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A simple general proof of the Krazer–Prym theorem and related famous formulae resolving convergence properties of Coulomb series in crystals

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Abstract

The Krazer–Prym theorem extending the Poisson summation formula to oblique lattices is proved as a direct consequence of translational symmetry. A generalized Ewald approach based on this theorem is reproduced. The two other famous approaches proposed by Nijboer and De Wette, and by Harris and Monkhorst, are derived in the same fashion. The absence of any uniform contribution to bulk electrostatic potentials in each of those treatments is emphasized as a property of locally neutral systems subject to translational symmetry. It is found that an analytic evaluation of the Ewald variable parameter naturally follows from the treatment of the Coulomb lattice characteristic in terms of the Krazer–Prym theorem. The extension of those characteristics to off-lattice points is also discussed.

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1. Introduction

The problem of lattice summation remains the subject of active interest [1–8]. Nevertheless, of various methods of lattice summation proposed earlier [9–11], the classical approach developed by Epstein [12] and Ewald [13] and based on the Krazer–Prym theorem [14] is still one of the most widespread [15–22]. In this connection, it is worth noting that there are many treatments of conditionally convergent Coulomb series, where the influence of a remote surface is anyhow taken into account, in conjunction with the customary representation that every real crystal is eventually bounded [23, 24]. Of course, the solution appropriate to perfect crystals can also be obtained within such treatments [11], though some skill is necessary to solve this task [25]. In particular, it appears that the Krazer–Prym theorem can in turn be verified by making use of periodic boundary conditions imposed at infinity as well [26].

In the present paper we show that sophisticated approaches dealing with conditions at infinity, which are typical of methods of lattice summation in direct space [11], are not principal for descriptions based on functional transforms. It is significant that the most fundamental functional transforms of interest are conventionally introduced by the Krazer–Prym theorem. It implies that the set of statements necessary to prove this theorem, in turn, determine the properties of solutions associated with its application. This is the reason why the proof of the Krazer–Prym theorem is proposed here, simplifying that treatment in comparison with the original one [14]. As a result, we confirm that the problems of conditional convergence of Coulomb series are definitely resolved within the Ewald approach making use of this theorem. It is important that the above issue is intrinsic to perfect crystals associated with the thermodynamic limit only. In other words, it is not the case if we deal with metastable bulk states associated with unstable surfaces of bounded crystals [11]. Inasmuch as the problem of summation over low-dimensional periodic lattices is sometimes of interest [18, 19, 27], here we give the proof of the Krazer–Prym theorem in the general case of an arbitrary dimensionality.

One more insight into the physical nature of efficiency of the Ewald approach arises within the important generalizing treatment proposed by Nijboer and De Wette [28] that is based on the application of screened potentials. As a result, the classical consideration of Ewald actually deals with the complementary error function as a screening one, though different other forms of screening are possible as well.

But the latter generalization also turns out to be more general from the standpoint of conditional convergence. Indeed, the direct application of Parseval’s formula in the original paper [28] admits the appearance of an additional contribution described by the reciprocal lattice vector $\mathbf{h} = 0$. This is a matter of intensive discussion for a long time [2, 11, 23, 24] and eventually implies the inclusion of metastable states typical of finite crystals [11]. On the other hand, it is obvious that the translationally symmetric solution characteristic of the generalization at hand does not still contain such a contribution. In the present paper, this result is readily confirmed by making use of the approach similar to that describing the Krazer–Prym theorem, providing that the question about other solutions does not arise. The exclusion of the $\mathbf{h} = 0$ contribution is also inherent in the Harris–Monkhorst formula [25], where this property is originally established by a tedious procedure of examining a remote surface [25, 29]. Here we simplify this analysis as well. Moreover, based on the Krazer–Prym theorem [9, 11, 13, 14] as an extension of the many-dimensional Poisson summation formula [30, 31] to oblique lattices, a general expression for the Coulomb characteristic of a Bravais lattice specified by the Harris–Monkhorst formula is obtained for arbitrary lattices. The latter approach enables us to derive an analytic estimate of the Ewald variable parameter as well. The extension of the concept of the Coulomb characteristic of an arbitrary Bravais lattice to off-lattice points is also proposed.

2. The Krazer–Prym theorem

Let us consider a series of the form

$$S(\mathbf{r}) = \sum_i \exp[-t|\mathbf{r} - \mathbf{R}_i|^2 + i\mathbf{q}(\mathbf{r} - \mathbf{R}_i)], \quad (1)$$

where the summation over i is carried out over sites of an m -dimensional oblique Bravais lattice described by vectors \mathbf{R}_i , \mathbf{r} is an arbitrary m -dimensional position vector, t is a positive parameter and \mathbf{q} is any m -dimensional momentum. It is evident that $S(\mathbf{r})$ is subject to

translational symmetry. As a result, $S(\mathbf{r})$ can be cast in terms of a series over m -dimensional reciprocal lattice vectors \mathbf{h} :

$$S(\mathbf{r}) = \sum_{\mathbf{h}} S(\mathbf{h}) \exp(2\pi i \mathbf{h} \mathbf{r}), \tag{2}$$

where

$$S(\mathbf{h}) = \frac{1}{v} \int_{\text{cell}} S(\mathbf{r}_1) \exp(-2\pi i \mathbf{h} \mathbf{r}_1) d\mathbf{r}_1, \tag{3}$$

with v being the unit-cell volume; the integration in equation (3) is carried out over the unit cell defined as an m -dimensional parallelepiped whose edges are described by m vectors of elementary translations considered as basic ones for producing the Bravais lattice in question. It implies that the same m vectors are employed upon defining the set of elementary translations in reciprocal space. It is significant that equations (2) and (3) are connected by periodic boundary conditions on each couple of opposite faces of the unit-cell parallelepiped.

