Madelung energy of Yukawa lattices

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We propose a method to obtain an approximate closed form expression for the Madelung energy (ME) of Yukawa lattices. Such a method is applied for lattices of different topologies and dimensions. The obtained Madelung energies have a satisfactory accuracy for all ranges of the screening parameter κ of the Yukawa potential, and it becomes exact in the asymptotic limits $\kappa \to 0$ and $\kappa \to +\infty$. For instance, for the triangular lattice, the maximum relative error of the ME given by the method is about 0.0047. Also, satisfactory results are obtained for the one-component plasma limit. The Madelung constants of the two-dimensional hexagonal BN and square NaCl and the three-dimensional cubic NaCl crystals are estimated with a relative error of 0.004, 0.006, and 0.03, respectively. Finally, different ways to improve the method are presented and discussed.

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I. INTRODUCTION

Consider a one-component Yukawa lattice, i.e., a lattice of identical charged particles interacting through a pairwise Yukawa potential (Debye-shielded Coulomb potential):

$$V_p(r) = \frac{qe^{-\kappa r}}{r}, \tag{1}$$

where r is the distance between two particles, $1/\kappa$ is the screening length, and q is the particle's charge. Yukawa lattices appear in a variety of physical systems [1–3].

The total potential over a test particle i of the lattice is given by the following sum:

$$\phi = q\sum_{j\neq i}\frac{e^{-\kappa r_{ij}}}{r_{ij}}, \tag{2}$$

where r_{ij} is the distance between two distinct particles i and j. We will consider, in this article, only lattices with a well-defined Wigner-Seitz cell. The lattice sum given by Eq. (2), when multiplied by the particle's charge q, is known as the Madelung energy (ME) of the lattice. For most of the lattices, the ME does not have a known closed form expression and converges only for $\kappa > 0$. A neutralizing background is sufficient to guarantee the convergence when $\kappa = 0$ [4], however this convergence is very slow. Due to the latter reason, sophisticated methods, such as the Ewald's method [4,5], were developed to speed up the convergence of the ME.

In this article, we propose a method to obtain an approximate closed form expression for the ME of Yukawa lattices. Beyond the mathematical importance, closed form expressions of the ME must have many different applications, e.g., for the investigation of the thermodynamics and phase diagrams in complex plasmas [6–8], and for the understanding of correlation influences in the wave spectra [9] and in the structure of Yukawa crystals [10–12] and Yukawa balls [13–16].

The paper is organized as follows: in the next section, the asymptotic limits of the ME, i.e., when the parameter κ assumes large and small values, will be considered. The continuum and the nearest-neighbor approaches are revised and an improvement for the continuum approach, where self-interaction contributions are avoided, is proposed. In Sec. III, a method to obtain an approximate closed form expression for the ME of two-dimensional (2D) lattices with a good accuracy in the entire range of the parameters is proposed. In Sec. IV our method is applied for the triangular, hexagonal, and square lattices where results and improvements are discussed. In Sec. V, we investigate the behavior of the ME in the Coulomb limit and show how to use the results of Sec. IV to obtain approximations for the Madelung constants of 2D lattices. Finally, in the last section, an extension of the method for three-dimensional (3D) lattices and the one-dimensional (1D) chain is presented.

II. ASYMPTOTIC LIMITS

For all practical purposes, we can make $r_{ij} = p_{ij}x$, where x is the distance between two nearest-neighbor particles in the lattice. Then Eq. (2) can be written as

$$\phi(\kappa,x) = \frac{q^2}{x}\sum_{j\neq i}\frac{e^{-\kappa x p_{ij}}}{p_{ij}} = \frac{q^2}{x}\psi(\kappa'), \tag{3}$$

where $\psi(\kappa')$ is a dimensionless function of the product $\kappa' = \kappa x$. For the Coulomb case, $\kappa = 0$ and $\psi(\kappa')$ diverges. But when positive and negative charged particles are equally distributed in the lattice, the total potential [Eq. (2)] has positive and negative terms and $\psi(\kappa')$ converges conditionally for $\kappa' = 0$ giving the well known Madelung constant. From Eq. (3) one can see that the behavior of $\psi(\kappa')$, and consequently of $\phi(\kappa,x)$, when $\kappa \to 0$ (Coulomb limit) is the same as when $x \to 0$ (continuum limit). In the latter case, the ME is given by an integral, which for the 2D and 3D lattices becomes

$$\phi_{2D}(\kappa,x) = \int_{\mathbb{R}^2} q^2\rho_{2D}(x)\frac{e^{-\kappa|\vec{r}|}}{|\vec{r}|}d\vec{r} = \frac{2\pi q^2\rho_{2D}(x)}{\kappa^2} \tag{4}$$

and

$$\phi_{3D}(\kappa,x) = \int_{\mathbb{R}^3} q^2\rho_{3D}(x)\frac{e^{-\kappa|\vec{r}|}}{|\vec{r}|}d\vec{r} = \frac{4\pi q^2\rho_{3D}(x)}{\kappa^2}, \tag{5}$$

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respectively, where $\rho_{2D}(x) \propto 1/x^2$ and $\rho_{3D}(x) \propto 1/x^3$ are the particle densities of the lattices. Although the relative error of these approximations diverges with the increasing of κ', they are exact in the limit $\kappa' \to 0$. In fact, the continuum approach represents the lowest order term of the series expansion of $\psi(\kappa')$ [4].

