows to "map" $\mathscr{S}^3$ onto $\mathscr{C}^3$. If we apply this mapping to the dielectric constant (2.4) and define

$$\varepsilon(L) = 1 + \frac{\alpha^2 R^2}{L(L+2)} \tag{4.39}$$

then Eq. (4.36) can be rewritten as

$$\begin{aligned} V^{\mathscr{S}3}_{\mathbf{YOCP}} &= N\mathscr{A}^{\mathscr{S}3}_{\mathbf{YOCP}} + \frac{q^2}{2} \sum_{i \neq j}^{N} \bar{\varphi}^{\mathscr{S}3}_{ij} \\ \mathscr{A}^{\mathscr{S}3}_{\mathbf{YOCP}} &= \mathscr{A}^{\mathscr{S}3}_{\mathbf{OCP}} + \delta\mathscr{A}^{\mathscr{S}3}_{\mathbf{YOCP}} \end{aligned} \tag{4.40}$$

The additional constant $\delta\mathscr{A}^{\mathscr{S}3}_{\mathbf{YOCP}}$ originates from the terms $i = j$ in the r.h.s. of Eq. (4.36)

$$\begin{aligned} \delta\mathscr{A}^{\mathscr{S}3}_{\mathbf{YOCP}} &= \frac{q^2}{2} \frac{4\pi}{R} \sum_{L=1}^{\infty} \sum_{\mathbf{m}} \left[\frac{1}{\varepsilon(L)} - 1 \right] \frac{1}{L(L+2)} Y^*_{L,\mathbf{m}}(M_i)\, Y_{L,\mathbf{m}}(M_i) \\ &= \frac{q^2}{2} \lim_{w \to 0} \left[\bar{\varphi}^{\mathscr{S}3}(w) - \psi(w) \right] \end{aligned} \tag{4.41}$$

One can compute explicitly the limit in (4.41), which gives

$$\begin{aligned} \beta\delta\mathscr{A}^{\mathscr{S}3}_{\mathbf{YOCP}} &= \frac{\Gamma}{2} \left[\frac{3}{2\pi R^*} - \frac{\omega \coth \omega\pi}{R^*} - \frac{4\pi}{\alpha^{*2} \Lambda^*} \right] \qquad (\alpha R \geqslant 1) \\ &= \frac{\Gamma}{2} \left[\frac{3}{2\pi R^*} - \frac{\omega \cot \omega\pi}{R^*} - \frac{4\pi}{\alpha^{*2} \Lambda^*} \right] \qquad (\alpha R \leqslant 1) \end{aligned} \tag{4.42}$$

where we have introduced the reduced volume $\Lambda^* = \Lambda/(a^{\mathscr{S}3})^3$ and the reduced screening parameter $\alpha^* = \alpha a^{\mathscr{S}3}$. Note that in the limit $\alpha \to 0$, $\delta\mathscr{A}^{\mathscr{S}3}_{\mathbf{YOCP}} \to 0$, as it should. Moreover in the limits $\alpha \to \infty$, R fixed or alternatively $R \to \infty$, α fixed one has $\beta\delta\mathscr{A}^{\mathscr{S}3}_{\mathbf{YOCP}} \sim -\alpha^* \Gamma/2$.

The expression (4.40) of $V^{\mathscr{S}3}_{\mathbf{YOCP}}$ corresponds to the expression (3.30) of $V^{\mathscr{C}3}_{\mathbf{YOCP}}$. An expression analogous to (3.31) involving the potentials of bare Yukawa charges is easily derived from (4.40) and reads

$$\begin{aligned} V^{\mathscr{S}3}_{\mathbf{YOCP}} &= N\bar{\mathscr{A}}^{\mathscr{S}3}_{\mathbf{YOCP}} - \frac{N}{2} \frac{4\pi n}{\alpha^2} + \frac{q^2}{2} \sum_{i \neq j}^{N} \varphi^{\mathscr{S}3}_{ij} \\ \bar{\mathscr{A}}^{\mathscr{S}3}_{\mathbf{YOCP}} &= \mathscr{A}^{\mathscr{S}3}_{\mathbf{YOCP}} + \frac{q^2}{2} \frac{4\pi}{\alpha^2 \Lambda} \end{aligned} \tag{4.43}$$

With arguments similar to those of Section IIID one can derive an extensive lower bound for $V^{\mathscr{S}3}_{\mathbf{YOCP}}$. By analogy with Eq. (3.35) one thus has

$$\begin{aligned} V^{\mathscr{S}3}_{\mathbf{YOCP}} &\geqslant N\mathscr{B}^{\mathscr{S}3}_{\mathbf{YOCP}}(a) \\ \mathscr{B}^{\mathscr{S}3}_{\mathbf{YOCP}}(a) &= \bar{\mathscr{A}}^{\mathscr{S}3}_{\mathbf{YOCP}} - \mathscr{E}^{\mathscr{S}3}_{\rho}(a) - \frac{1}{2} \frac{4\pi n}{\alpha^2} \left[q^2 - q_0^2(a) \right] \end{aligned} \tag{4.44}$$