Substituting equation (1) into formula (3) and keeping in mind that the integral over the unit cell together with the summation over i is converted into the integral over all m -dimensional space [32], we easily obtain

$$S(\mathbf{h}) = \frac{1}{v} \int \exp[-t|\mathbf{r}_1|^2 + i(\mathbf{q} - 2\pi \mathbf{h})\mathbf{r}_1] d\mathbf{r}_1. \tag{4}$$

Since the integration is over uniform and isotropic space now, we may introduce Cartesian components x_j of \mathbf{r}_1 , in terms of which equation (4) takes the form

$$S(\mathbf{h}) = \frac{1}{v} \prod_{j=1}^m \int_{-\infty}^{\infty} \exp[-tx_j^2 + i(q_j - 2\pi h_j)x_j] dx_j, \tag{5}$$

where q_j and h_j , respectively, are the components of \mathbf{q} and \mathbf{h} parallel to x_j ,

$$\int_{-\infty}^{\infty} \exp[-tx_j^2 + i(q_j - 2\pi h_j)x_j] dx_j = 2 \int_0^{\infty} \exp(-tx_j^2) \cos[(q_j - 2\pi h_j)x_j] dx_j. \tag{6}$$

It is important that upon transformation from equation (4) to equation (5), it is not necessary to convert the quadratic form in the exponent of formula (4), which is described initially in terms of triclinic components of \mathbf{r}_1 , into the diagonal form in an explicit manner, though it is always possible [14].

The latter relation in equation (6) is just the integral of Poisson [30]:

$$\int_0^{\infty} \exp(-tz^2) \cos(uz) dz = \frac{1}{2} \sqrt{\frac{\pi}{t}} \exp\left(-\frac{u^2}{4t}\right). \tag{7}$$

Substituting formula (7) into relation (6) and taking this result into account in equation (5) combined with equations (1) and (2), we obtain the Krazer–Prym formula:

$$\sum_i \exp[-t|\mathbf{r} - \mathbf{R}_i|^2 + i\mathbf{q}(\mathbf{r} - \mathbf{R}_i)] = \frac{1}{v} \left(\frac{\pi}{t}\right)^{m/2} \sum_{\mathbf{h}} \exp\left(-\frac{|\mathbf{q} - 2\pi \mathbf{h}|^2}{4t} + 2\pi i \mathbf{h} \mathbf{r}\right). \tag{8}$$

On multiplying both the sides of (8) by $\exp(-i\mathbf{q}\mathbf{r}/2)$, this relation takes a symmetric form

$$\begin{aligned} & \sum_i \exp\left[-t|\mathbf{r} - \mathbf{R}_i|^2 + i\mathbf{q}\left(\frac{\mathbf{r}}{2} - \mathbf{R}_i\right)\right] \\ &= \frac{1}{v} \left(\frac{\pi}{t}\right)^{m/2} \sum_{\mathbf{h}} \exp\left[-\frac{|\mathbf{q} - 2\pi \mathbf{h}|^2}{4t} + i\left(2\pi \mathbf{h} - \frac{\mathbf{q}}{2}\right) \mathbf{r}\right]. \end{aligned} \tag{9}$$

This symmetry between the real space and reciprocal space representations is especially pronounced in the particular case of $\mathbf{r} = 0$ and $\mathbf{q} = 0$. Then formulae (8) and (9) coincide and may be written in the two mutually connected forms

$$\sum_i \exp(-t|\mathbf{R}_i|^2) = \frac{1}{v} \left(\frac{\pi}{t}\right)^{m/2} \sum_h \exp\left(-\frac{\pi^2|\mathbf{h}|^2}{t}\right), \quad (10)$$

$$\sum_h \exp(-u|\mathbf{h}|^2) = v \left(\frac{\pi}{u}\right)^{m/2} \sum_i \exp\left(-\frac{\pi^2|\mathbf{R}_i|^2}{u}\right). \quad (11)$$

Equation (11) results from formula (10) upon changing the parameter: $u = \pi^2/t$. However, it is much more important that relation (11) is just relation (10), where the following formal transformations are proposed: $\mathbf{R}_i \leftrightarrow \mathbf{h}$, $t \rightarrow u$ and $v \rightarrow v^{-1}$. The latter transformation is natural because v^{-1} is the volume of a unit cell describing the reciprocal lattice. The meaning of this connection between equations (10) and (11) is evident because the lattices composed of \mathbf{R}_i and \mathbf{h} are mutually reciprocal.