For the sake of simplicity, we will define the convenient dimensionless Madelung energies (DMEs):

$$\varphi_{2D}(\kappa') = \kappa' \psi(\kappa') = \frac{\kappa x^2}{q^2} \phi_{2D}(\kappa, x) \tag{6}$$

and

$$\varphi_{3D}(\kappa') = \kappa'^2 \psi(\kappa') = \frac{\kappa^2 x^3}{q^2} \phi_{3D}(\kappa, x). \tag{7}$$

For these functions we have $\varphi_{2D}(0) = 2\pi\rho_{2D}(x)x^2$ and $\varphi_{3D}(0) = 4\pi\rho_{3D}(x)x^3$.

With the increasing of κ (or x) we must consider lattice correlation (discretization) effects. Notice that to calculate the total potential energy over a given test particle in Eq. (4) [or Eq. (5)] we integrated throughout the plane (or space), even including the region "occupied" by the test particle. To avoid such a self-interaction in the calculation of the ME, we propose to integrate the radial component from the Wigner-Seitz radius to infinity; i.e., we consider the Wigner-Seitz cell as the region occupied by the test particle in the lattice. The Wigner-Seitz radii are given by $(\pi\rho)^{-1/2}$ and $(4\pi\rho/3)^{-1/3}$ for 2D and 3D lattices, respectively, and therefore their DMEs become

$$\varphi_{2D}(\kappa') = 2\pi\rho_{2D}(x)x^2 e^{-\kappa r_{WS}} \tag{8}$$

and

$$\varphi_{3D}(\kappa') = 4\pi\rho_{3D}(x)x^3 e^{-\kappa r_{WS}}(1 + \kappa r_{WS}). \tag{9}$$

When $\kappa \gg 1$ (strong screening) just the interaction between neighbor particles is enough to be considered (the pair potential goes to zero very fast with the distance). If each particle in the lattice has N nearest-neighbor particles, then we can make the asymptotic approximation for $\kappa \gg 1$:

$$\varphi(\kappa') = N\kappa' e^{-\kappa'}. \tag{10}$$

Hebner *et al.* [11] used this approximation in the 2D triangular lattice ($N = 6$) and proposed a correction for non-nearest-neighbor interaction effects which can be written as

$$\varphi(\kappa') = \frac{6\kappa x^2}{q} \sum_{n=1}^{\infty} n V_p(\kappa, nx) = \frac{6\kappa' e^{-\kappa'}}{1 - e^{-\kappa'}}. \tag{11}$$

Although this equation goes to a finite constant in the limit $\kappa x \to 0$, it does not become equal to the correct value $2\pi\rho_{2D}(x)x^2$ obtained in the continuum limit. In order to obtain a closed form expression for the ME, which works well for all values of the parameter κ', including both asymptotic limits given by Eqs. (4) and (10), a method is proposed in the next section.

III. METHOD FOR 2D LATTICES

We present in this section a method to obtain an approximate closed form expression for the ME as a function of the lattice's and the interparticle potential's parameters. Such a method can be applied for 1D, 2D, and 3D lattices. In order to simplify the presentation of the method and gain in clarity we will first present it for a 2D lattice.

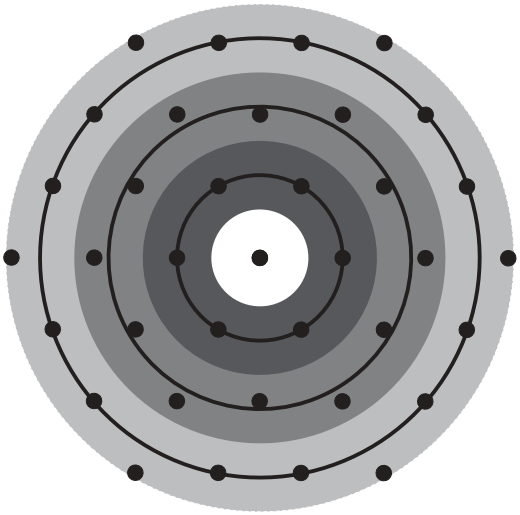

FIG. 1. Schematic representation of a 2D lattice where particles are indicated by closed dark circles. The test particle is located in the center of the figure within the white circle. The first three most internal annuli A_0, A_1, and A_2 are indicated, respectively, by the decreasing gray darkness regions.

The ME related to a single test particle is the total potential energy due to the interaction between the test particle and the rest of the lattice. Figure 1 shows a schematic representation of a regular lattice of Yukawa particles where the test particle was chosen to be the central particle (see closed black circle within the central white circular region in Fig. 1).

The method is as follows: we divide the plane of the 2D lattice in a set of concentric annuli denoted by A_n ($n = 0, 1, 2, \ldots$) of same thickness equal to y and with average radii $r_n = r_0 + ny$. The first (A_0), second (A_1), and third (A_2) annuli are represented, respectively, by decreasing gray darkness regions in Fig. 1.