where q_0 is the charge of a sphere of radius a such that the associated renormalized charge $q_{0,\rho}^{\mathscr{S}^3}(\alpha)=q$ (cf. Eq. (4.28), $\mathscr{E}_{\rho}^{\mathscr{S}^3}(a)$ being the associated self-energy (4.30). The "best" bound is obtained by searching the maximum of $\mathscr{B}_{\text{YOCP}}^{\mathscr{S}3}(a)$ as a function of a. After tremendously tedious calculations one finds that the best bound is obtained for a equal to the ionic radius $a^{\mathscr{S}^3}$ in both cases $\alpha R \geqslant 1$ and $\alpha R \leqslant 1$. Therefore $\mathscr{B}_{\text{YOCP}}^{\mathscr{S}3} \equiv \mathscr{B}_{\text{YOCP}}^{\mathscr{S}3}(a^{\mathscr{S}^3})$. This expression does not coincide with $\mathscr{B}_{\text{YOCP}}^{\mathbb{R}^3}$ but the differences are exponentially small with system size R^*. As for the YRPM one could redefine the additive constant $\bar{\mathscr{A}}_{\text{YOCP}}^{\mathscr{S}^3}$ in such a way that the two bounds $\mathscr{B}_{\text{YOCP}}^{\mathscr{S}^3}$ and $\mathscr{B}_{\text{YOCP}}^{\mathbb{R}^3}$ coincide. It turns out that the numerical differences between these two distinct expressions of the zero of energy are extremely small for the cases usually considered in MC simulations (i.e., $N \geqslant 100$).

5. CONCLUSION

In this article we have derived all the formal expressions which are needed for numerical simulations of Yukawa systems either in cubico-periodic or hyperspherical boundary conditions. By passing, a new lower bound for the YRPM has also been obtained. In the companion paper, we report extensive Monte Carlo simulations of the thermodynamic and structural properties of the YOCP performed on a hypersphere. We shall show that the hypersphere method allows an efficient determination of the internal energy as well as the pressure. Part of these numerical results have been used in a recent theoretical study of the equation of state of the Deuterium.[14]

APPENDIX A. SPHERICAL AVERAGE OF YUKAWA POTENTIAL

We consider a potential $\Phi(M)$ which is a solution of the homogeneous Helmholtz equation in a region $\mathscr{D}$ of $\mathbb{R}^3$, i.e.,

$$(\Delta - \alpha^2)\,\Phi(M) = 0 \qquad (\forall M \in \mathscr{D}) \tag{A.1}$$

The charges which create $\Phi(M)$ lie somewhere outside $\mathscr{D}$. Let $S(O, a)$ a sphere of center O—which, henceforth, will be the origin of the coordinates—and radius a which is totally included in $\mathscr{D}$. In order to obtain an expression for the spherical average $\langle \Phi \rangle(a)$ defined at Eq. (2.8) we apply one of Green's identities[23] to the potentials Φ and $\Psi \equiv \exp(-\alpha r)/r$ i.e.,

$$\int_{B(O,a)} (\Phi \Delta \Psi - \Psi \Delta \Phi)\, d\tau = \int_{S(O,a)} (\Phi \nabla \Psi - \Psi \nabla \Phi) \cdot d\mathbf{S} \tag{A.2}$$

where $B(O, a)$ denotes the interior of the sphere $S(O, a)$ and $d\mathbf{S}$ is the (vectorial) outwards surface element. Since $\Psi(r)$ is the Green function of Helmholtz Eq. (2.1) the l.h.s of Eq. (A.2) can be written as

$$\int_{B(O,a)} (\Phi[\alpha^2\Psi - 4\pi\delta(\mathbf{r})] - \Psi\alpha^2\Phi)\, d\tau = -4\pi\Phi(O) \tag{A.3}$$

The r.h.s. of Eq. (2.1) is easily related to the spherical average $\langle\Phi\rangle(a)$. Indeed, since $\nabla\psi = -(1+\alpha a)\exp(-\alpha a)\,\mathbf{a}/a$, we have

$$\begin{aligned}\int_{S(O,a)} \Phi\nabla\Psi\cdot d\mathbf{S} &= -(1+\alpha a)\exp(-\alpha a)\int_{S(O,a)} d\Omega(\mathbf{a})\,\Phi(\mathbf{a})\\ &= -4\pi(1+\alpha a)\exp(-\alpha a)\langle\Phi\rangle(a)\end{aligned} \tag{A.4}$$

Moreover

$$\begin{aligned}\int_{S(O,a)} \Psi\nabla\Phi\cdot d\mathbf{S} &= \frac{\exp(-\alpha a)}{a}\int_{B(O,a)} \Delta\Phi\, d\tau\\ &= \frac{\alpha^2}{a}\exp(-\alpha a)\int_{B(O,a)} \Phi\, d\tau\\ &= \frac{4\pi\alpha^2}{a}\exp(-\alpha a)\int_0^a dr\, r^2\langle\Phi\rangle(r)\end{aligned} \tag{A.5}$$

Reporting the intermediate results (A.3), (A.4), and (A.5) in Eq. (A.2) yields the following integral equation for $\langle\Phi\rangle$:

$$\Phi(O) = (1+\alpha a)\exp(-\alpha a)\langle\Phi\rangle(a) + \frac{\alpha^2}{a}\exp(-\alpha a)\int_0^a r^2\langle\Phi\rangle(r)\, dr \tag{A.6}$$

Examining the limit $a \to 0$ of Eq. (A.6) yields $\Phi(O) = \langle\Phi\rangle(0)$. Taking into account this result and deriving both sides of Eq. (A.6) with respect to a gives a simple differential equation for $\langle\Phi\rangle(a)$:

$$a\frac{d}{da}\langle\Phi\rangle(a) + (1+\alpha a)\langle\Phi\rangle(a) = \exp(\alpha a)\langle\Phi\rangle(0) \tag{A.7}$$

the solution of which may be cast under the form

$$\langle\Phi\rangle(a) = \frac{\sinh(\alpha a)}{\alpha a}\Phi(O) \tag{A.8}$$

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