3. The Ewald approach

In order to emphasize subtle points associated with the conditional convergence of Coulomb series over crystal lattices, as well as the application of theorem (8) to this problem, here we concentrate on the Ewald approach [13]. We start from a charge distribution $\rho_c(\mathbf{r})$ subject to translational symmetry in a three-dimensional crystal. In addition, $\rho_c(\mathbf{r})$ can also be cast in terms of a charge distribution $\rho(\mathbf{r})$ attributed to the unit cell:

$$\rho_c(\mathbf{r}) = \sum_i \rho(\mathbf{r} - \mathbf{R}_i), \quad (12)$$

where the summation is over the sites of the corresponding Bravais lattice specified by \mathbf{R}_i as well. Note that representation (12) is not unique due to an optional character of $\rho(\mathbf{r})$ subject to the sole condition of local electrical neutrality

$$\int_V \rho(\mathbf{r}) d\mathbf{r} = 0, \quad (13)$$

where the integration is carried out over the volume V occupied by $\rho(\mathbf{r})$. Like equations (2)–(4), $\rho_c(\mathbf{r})$ can be cast in terms of a series over three-dimensional reciprocal lattice vectors \mathbf{h} :

$$\rho_c(\mathbf{r}) = \sum'_h F(\mathbf{h}) \exp(2\pi i\mathbf{h}\mathbf{r}). \quad (14)$$

Here the structure factor is equal to

$$\begin{aligned} F(\mathbf{h}) &= \frac{1}{v} \int_{\text{cell}} \rho_c(\mathbf{r}) \exp(-2\pi i\mathbf{h}\mathbf{r}) d\mathbf{r} \\ &= \frac{1}{v} \int_V \rho(\mathbf{r}) \exp(-2\pi i\mathbf{h}\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (15)$$

where the integral over the interior of a unit-cell parallelepiped of volume v in the first expression is transformed into the integral over all space after substituting relation (12). The fact that $(\mathbf{h}\mathbf{R}_i)$ is an integer by definition is taken into account upon deriving the last relation of equation (15) as well. Comparing equation (15) with formula (13), we see that $F(0) = 0$ and so the $\mathbf{h} = 0$ contribution is absent in equation (14), as pointed out by the prime on the summation sign there.

The electrostatic potential $U(\mathbf{r})$ generated by the charge distribution (12) at any point \mathbf{r} can be written down as

$$U(\mathbf{r}) = \int' \frac{\rho_c(\mathbf{r}_1) d\mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{r}|} = \int' \frac{d\mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{r}|} \sum_i \rho(\mathbf{r}_1 - \mathbf{R}_i), \tag{16}$$

where the prime on the integral sign implies that the singular contribution of any point charge if it happens at \mathbf{r} must be omitted. It is important that in the last relation of (16) and in what follows this prime can equally be associated with the corresponding restriction upon summation over i .

Note that we cannot go over to a new variable of integration $\mathbf{r}' = \mathbf{r}_1 - \mathbf{R}_i$ in equation (16) yet, because the sum over i would be divergent. In order to overcome this obstacle, we represent the Coulomb denominator in an obvious form

$$\frac{1}{|\mathbf{r}|} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp(-u^2|\mathbf{r}|^2) du. \tag{17}$$

On substituting expression (17) into equation (16) and going over to the variable \mathbf{r}' mentioned above, equation (16) takes the form

$$U(\mathbf{r}) = \frac{2}{\sqrt{\pi}} \int_V \rho(\mathbf{r}') d\mathbf{r}' \int_0^\infty du \sum_i \exp(-u^2|\mathbf{R}_i + \mathbf{r}' - \mathbf{r}|^2). \tag{18}$$

One can see that all the contributions to formula (18) are definite and convergent in the interval $0 < u < \infty$. The only problem appears as u tends to zero. In order to explore this particular case, we define

$$U_1(\mathbf{r}) = \frac{2}{\sqrt{\pi}} \int_V \rho(\mathbf{r}') d\mathbf{r}' \int_0^\mu du \sum_i \exp(-u^2|\mathbf{R}_i + \mathbf{r}' - \mathbf{r}|^2) - \left\{ \frac{2\mu q_j}{\sqrt{\pi}} \right\}_{r=b_j}, \tag{19}$$

where μ is a certain finite positive parameter. The contribution excluded earlier, as was shown by the prime on the integral sign, is finite here. So it is now added and subtracted, as indicated by omitting that prime, as well as by the facultative last term corresponding to a point charge q_j at a point \mathbf{b}_j if it happens that $\mathbf{r} = \mathbf{b}_j$.

Since there is no restriction on summation over i in equation (19) now, the Krazer–Prym theorem in form (10) still addressed to crystals subject to translational symmetry can be directly incorporated into formula (19), with the result

$$U_1(\mathbf{r}) = \frac{2\pi}{v} \int_V \rho(\mathbf{r}') d\mathbf{r}' \int_0^\mu \frac{du}{u^3} \sum_h \exp \left[-\frac{\pi^2|\mathbf{h}|^2}{u^2} + 2\pi i\mathbf{h}(\mathbf{r} - \mathbf{r}') \right] - \left\{ \frac{2\mu q_j}{\sqrt{\pi}} \right\}_{r=b_j}. \tag{20}$$

The fact that there is a singularity associated with the limit $u \rightarrow 0$ is confirmed by equation (20). But in the latter case it is also evident that the divergent term in question is associated with the $\mathbf{h} = 0$ contribution, which is independent of \mathbf{r}' at every value of u and so has to be removed from equation (20) due to restriction (13).

Because the rest of equation (20) is absolutely convergent, the integration can be carried out first there and results in

$$U_1(\mathbf{r}) = \frac{1}{\pi} \sum'_h \frac{F(\mathbf{h})}{|\mathbf{h}|^2} \exp \left(-\frac{\pi^2|\mathbf{h}|^2}{\mu^2} + 2\pi i\mathbf{h}\mathbf{r} \right) - \left\{ \frac{2\mu q_j}{\sqrt{\pi}} \right\}_{r=b_j}, \tag{21}$$

where the prime on the summation sign over \mathbf{h} implies missing the $\mathbf{h} = 0$ term and the structure factor $F(\mathbf{h})$ is determined by formula (15).