Concerning the first annulus, A_0, we request the following two conditions to be satisfied: (1) the average radius r_0 of the annulus A_0 must have the value x and (2) the total charge within the annulus A_0 must be equal to Nq, where N is the total number of nearest neighbors of the lattice (number of particles at the distance x from the test particle).

The total charge Q_n of a given annulus A_n, in the continuous limit, is given by

$$Q_n = \int_{A_n} \rho q dA = 2\pi\rho q \int_{r_n - y/2}^{r_n + y/2} r dr = 2\pi\rho q y r_n. \tag{12}$$

The value of y can be obtained by using the second requirement concerning the first annulus, which results in the equation

$$N = \int_{A_0} \rho(x) dA = 2\pi\rho \int_{r_0 - y/2}^{r_0 + y/2} r dr, \tag{13}$$

where $r_0 = x$, and then

$$y = \frac{N}{2\pi\rho x}. \tag{14}$$

For the last step of our method, we consider that the total charge of the annulus A_n is uniformly distributed over a ring of radius r_n, which is the average radius of the annulus. In doing so, we obtain an approximative expression for the DME which has the general closed form

$$\varphi(\kappa') = \frac{\kappa x^2}{q} \sum_{n=0}^{\infty} Q_n \frac{e^{-\kappa r_n}}{r_n} = \frac{N\kappa' e^{-\kappa'}}{1 - e^{-\kappa y}}. \tag{15}$$

Notice that the expression for the DME depends on the lattice's topology via the number of nearest-neighbor particles N and the density of particles ρ.

IV. APPLICATIONS OF THE METHOD (2D LATTICES)

Here, the method described in the latter section is applied to obtain the Madelung energies of 2D lattices. We start by considering the triangular lattice, since it is the most energetically favorable arrangement in 2D crystallizations.

A. Triangular lattice

The DME of the triangular lattice can be calculated directly by Eq. (3) or alternatively by the sum

$$\varphi_{\text{exact}}(\kappa, x) = 6\kappa' \sum_{l=0}^{\infty} \sum_{m=1}^{\infty} \frac{e^{-\kappa'\sqrt{l^2+m^2+lm}}}{\sqrt{l^2+m^2+lm}}, \tag{16}$$

where the particle's positions in the lattice were written in terms of the lattice's parameter x and the integer numbers l and m. Figure 2(a) (see opened circles) shows the result of the numerical calculation of the DME given by Eq. (16). In the same figure, the nearest-neighbor approximation [Eq. (10)], which takes into account only the contribution of the first neighbor particles, is also presented (see dotted traced line). As expected, the latter approximation is only good for large values of κ'. We can also see that Eq. (11) [see long traced line in Fig. 2(a)] does not give a satisfactory accuracy for small values of κ'. On the other hand, Eq. (8) [see dotted line in Fig. 2(a)], i.e., the calculated DME when self-interaction effects were excluded, has a satisfactory accuracy only for small values of κ'.

In order to obtain a more accurate approximation for this Madelung energy which works for a wider range of the parameter κ', we will now apply the method described in the latter section. For the triangular lattice we use, in Eq. (15), the quantities $\rho = 2/(\sqrt{3}x^2)$ and $N = 6$, respectively, for the particle density and the total number of nearest neighbors, which gives

$$\varphi_t(\kappa, x) = \frac{6\kappa' e^{-\kappa'}}{1 - e^{-\frac{3\sqrt{3}}{2\pi}\kappa'}}. \tag{17}$$

Notice that the only difference between this equation and Eq. (11) is the exponential's argument in the denominator. From Fig. 2(a), it is clear that Eq. (17) (full line) is in excellent agreement with the DME computed numerically.

Figure 2(b) (see opened circles) shows the relative error of Eq. (17), which is calculated by

$$E_t(\kappa') = \frac{|\phi_{\text{exact}} - \phi_t|}{\phi_{\text{exact}}}, \tag{18}$$

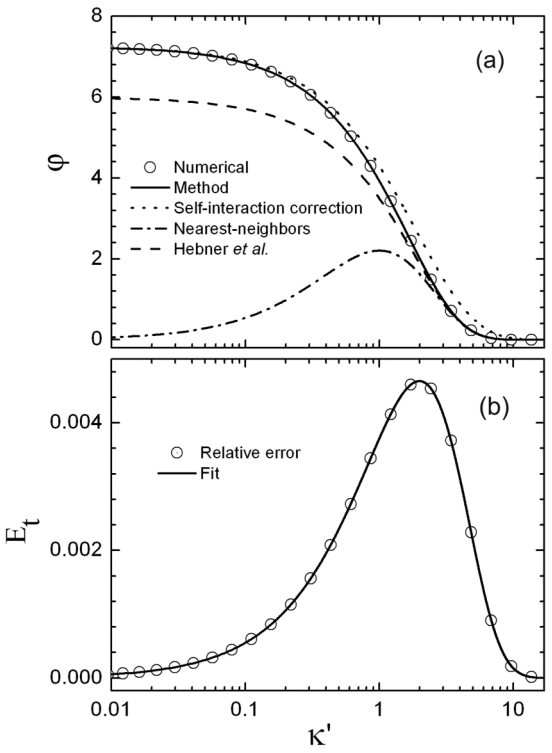

FIG. 2. (a) DME obtained numerically, as a function of κ', for the triangular lattice (circles) and by different analytical approaches as indicated within figure. (b) Relative error [Eq. (18), circles] between the DME of a triangular lattice calculated analytically by our method [Eq. (17)] and numerically [Eq. (16)], and fit of the error [Eq. (19), full line], as a function of the parameter κ'. Both figures have the horizontal axis in the same logarithmic scale.