Extracting expression (19) from equation (18) and keeping in mind that the remainder is absolutely convergent, we easily obtain that this remainder takes the form

$$\begin{aligned} U_2(\mathbf{r}) &= \frac{2}{\sqrt{\pi}} \int_V' \rho(\mathbf{r}') d\mathbf{r}' \int_\mu^\infty du \sum_i \exp(-u^2 |\mathbf{R}_i + \mathbf{r}' - \mathbf{r}|^2) \\ &= \sum_i' \int_V \frac{\rho(\mathbf{r}') \operatorname{erfc}(\mu |\mathbf{R}_i + \mathbf{r}' - \mathbf{r}|) d\mathbf{r}'}{|\mathbf{R}_i + \mathbf{r}' - \mathbf{r}|}, \end{aligned} \quad (22)$$

where the integration over u leads to the last relation, the prime on the summation sign stands for missing the singular term associated with zero of the Coulomb denominator in agreement with the comment after equation (16),

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-u^2) du \quad (23)$$

is the complementary error function.

The total electrostatic potential is then of the form

$$U(\mathbf{r}) = U_1(\mathbf{r}) + U_2(\mathbf{r}), \quad (24)$$

where formulae (21) and (22) are taken into account.

It is important that the mean potential is equal to zero:

$$\bar{U} = \frac{1}{v} \int_{\text{cell}} U(\mathbf{r}) d\mathbf{r} = 0. \quad (25)$$

Indeed, the contribution of result (21) to equation (25) is zero due to the absence of the $\mathbf{h} = 0$ term there, providing that the contributions of all q_j associated with the last term in formula (21) compose a set of measure zero and so do not affect the integral in equation (25). On the other hand, after substituting equation (22) into equation (25), in agreement with relation (24), a further integration over \mathbf{r} replaced by $\mathbf{r} - \mathbf{R}_i - \mathbf{r}'$ results in the appearance of the output (13).

In the particular case of $\rho(\mathbf{r})$ composed of point charges q_j at positions \mathbf{b}_j in a unit cell, we have

$$\rho(\mathbf{r}) = \sum_j q_j \delta(\mathbf{r} - \mathbf{b}_j), \quad (26)$$

$$F(\mathbf{h}) = \frac{1}{v} \sum_j q_j \exp(-2\pi i \mathbf{h} \mathbf{b}_j), \quad (27)$$

in agreement with formula (15). Utilizing relation (26) in equations (21)–(22) and keeping equation (24) in mind, we obtain the classical formula of Ewald [13]:

$$\begin{aligned} U(\mathbf{r}) &= \frac{1}{\pi v} \sum_{h,j}' \frac{q_j}{|\mathbf{h}|^2} \exp \left[-\frac{\pi^2 |\mathbf{h}|^2}{\mu^2} + 2\pi i \mathbf{h}(\mathbf{r} - \mathbf{b}_j) \right] \\ &\quad + \sum_{i,j}' \frac{q_j \operatorname{erfc}(\mu |\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|)}{|\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|} - \left\{ \frac{2\mu q_j}{\sqrt{\pi}} \right\}_{\mathbf{r}=\mathbf{b}_j}. \end{aligned} \quad (28)$$

For completeness, the Coulomb energy per unit cell is as follows:

$$\mathcal{E}_{\text{tot}} = \frac{1}{2} \int_V \rho(\mathbf{r}) U(\mathbf{r}) d\mathbf{r}. \quad (29)$$

According to the meaning of $U(\mathbf{r})$, one can see that the value of \mathcal{E}_{tot} is an exact bulk energy appropriate to the thermodynamic limit as well [11].

4. General screened-potentials treatment of Nijboer and De Wette

It is significant that the Ewald approach may also be regarded as a particular case of a more general description discussed by Nijboer and De Wette [28]. In this case taking screened potentials into account leads to the enhancement of the rate of convergence of Coulomb series. For completeness, here we consider the latter treatment in our present manner. The electrostatic potential described by (16) is then expressed as

$$U(\mathbf{r}) = U_1(\mathbf{r}) + U_2(\mathbf{r}), \tag{30}$$

where

$$U_1(\mathbf{r}) = \int' \frac{\rho_c(\mathbf{r}_1)g(|\mathbf{r}_1 - \mathbf{r}|) d\mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{r}|}, \tag{31}$$

$$U_2(\mathbf{r}) = \int' \frac{\rho_c(\mathbf{r}_1)[1 - g(|\mathbf{r}_1 - \mathbf{r}|)] d\mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{r}|}, \tag{32}$$

a screening function $g(x)$ is assumed to fall off rapidly with increasing x , but $g(0) = 1$. Substituting expression (12) into equation (31), we derive

$$U_1(\mathbf{r}) = \sum'_i \int_V \frac{\rho(\mathbf{r}_1)g(|\mathbf{R}_i + \mathbf{r}_1 - \mathbf{r}|) d\mathbf{r}_1}{|\mathbf{R}_i + \mathbf{r}_1 - \mathbf{r}|}, \tag{33}$$

where the meaning of the prime on the summation sign is the same as in equation (31). It is obvious that the series in formula (33) then converges rapidly.

Since the restriction marked by the prime is not principal in equation (32), where the excluded term is actually finite, we can add and subtract this contribution. Thus equation (32) takes the form

$$U_2(\mathbf{r}) = \int \frac{\rho_c(\mathbf{r}_1)[1 - g(|\mathbf{r}_1 - \mathbf{r}|)] d\mathbf{r}_1}{|\mathbf{r}_1 - \mathbf{r}|} + \{q_j g'(0)\}_{\mathbf{r}=\mathbf{b}_j}, \tag{34}$$

where the last term is associated with any point charge q_j at the position \mathbf{b}_j if $\mathbf{r} = \mathbf{b}_j$,

$$g'(0) = \lim_{x \rightarrow 0} \frac{dg(x)}{dx}. \tag{35}$$

Substituting equation (12) into formula (34), we easily obtain

$$U_2(\mathbf{r}) = \sum'_h F(\mathbf{h})G(-\mathbf{h}) \exp(2\pi i\mathbf{h}\mathbf{r}) + \{q_j g'(0)\}_{\mathbf{r}=\mathbf{b}_j}, \tag{36}$$

where

$$G(-\mathbf{h}) = \int \frac{[1 - g(|\mathbf{r}|)] \exp(2\pi i\mathbf{h}\mathbf{r}) d\mathbf{r}}{|\mathbf{r}|}. \tag{37}$$

The integration over the angular variables of \mathbf{r} in equation (37) is straightforward. As a result, one can show that

$$G(-\mathbf{h}) = \frac{1}{\pi|\mathbf{h}|^2} \int_0^\infty \left[1 - g\left(\frac{u}{2\pi|\mathbf{h}|}\right) \right] \sin u du. \tag{38}$$

In the particular case of point-charge lattices, the substitution of equations (26) and (27) into equations (33) and (36), respectively, with keeping formula (30) in mind, leads to

$$U(\mathbf{r}) = \frac{1}{v} \sum'_h G(-\mathbf{h}) \sum_j q_j \exp[2\pi i\mathbf{h}(\mathbf{r} - \mathbf{b}_j)] + \sum'_{i,j} \frac{q_j g(|\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|)}{|\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|} + \{q_j g'(0)\}_{\mathbf{r}=\mathbf{b}_j}. \tag{39}$$

Because the series in the second term on the right-hand side of equation (39) is absolutely convergent, the order of summation over i and j may be thought of as arbitrary there. But in the first term of equation (39) the structure factor generating $G(-\mathbf{h})$ must be considered as an indivisible entity. This leads to the prime on the sign of summation over \mathbf{h} . Only if this prime is already present, the summation over \mathbf{h} and j can be carried out in an arbitrary order.

It is significant that results (33), (36) and (39) are independent of a particular choice of $\rho(\mathbf{r})$. Indeed, if we add some charge q_0 at a point \mathbf{r}_0 to $\rho(\mathbf{r})$ and subtract the same charge at a point shifted by a translation vector from \mathbf{r}_0 , then the foregoing results remain unchanged.

Different examples of $g(x)$ have been studied [20, 33]. If we choose $g(x)$ in the form of the complementary error function,

$$g(x) = \operatorname{erfc}(\mu x) = \frac{2}{\sqrt{\pi}} \int_{\mu x}^{\infty} \exp(-u^2) du, \quad (40)$$

then $g'(0) = -2\mu/\sqrt{\pi}$, whereas equation (37) is readily converted into

$$G(-\mathbf{h}) = \frac{1}{\pi|\mathbf{h}|^2} \exp\left(-\frac{\pi^2|\mathbf{h}|^2}{\mu^2}\right). \quad (41)$$

Substituting these relations into equation (39), we return to the result of Ewald (28). Results (40) and (41) utilized directly in equations (33) and (36) reproduce the generalized version of the Ewald approach driven by formulae (21)–(24).

It is important that formula (36), as well as formula (39), with taking equation (27) into account, may in turn be regarded as a modified employment of Parseval's formula in the particular case of translationally symmetric systems. On the other hand, an additional $\mathbf{h} = 0$ contribution would still arise if one substituted the last relation of equation (15) into equation (36) and interchanged the order of summation and integration, with ignoring the prime on the summation sign over \mathbf{h} . Although the latter procedure results in some ambiguity in the potential value, it is worth noting that due to a more general character of the issues, in other cases significant results could be obtained in such a generalized fashion for perfect crystals, as will be discussed elsewhere.

5. Coulomb lattice characteristic put forth by Harris and Monkhorst

Harris and Monkhorst [25] first derived one more important formula. It is based on the following Fourier integral for the Coulomb denominator:

$$\frac{1}{|\mathbf{r}|} = \frac{1}{2\pi^2} \int \frac{\exp(i\mathbf{p}\mathbf{r})}{|\mathbf{p}|^2} d\mathbf{p}. \quad (42)$$

Substituting equation (42) into equation (16), we obtain

$$U(\mathbf{r}) = \frac{1}{2\pi^2} \int' \rho_c(\mathbf{r}_1) d\mathbf{r}_1 \int \frac{\exp[i\mathbf{p}(\mathbf{r}_1 - \mathbf{r})]}{|\mathbf{p}|^2} d\mathbf{p}. \quad (43)$$

First, we are interested in a general point \mathbf{r} without any point charge. In this case the prime on the integral sign is immaterial in formula (43) and can be omitted there. By making use of equation (14), relation (43) is then transformed into

$$U(\mathbf{r}) = \frac{1}{\pi} \sum_h' \frac{F(\mathbf{h})}{|\mathbf{h}|^2} \exp(2\pi i\mathbf{h}\mathbf{r}). \quad (44)$$