and is a function of κ'. We can see that the relative error has a maximum value of about $E_t \simeq 0.0047$ at $\kappa' \simeq 2.0$, and that it goes to zero in both asymptotic limits $\kappa' \to 0$ and $\kappa' \to \infty$. This relative error is well fitted by the function

$$E_t(\kappa') = \frac{c\kappa'^2}{e^{d\kappa'} - 1}, \tag{19}$$

where $c = 0.00462$ and $d = 0.8016$ [see full line in Fig. 2(b)]. Finally, by using the latter fit to improve the accuracy of Eq. (17), we obtain the following expression:

$$\varphi_t^{\text{imp}}(\kappa') = \frac{\varphi_t(\kappa')}{1 - E_t(\kappa')}. \tag{20}$$

The maximum relative error of this semianalytic approximation is expressively reduced to a value smaller than 0.000007. In fact, independently of the lattice choice, Eq. (15) can always be improved, as much as we want, by fitting the relative error, calculated by Eq. (18) without the modulus, with a function of the form

$$E(\kappa') = \kappa'^2 \frac{(a_0 + a_1\kappa' + a_2\kappa'^2 + \cdots)}{e^{b\kappa'} - 1}, \tag{21}$$

where a_i, for $i = 0, 1, 2, \ldots$, and b are numerical fitting parameters to be appropriately chosen. For the triangular lattice, two parameters are enough to obtain a satisfactory fit. It may be necessary to use three or more parameters for the other lattices. Notice that, in the asymptotic limits where the

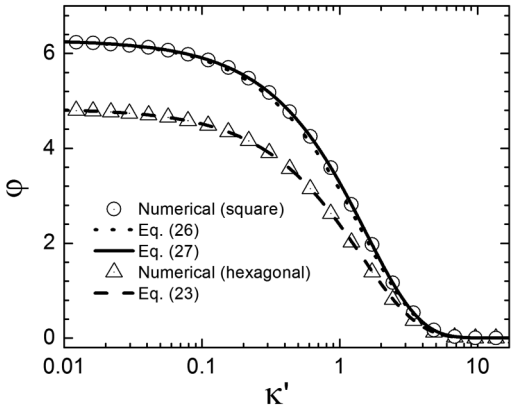

FIG. 3. DME obtained numerically, as a function of the parameter κ', for the square (circles) and hexagonal (triangles) lattices and by different analytical approaches as indicated within figure. The horizontal axis is in logarithmic scale.

parameter κ' goes to zero or infinity, the DME has a polynomial or an exponential behavior, respectively. Such a fact justifies the form of Eq. (21) since it is natural to expect that both the DME and its relative error have similar behaviors in the asymptotic limits of κ'.

If we use only the first rings while the rest of the lattice is considered continuum, another semianalytic improvement is obtained. It can be written as

$$\phi_{\rm PC} = q\sum_{n=0}^{m} Q_n \frac{e^{-\kappa r_n}}{r_n} + \int_{r_m+\frac{y}{2}}^{\infty} \rho q^2 \frac{e^{-\kappa r}}{r} 2\pi r dr$$
$$= \frac{Nq^2 e^{-\kappa x}}{x}\left[\frac{1-e^{-(m+1)\kappa y}}{1-e^{-\kappa y}} + \frac{e^{-(m+\frac{1}{2})\kappa y}}{\kappa y}\right], \qquad (22)$$

where the integral must start at the end of the annulus A_m, i.e., from the radius $r_m + y/2$. The best value of the cutoff m is chosen by comparing the improved DME $\phi_{\rm PC}$ with the exact numerical result. Here and after, we will refer to this improvement method as the partially continuous (PC) improvement. For the triangular lattice, we found that $m = 1$ gives the best approximation with a maximum relative error of 0.00248, while the choice $m = 0$ gives an accuracy worse than the one of Eq. (17).

B. Hexagonal (honeycomb) lattice

Now, applying the method for the hexagonal (honeycomb) lattice, we obtain the following expression for its DME:

$$\varphi_h(\kappa') = \frac{3\kappa' e^{-\kappa'}}{1-e^{-\frac{9\sqrt{3}}{8\pi}\kappa'}}, \qquad (23)$$

where we used in Eq. (15) the values $\rho = 4/(3\sqrt{3}x^2)$ and $N = 3$, respectively, for the particle density and the total number of nearest neighbors of a hexagonal lattice. Figure 3 shows the plot of Eq. (23) (long traced line) together with the DME obtained numerically (opened triangles). Notice that, for this lattice, the PC improvement [Eq. (22)] is not useful; i.e., there is not a finite value of m resulting in a better accuracy than the one found in Eq. (23).