However, if $\mathbf{r} = \mathbf{b}_0$, where a point charge q exists, then it is expedient to rewrite $\rho(\mathbf{r})$ in the form

$$\rho(\mathbf{r}) = \tilde{\rho}_0(\mathbf{r}) + q\delta(\mathbf{r} - \mathbf{b}_0) \quad (45)$$

and designate the contribution of $\tilde{\rho}_0(\mathbf{r})$ to formula (15) as $\tilde{F}_0(\mathbf{h})$. The potential of interest can be written as

$$U(\mathbf{b}_0) = U_1(\mathbf{b}_0) + U_2(\mathbf{b}_0), \tag{46}$$

where

$$U_1(\mathbf{b}_0) = \frac{1}{\pi} \sum'_h \frac{\tilde{F}_0(\mathbf{h})}{|\mathbf{h}|^2} \exp(2\pi i \mathbf{h} \mathbf{b}_0), \tag{47}$$

$$U_2(\mathbf{b}_0) = q \left(\frac{1}{\pi v} \sum'_h \frac{1}{|\mathbf{h}|^2} - \frac{1}{2\pi^2} \int \frac{d\mathbf{p}}{|\mathbf{p}|^2} \right)_{\text{consist}}. \tag{48}$$

The primes on the summation signs over \mathbf{h} still exist here as a direct consequence of relation (44). The elimination of the Coulomb singularity in equation (48) is accomplished just in form (42) [25]. The fact that both the terms in the parentheses of equation (48) must be calculated in a consistent manner is pointed out there. In particular [25, 34], we may suggest that both the summation and integration are performed over a common domain \mathcal{P} extending to infinity. It is convenient to write down this result as

$$U_2(\mathbf{b}_0) = q C_1, \tag{49}$$

$$C_1 = \lim_{\mathcal{P} \rightarrow \infty} \left(\frac{1}{\pi v} \sum'_{2\pi \mathbf{h} \in \mathcal{P}} \frac{1}{|\mathbf{h}|^2} - \frac{1}{2\pi^2} \int_{\mathcal{P}} \frac{d\mathbf{p}}{|\mathbf{p}|^2} \right), \tag{50}$$

where C_1 is the Coulomb characteristic of a Bravais lattice [25]. In the particular case of equations (26) and (27), formulae (44), (45) and (47) are reduced to the original results of Harris and Monkhorst [25, 29], providing that results (48)–(50) remain the same.

It is significant that averaging equation (44) over a unit-cell parallelepiped gives rise to result (25) again, providing that the discussion after equation (25) is still valid as addressed to the contribution of (46)–(50) now.

As far as the effect of C_1 is concerned, it is especially pronounced in the particular case of a jellium model [25], where a Bravais lattice composed of point charges of a sole species q is immersed in a neutralizing uniform background. The charge distribution localized within a unit-cell parallelepiped is then of the form

$$\rho(\mathbf{r}) = q \delta(\mathbf{r} - \mathbf{b}_1) - \frac{q}{v}, \tag{51}$$

where \mathbf{b}_1 is the position vector of q . In this case the potential effect of a background follows from equation (47), where a uniform charge distribution $\tilde{\rho}_0(\mathbf{r}) = -q/v$ results in zero value of $U_1(\mathbf{b}_0)$ [25]. But the interaction of a background with the total potential is also absent due to equation (25). The latter is a classical result [35], though it caused some discussion in the literature [11]. Thus, in a jellium model specified by a lattice without basis, the total Coulomb energy per unit cell is equal to

$$\mathcal{E}_{\text{tot}} \equiv \mathcal{E}_1 = \frac{q^2}{2} C_1. \tag{52}$$

6. Application of the Krazer–Prym theorem to Coulomb characteristic problems

Of the different methods for calculating C_1 , we consider only one associated with the Poisson summation formula [31]. Here we generalize this approach to oblique lattices by making use

of the Krazer–Prym theorem in form (11). Separating out the terms at $\mathbf{h} = 0$ and $\mathbf{R}_i = 0$ there, we rewrite equation (11) as follows:

$$\sum'_h \exp(-u|\mathbf{h}|^2) - v \left(\frac{\pi}{u}\right)^{3/2} \sum'_i \exp\left(-\frac{\pi^2|\mathbf{R}_i|^2}{u}\right) = v \left(\frac{\pi}{u}\right)^{3/2} - 1. \quad (53)$$

In the case of $0 < u < \infty$ both the series on the left-hand side of equation (53) are uniformly convergent. So, equation (53) can be integrated with respect to u . As a result, we reach

$$\sum'_h \frac{\exp(-u|\mathbf{h}|^2)}{|\mathbf{h}|^2} + \pi v \sum'_i \frac{1}{|\mathbf{R}_i|} \operatorname{erfc}\left(\frac{\pi|\mathbf{R}_i|}{\sqrt{u}}\right) = \frac{2\pi^{3/2}v}{\sqrt{u}} + u + \tilde{C}, \quad (54)$$

where \tilde{C} is a constant of integration. In other words, \tilde{C} is independent of u and equation (54) may be treated as an identity determining \tilde{C} . In particular, it implies that, according to formula (54), the value of \tilde{C} can be considered in the limit of $u \rightarrow 0$:

$$\tilde{C} = \lim_{u \rightarrow 0} \left[\sum'_h \frac{\exp(-u|\mathbf{h}|^2)}{|\mathbf{h}|^2} - \frac{2\pi^{3/2}v}{\sqrt{u}} \right]. \quad (55)$$

Likewise, equation (50) can be rewritten in the same manner:

$$C_1 = \lim_{u \rightarrow 0} \left[\frac{1}{\pi v} \sum'_h \frac{\exp(-u|\mathbf{h}|^2)}{|\mathbf{h}|^2} - \frac{1}{2\pi^2} \int \frac{d\mathbf{p}}{|\mathbf{p}|^2} \exp\left(-\frac{u|\mathbf{p}|^2}{4\pi^2}\right) \right]. \quad (56)$$

The calculation of the integral over \mathbf{p} in equation (56) is straightforward. Comparing the resulting expression with equation (55), we draw a conclusion that $\tilde{C} = \pi v C_1$.