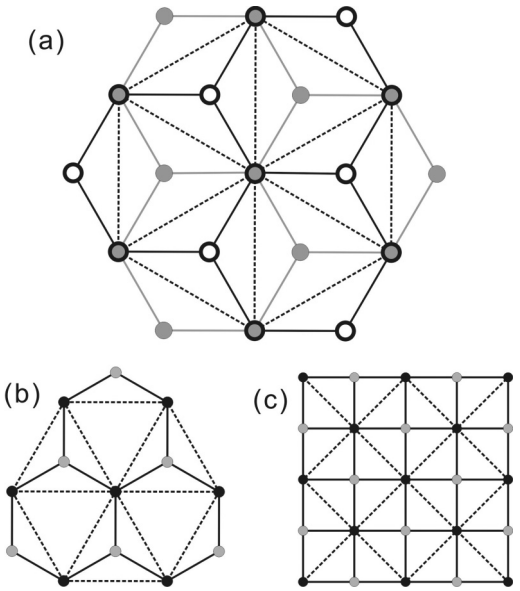

FIG. 4. (a) The set of all sites, i.e., gray dots and black circles, forming a triangular lattice with nearest particle distance x. Black circles and gray dots form, each one, two distinct hexagonal lattices with nearest particle distance x, while the intersection between them forms another triangular lattice with larger nearest particle distance $\sqrt{3}x$. (b) Hexagonal lattice with nearest site distance x formed by negative (black) and positive (gray) charges. The gray dots form a triangular lattice with a larger nearest site distance equal to $\sqrt{3}x$. (c) Square lattice with nearest site distance x formed by negative (black) and positive (gray) charges. The gray dots form a square lattice with a larger nearest site distance equal to $\sqrt{2}x$.

Alternatively, we can also obtain the ME for the hexagonal lattice directly from the ME of a triangular lattice by using the following functional relation:

$$2\phi_h(\kappa,x) = \phi_t(\kappa,x) + \phi_t(\kappa,\sqrt{3}x), \qquad (24)$$

or, for the DME, $2\varphi_h(\kappa') = \varphi_t(\kappa') + 3^{-1}\varphi_t(\sqrt{3}\kappa')$. The above functional relation is obtained by observing that from any triangular lattice we can always draw two distinct hexagonal lattices having the same nearest particle distance. In Fig. 4(a), the set of all particles forms a representative part of a triangular lattice with nearest particle distance equal to x. Accordingly, in the same figure, open black and closed gray circles form two distinct hexagonal lattices with nearest particle distance also equal to x. Still, notice that the intersections between the two hexagonal lattices constitute another triangular lattice with larger nearest particle distance equal to $\sqrt{3}x$. Based on these facts, which involve few simple geometric relations, we can easily construct Eq. (24).

From Eqs. (17) and (24), we can obtain directly a new analytical expression for the DME of a hexagonal lattice where the maximum relative error is smaller than 0.005. Inversely, another expression for the DME of the triangular lattice φ_t can be obtained by solving Eq. (24) where φ_h is given by Eq. (23). Such a solution of this linear functional equation is given by the following power series [17]:

$$\varphi_t(\kappa') = 2\sum_{n=0}^{\infty} \frac{\kappa'^n}{n!} \frac{1}{\left(1+3^{\frac{n-2}{2}}\right)} \frac{d^n\varphi_h}{d\kappa'^n}\bigg|_{\kappa'=0}. \qquad (25)$$

For small values of κ', i.e., $\kappa' \lesssim 0.7$, we found that the latter approximation has better accuracy than Eq. (17). Fortunately, for this range of κ', such a series has a fast convergence. We will see, in Sec. V, that the second term of this series is useful to obtain a better approximate closed form expression for some lattice constants.

C. Square lattice

Finally, we consider the calculation of the DME for a square lattice. The corresponding particle density and number of first neighbors of a square lattice are, respectively, $\rho = 1/x^2$ and $N = 4$. Using these values in Eq. (15) we obtain the following DME:

$$\varphi_s(\kappa') = \frac{4\kappa' e^{-\kappa'}}{1 - e^{-\frac{2}{\pi}\kappa'}}. \tag{26}$$

We found that the relative error of this approximation has a maximum value of ≈ 0.0650. Notice that, for the square lattice, the PC improvement achieves the best accuracy at $m = 0$, where the maximum relative error becomes ≈ 0.0446.

A great improvement is obtained if we modify Eq. (26) by including the exact contribution due to particles belonging to the annuli A_1 and A_2 and, in the sequence, subtracting the contribution due to the total charges Q_1 and Q_2, which are distributed along the rings of radii r_1 and r_2, respectively. In doing so, we obtain the following improved expression for the DME of a square lattice:

$$\varphi_s^{\text{imp}}(\kappa') = \frac{\kappa x^2}{q}[4V_p(\sqrt{2}x) + 4V_p(2x) + 8V_p(\sqrt{5}x)] + \varphi_s(\kappa,x) - \frac{\kappa x^2}{q}\left(\frac{Q_1 e^{-\kappa r_1}}{r_1} + \frac{Q_2 e^{-\kappa r_2}}{r_2}\right). \tag{27}$$

The new maximum relative error decreases now to ≈ 0.0017. Plots of the approximations Eqs. (26) (short traced line) and (27) (full line) are shown in Fig. 3 together with the numerical calculation of the DME of the square lattice (opened circles).

The previous improvement can be generalized by subtracting, from the ME of the method, the potential contributions due to the first $(m + 1)$ rings and adding to it the exact potential generated by all particles having radial distance smaller or equal to r_m for $m > 0$ (one can see that the case $m = 0$ is useless). In the rest of the article we will call such a correction the particle ring (PR) improvement. We tested the accuracy of this approximation for the three lattices investigated in this section, where we considered small values of m. Only for the square lattice, Eq. (27), we found good results for a sufficiently small value of m $(m = 2)$.

V. OCP LIMIT AND MADELUNG CONSTANTS

The divergence of the ME when $\kappa \to 0$ vanishes if the system is embedded in a neutralizing background [18]. For a background with uniform charge density $-q\rho_b$, the total potential energy is given by [19]

$$\Phi(\kappa,x) = \phi(\kappa,x) - \frac{2\pi q^2 \rho_b}{\kappa}, \tag{28}$$

which is the sum of the lattice and the background contributions. Considering that the series expansion of the 2D ME has the functional form [4]

$$\phi_{2D}(\kappa,x) = \frac{2\pi q^2 \rho(x)}{\kappa} + \frac{q^2 C}{x} + O(\kappa), \tag{29}$$

and setting $\rho_b = \rho(x)$, we obtain, in the one-component-plasma (OCP) limit, the following relation:

$$\Phi^{\text{OCP}}(x) = \lim_{\kappa \to 0} \Phi(\kappa,x) = \frac{q^2 C}{x}, \tag{30}$$

where C is a constant of the lattice.

Notice that, for the triangular lattice, we can determine an approximate value of the constant C_t by comparing the series expansion of Eq. (17), resulting from the method, with the right hand side of Eq. (29). Following this procedure, we obtain $C_t = 3 - 4\pi/\sqrt{3} = -4.255197$, which compared with the correct value -4.213425 [18] gives a relative error of ≈ 0.0099. Alternatively, we can substitute Eq. (23) in Eq. (25) to get the value

$$C_t = \frac{1}{1 + \sqrt{3}}\left(3\sqrt{3} - \frac{16\pi}{3}\right) = -4.230891, \tag{31}$$

which has a relative error of ≈ 0.0041.

The same procedure can be made now for the square lattice. The series expansion of Eq. (26), obtained by our method, gives $C_s = 2(1 - \pi) = -4.283185$ with a relative error of ≈ 0.0982, when compared to the correct value -3.900265 [18]. We can obtain a better approximation for C_s if we use Eq. (27) instead of Eq. (26), which gives

$$C_s = 2\sqrt{2} + \frac{8}{\sqrt{5}} - 4 - 2\pi = -3.877049, \tag{32}$$

with a relative error of ≈ 0.0060.

When positive and negative charges are equally distributed on a lattice, the ME in the OCP limit converges to q^2/x multiplied by a constant of the lattice known as the Madelung constant. From the previous results obtained for the constant C we can calculate the Madelung constants by using functional relations for the positive and negative lattices. For the hexagonal lattice, with positive and negative charges equally distributed [see Fig. 4(b) for a schematic representation of part of such a lattice], the Madelung constant H_2 [20] can be obtained by

$$\frac{q^2 H_2}{x} = \lim_{\kappa \to 0} |\phi_+(\kappa,x) + \phi_-(\kappa,x)| = \lim_{\kappa \to 0} \frac{|\phi_t(\kappa,x) - 3\phi_t(\kappa,\sqrt{3}x)|}{2} = \frac{q^2}{x}\frac{C_t(1 - \sqrt{3})}{2}. \tag{33}$$

In the latter, we used the relation Eq. (24), and the Madelung energies of the negative and positive lattices are, respectively, equal to $\phi_- = \phi_t(\sqrt{3}x)$ and $\phi_+ = -[\phi_h(x) - \phi_t(\sqrt{3}x)]$. The expressions for ϕ_- and ϕ_+ are obtained by employing basic geometric relations in the lattice of Fig. 4(b). An approximative value for H_2 is obtained by setting Eq. (31) in Eq. (33), which gives $H_2 = 1.54861$, against the correct value 1.54222 [21] with a relative error of ≈ 0.0041.

For the Madelung constant M_2 of the square lattice with positive and negative charges [see Fig. 4(c) for a schematic

representation of this lattice] [20], one can repeat the same procedure made for the constant H_2, which gives

$$\frac{q^2 M_2}{x} = \lim_{\kappa\to 0} |\phi_s(\kappa,x) - 2\phi_s(\kappa,\sqrt{2}x)| = \frac{q^2}{x} C_s(1-\sqrt{2}), \tag{34}$$

where in this case we have $\phi_- = \phi_s(\sqrt{2}x)$ and $\phi_+ = -[\phi_s(x) - \phi_s(\sqrt{2}x)]$ for a central particle with charge $-q$. The values of ϕ_+ and ϕ_-, for the square lattice having alternating positive and negative charges, are directly obtained from Fig. 4(c) by employing simple geometric relations. A more rigorous way to obtain the lattice-sublattice relations used in this section is described in [22]. Finally, setting the value $C_s = -3.877049$ [see Eq. (32)] in Eq. (34) we obtain $M_2 = 1.60593$ against the correct value 1.61554 [21] with a relative error of ≈ 0.0060.