But relation (54) also admits another continuation. Indeed, the right-hand side of equation (54) as a function of u has a minimum and the same is expected for the left-hand side. It implies that an optimum magnitude of u can be evaluated from the condition

$$\frac{d}{du} \left(\frac{2\pi^{3/2}v}{\sqrt{u}} + u \right) = -v \left(\frac{\pi}{u}\right)^{3/2} + 1 = 0, \quad (57)$$

with the result $u_{\text{opt}} = \pi v^{2/3}$. As anticipated, this special value of u_{opt} is the most favourable for practical calculations of \tilde{C} transforming further into C_1 . Making use of the value u_{opt} in equation (54) and going over to C_1 , we derive

$$C_1 = \frac{1}{\pi v} \sum'_h \frac{\exp(-\pi v^{2/3}|\mathbf{h}|^2)}{|\mathbf{h}|^2} + \sum'_i \frac{1}{|\mathbf{R}_i|} \operatorname{erfc}\left(\frac{\sqrt{\pi}|\mathbf{R}_i|}{v^{1/3}}\right) - 3v^{-1/3}. \quad (58)$$

It is interesting to note that the evaluation of C_1 in form (58) can be also obtained in a somewhat different fashion. Indeed, inserting issue (28) at $\mathbf{r} = \mathbf{b}_0$ into formula (49), one can show that

$$C_1 = \frac{1}{\pi v} \sum'_h \frac{1}{|\mathbf{h}|^2} \exp\left(-\frac{\pi^2|\mathbf{h}|^2}{\mu^2}\right) + \sum'_i \frac{\operatorname{erfc}(\mu|\mathbf{R}_i|)}{|\mathbf{R}_i|} - \frac{\pi}{v\mu^2} - \frac{2\mu}{\sqrt{\pi}}, \quad (59)$$

where the third term on the right-hand side of equation (59) is associated with the background contribution to the second term on the right-hand side of equation (28), the last terms on the right-hand sides of relations (59) and (28) are correspondent. Comparing results (54) and (59), we see that the Ewald variable parameter μ is connected with u as follows:

$$\mu = \pi/\sqrt{u}, \quad \mu_{\text{opt}} = \pi/\sqrt{u_{\text{opt}}} = \sqrt{\pi}v^{-1/3}. \quad (60)$$

It seems to be natural that the value μ_{opt} agrees with earlier estimates [13, 27, 36]. Substituting the value of μ_{opt} into equation (59), we return to C_1 in form (58). It is obvious that an optimum

value of μ mentioned above can be obtained immediately from equation (59), providing that the negative of the last two terms on the right-hand side of (59) be a minimum as well.

It is worth noting that Harris and Monkhorst [25] have proposed another, albeit consistent with equation (59), expression for C_1 , in terms of which the inhomogeneous potential contribution of a uniform background disappears in an explicit manner. In other words, C_1 describes the inhomogeneous potential effect exerted by a Bravais lattice composed of unit point charges at a lattice site, in agreement with (49).

Likewise, if there is a jellium model with two equal point charges q described by basis vectors \mathbf{b}_1 and \mathbf{b}_2 in the unit-cell parallelepiped, then relation (51) is replaced by

$$\rho(\mathbf{r}) = q[\delta(\mathbf{r} - \mathbf{b}_1) + \delta(\mathbf{r} - \mathbf{b}_2)] - \frac{2q}{v}. \tag{61}$$

The corresponding energy is calculated in the same manner. It is convenient here to normalize this energy per point charge and represent it in the form

$$\mathcal{E}_{\text{tot}} = \mathcal{E}_1 + \mathcal{E}_2, \quad \mathcal{E}_j = \frac{q^2}{2} C_j, \tag{62}$$

where $j = 1, 2$. The value of C_1 is then still described by formula (58), whereas

$$C_2 = \frac{1}{\pi v} \sum'_h \frac{\exp(-\pi v^{2/3} |\mathbf{h}|^2)}{|\mathbf{h}|^2} \cos[2\pi \mathbf{h}(\mathbf{b}_1 - \mathbf{b}_2)] + \sum_i \frac{\text{erfc}(\sqrt{\pi} v^{-1/3} |\mathbf{R}_i + \mathbf{b}_1 - \mathbf{b}_2|)}{|\mathbf{R}_i + \mathbf{b}_1 - \mathbf{b}_2|} - \frac{1}{v^{1/3}}, \tag{63}$$

with exploiting an optimum value $\mu_{\text{opt}} = \sqrt{\pi} v^{-1/3}$ again. The meaning of C_2 is apparently similar to that of C_1 , though C_2 is addressed to off-lattice points shifted by the vectors $\pm(\mathbf{b}_1 - \mathbf{b}_2)$ from the lattice sites.