VI. 3D LATTICES AND APPLICATIONS

A. Method

Although we have chosen, in Sec. III, to start presenting the method for 2D lattices, it can also be applied for the 1D and 3D ones. In the latter case, the appropriated elements must be the spherical annuli S_n ($n = 0,1,2,\ldots$) having average radii $x + ny$ and thickness y. According to the proposed method, the thickness of the annuli is obtained from the completeness relation $N = \int_{S_0} \rho dV$ imposed for the most internal spherical annulus S_0. In doing so, we obtain the cubic equation

$$12x^2 y + y^3 = \frac{3N}{\pi\rho}, \tag{35}$$

which has one real and two complexes solutions given in closed forms. The total charge of the nth spherical annuli must attend the condition $Q_n = \int_{S_n} \rho q dV$ which gives

$$Q_n = \frac{\pi\rho q y}{3}[12(x+ny)^2 + y^2]. \tag{36}$$

In this case, the DME is obtained by summing up the terms $Q_n e^{-\kappa r_n}/r_n$ from $n = 0$ to $+\infty$ and multiplying it by $\kappa^2 x^3/q$, which results in the expression

$$\varphi_{3D}(\kappa') = \frac{N\kappa^2 x^3}{12x^2+y^2}\left\{12e^{-\kappa x}\frac{[x - e^{-\kappa y}(x-y)]}{(1-e^{-\kappa y})^2} + L\right\}, \tag{37}$$

where L is given by

$$L = y^2 \sum_{n=0}^{\infty} \frac{e^{-\kappa(x+ny)}}{x+ny} = \frac{y^2 e^{-\kappa x}}{x} {}_2F_1\left(1, \frac{x}{y}; 1+\frac{x}{y}; e^{-\kappa y}\right), \tag{38}$$

and ${}_2F_1(a,b;c;z)$ is the hypergeometric function.

An attempt to use the method for the 1D chain returns to the exact lattice sum

$$\phi(x) = q\sum_{n=0}^{\infty} Q_n \frac{e^{-\kappa(x+ny)}}{x+ny} = 2q^2 \sum_{n=1}^{\infty} \frac{e^{-\kappa n x}}{nx} = -\frac{2q^2}{x}\log(1-e^{-\kappa x}), \tag{39}$$

where Q_n and y become, respectively, equal to $2q$ and x.

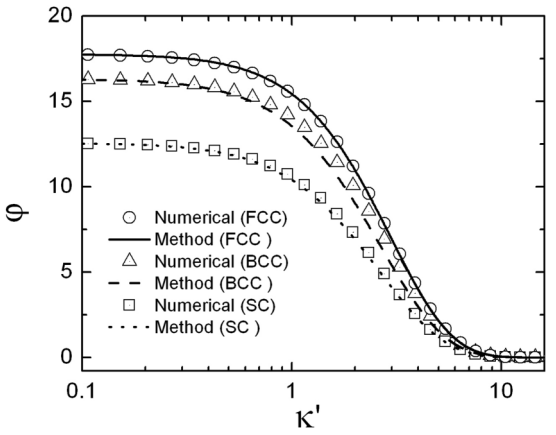

FIG. 5. DME obtained numerically, as a function of the parameter κ', for the FCC (circles), BCC (triangles), and SC (squares) lattices and by our analytical approach. The horizontal axis is in logarithmic scale.

B. Applications and improvements

Let the spherical annuli thickness be equal to $y = \alpha x$, βx, and γx, respectively, for the simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) lattices, where α, β, and γ are constants. The numbers of nearest neighbors and the particle densities for the SC, BCC, and FCC lattices are, respectively, $N = 6$ and $\rho = 1/x^3$, $N = 8$ and $\rho = 3\sqrt{3}/(4x^3)$, and $N = 12$ and $\rho = \sqrt{2}/x^3$. By replacing the latter parameters in Eq. (35), we obtain the following set of equations:

$$12\alpha + \alpha^3 = 18/\pi, \tag{40}$$

$$12\beta + \beta^3 = 32/(\pi\sqrt{3}), \tag{41}$$

and

$$12\gamma + \gamma^3 = 36/(\pi\sqrt{2}), \tag{42}$$

for the SC, BCC, and FCC lattices, respectively. Figure 5 shows the results obtained from the method and from the numerical calculations for these lattices. We found that the maximum relative errors for the FCC, SC, and BCC lattices are ≈ 0.014 at $\kappa' \approx 4.3$, ≈ 0.047 at $\kappa' \approx 3.2$, and ≈ 0.155 at $\kappa' \approx 5.4$, respectively.

Similar improvements, as those described in Sec. IV, can also be made here. For instance, the PC improvement, Eq. (22), when extended for the three lattices investigated in this section, reaches the best accuracy for $m = 0$. For this choice of m, the PC improvement can be written as

$$\phi_{PC} = \frac{Nq^2 e^{-\kappa x}}{x} + \int_{x+\frac{y}{2}}^{\infty} \rho q^2 \frac{e^{-\kappa r}}{r} 4\pi r^2 dr = \frac{Nq^2 e^{-\kappa x}}{x} + \frac{4\pi q^2\rho}{\kappa^2} e^{-\kappa z}(1+\kappa z), \tag{43}$$

where $z = x + y/2$. The new maximum relative errors for the FCC, SC, and BCC lattices are ≈ 0.009, ≈ 0.035, and ≈ 0.135, respectively.

The PR improvement, which was presented in Sec. IV.C, is also suitable for 3D lattices. By applying such a method,

we found the values $m = 2$ and 1, respectively, for the BCC and SC lattices. For the BCC lattice, there are 6, 12, and 24 particles, respectively, at the distances $r = 2x/\sqrt{3}$, $2\sqrt{2}x/\sqrt{3}$, and $x\sqrt{11/3}$, which are the particles between the first (S_1) and the third (S_3) spherical shells. The new improved expression of the ME is obtained by adding to Eq. (37) the potential generated by these particles and subtracting from it the contributions due to the spherical shells S_1 and S_2. In doing so, the maximum relative error decreases from 0.155 to 0.044. For the SC lattice, the potential generated by the shell S_1 is replaced by the 12 particles of position $r = x\sqrt{2}$. In this case, the improved expression of the ME has a maximum relative error of ≈0.0175.

C. OCP limit

The exact ME of 3D lattices has the following series expansion [4]:

$$\phi_{3D}(\kappa,x) = \frac{4\pi q^2 \rho(x)}{\kappa^2} + \frac{q^2 C}{x} + O(\kappa). \tag{44}$$

From this equation one can see that, as in the 2D case, the divergence of ϕ_{3D} when $\kappa \to 0$ vanishes in the presence of a uniform neutralizing background [Eq. (5)]. Notice that, in Eq. (37), the function L has a term of $\log(\kappa')$ in its series expansion. In order to avoid such a term and obtain a finite value of the total ME at $\kappa = 0$, we need a neutralizing background and an additional negative charge $Q_{\rm anc} = -\pi\rho q y^3/3$ in each spherical shell of our method. These additional negative charges in each spherical shell eliminate the divergent term L.

Finally, consider the Madelung constant M_3 [21] of a cubic NaCl-type crystal which can be obtained from the relation

$$\begin{aligned}\frac{q^2 M_3}{x} &= \lim_{\kappa\to 0} |\phi_+(\kappa,x) + \phi_-(\kappa,x)| \\ &= \lim_{\kappa\to 0} |\phi_{\rm SC}(\kappa,x) - 2\phi_{\rm FCC}(\kappa,\sqrt{2}x)|,\end{aligned} \tag{45}$$

where we have $\phi_- = \phi_{\rm FCC}(\sqrt{2}x)$ and $\phi_+ = -[\phi_{\rm SC}(x) - \phi_-] = -[\phi_{\rm SC}(x) - \phi_{\rm FCC}(\sqrt{2}x)]$. Notice that the evaluation of Eq. (45), when using our approximative method, will diverge due to the term L. However, we know that this divergent is not physically expected. In order to make the Madelung constant convergent we use the additional negative charges $Q_{\rm anc}$ as an additional regularization. Therefore, considering these negative charges in each spherical shell, and then eliminating L, we are able to determine the following approximative value for the Madelung constant:

$$\begin{aligned}\frac{q^2 M_3}{x} &= \frac{\pi q^2}{3x}[(6\alpha - \alpha^2 - 6) - 2(6\gamma - \gamma^2 - 6)] \\ &\approx 1.6948\frac{q^2}{x},\end{aligned} \tag{46}$$

by setting Eqs. (37), (40), and (42) in Eq. (45). Comparing with the correct value 1.7475 [21], it has a relative error of ≈0.03, which is better than the one obtained either by Eq. (9) ($M_3 \approx 1.4203$) or by Eq. (43) ($M_3 \approx 1.5520$).

VII. CONCLUSION

We presented in this letter a method to obtain an approximate closed form expression of the ME of Yukawa lattices. In order to test the accuracy of such a method we have applied it for lattices of different types and dimensions.

We have found that the ME obtained by our method becomes exact, independently of the lattice type, in both asymptotic limits of the screening parameter, $\kappa \to 0$ and $\kappa \to +\infty$. Moreover, at intermediate values of κ, the maximum relative error associated with such an energy, for most of the lattices, is satisfactorily small.

The maximum relative errors associated with the ME obtained by our method for the 2D triangular, hexagonal, and square lattices are, respectively, equal to 0.0047, 0.0199, and 0.0650. The method was also extended to 3D lattices, where we have found for the FCC, SC, and BCC lattices, respectively, the maximum relative errors 0.014, 0.047, and 0.155.

Moreover, we have shown that the accuracy of our closed form expression of the ME could be considerably improved by the following different ways: (1) by using the proposed fit of the relative error in the final expression of the ME, (2) via the substitution of some rings of the method by the particle's lattice or by a continuum system, or (3) by using functional relations which associate the ME of different lattices.

We also found that the present method works satisfactorily well for the calculation of the Madelung constants. For this latter, the relative errors associated with the 2D hexagonal and square lattices were found to be 0.0041 and 0.0060, respectively. For the 3D Madelung constant M_3 of the simple cubic lattice, a closed form approximation is also shown with a relative error of 0.03.

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