7. Some numerical results for tetragonal and hexagonal jellium-model lattices

In order to demonstrate the effect of the foregoing Coulomb characteristics, here we consider several one-parametric families of jellium-model lattices. We begin with simple tetragonal and body-centred (bc) tetragonal lattices at various $\xi = c/a$ ratios, where c is the lattice constant along the tetragonal axis, but a is the lattice constant in the perpendicular directions. In the simple tetragonal case $v = \xi a^3$ and vectors of elementary translations are immediately specified by a and c . As a result, the vectors describing the Bravais lattices in direct and reciprocal spaces, respectively, are of the form

$$|\mathbf{R}_i|^2 = a^2(n_1^2 + n_2^2 + \xi^2 n_3^2), \tag{64}$$

$$|\mathbf{h}|^2 = \frac{\xi^2(n_1^2 + n_2^2) + n_3^2}{a^2 \xi^2}, \tag{65}$$

where n_1, n_2 and n_3 are integers over which the summation in equation (58) is actually carried out. On substituting expressions (64) and (65) into formula (58) and performing the summation over n_j there, the results for the Coulomb energy per point charge is given by formula (52). The values obtained are listed in table 1.

If we deal with bc tetragonal lattices, then $v = \xi a^3/2$, though the lattice structure in direct space is still described by a Bravais lattice without basis. The vectors of elementary translations with a common origin are conventionally chosen so that each of them is directed from an apex to the centre of an elementary rectangular parallelepiped, providing that three

Table 1. The jellium-model Coulomb energy \mathcal{E} per point charge q determined by equations (52) and (58) for simple tetragonal and body-centred (bc) tetragonal lattices at different c/a ratios. \mathcal{E} is measured either in units of q^2/a (left columns) or in units of q^2/r_s , where $4\pi r_s^3/3 = v$ (right columns).

c/a	\mathcal{E} (simple tetragonal)		\mathcal{E} (bc tetragonal)	
	q^2/a units	q^2/r_s units	q^2/a units	q^2/r_s units
7.448 957 30	1.950 132 46	2.362 651 88	0	0
3.724 478 65	0	0	-0.975 099 20	-0.744 213 87
2.00	-0.902 920 90	-0.705 716 33	-1.433 594 02	-0.889 330 75
1.90	-0.955 268 51	-0.733 973 63	-1.462 296 74	-0.891 758 33
1.80	-1.007 605 33	-0.760 358 53	-1.491 881 54	-0.893 550 23
1.70	-1.059 921 89	-0.784 742 72	-1.522 644 45	-0.894 764 22
1.60	-1.112 200 30	-0.806 975 10	-1.554 972 46	-0.895 481 24
1.50	-1.164 406 85	-0.826 873 30	-1.589 365 42	-0.895 807 40
1.40	-1.216 477 77	-0.844 210 31	-1.626 458 41	-0.895 872 30
1.30	-1.268 292 14	-0.858 692 26	-1.667 039 18	-0.895 819 93
1.20	-1.319 619 92	-0.869 920 85	-1.712 050 24	-0.895 785 55
1.10	-1.370 021 19	-0.877 327 97	-1.762 553 57	-0.895 846 68
1.00	-1.418 648 74	-0.880 059 44 ^{ab}	-1.819 616 73	-0.895 929 26 ^{ab}
0.95	-1.441 831 28	-0.879 277 80	-1.850 881 36	-0.895 873 96
0.90	-1.463 854 49	-0.876 763 66	-1.884 038 47	-0.895 635 02
0.85	-1.484 256 85	-0.872 206 19	-1.919 049 04	-0.895 061 44
0.80	-1.502 383 98	-0.865 196 47	-1.955 750 58	-0.893 930 86
0.75	-1.517 301 33	-0.855 190 21	-1.993 792 62	-0.891 923 36
0.70	-1.527 661 95	-0.841 454 05	-2.032 540 16	-0.888 584 94
0.651 553 57	-1.531 506 80 ^a	-0.823 643 80	-2.069 753 63	-0.883 478 18
0.65	-1.531 502 34	-0.822 986 25	-2.070 925 93	-0.883 275 43
0.60	-1.525 918 52	-0.798 396 99	-2.107 217 00	-0.875 091 52
0.55	-1.506 536 57	-0.765 721 85	-2.138 631 48	-0.862 748 04
0.50	-1.466 614 89	-0.722 120 86	-2.160 680 32	-0.844 385 92
0.462 491 43	-1.416 964 17	-0.679 772 97	-2.166 791 25 ^a	-0.825 047 15
0.240 156 51	0	0	-1.443 115 62	-0.441 665 06
0.169 816 30	2.040 873 56	0.701 099 54	0	0

^a This is a minimum value in the corresponding column.

^b This value agrees with the result quoted in [25, 29, 37].

parallelepipeds of interest are adjacent to the first octant [38]. In this case one can show that relations (64) and (65) must be replaced by

$$|\mathbf{R}_i|^2 = \frac{a^2}{4} \{2[n_1^2 + (n_2 - n_3)^2] + \xi^2(n_1 - n_2 - n_3)^2\}, \quad (66)$$

$$|\mathbf{h}|^2 = \frac{(n_2 + n_3)^2 + \xi^2[n_2^2 + n_3^2 + 2n_1(n_1 + n_2 + n_3)]}{a^2\xi^2}, \quad (67)$$

with the same meaning of integers n_j . A further calculation is carried out in the same manner. The results are compiled in table 1 as well.

Table 1 shows that the change in \mathcal{E} as a function of ξ is not monotonic for both types of lattices. Moreover, the instability associated with $\mathcal{E} > 0$ is predicted in either case as well. Driven by the behaviour of C_1 , for simple tetragonal lattices this instability takes place if either $\xi > 3.724 478 65$ or $\xi < 0.240 156 51$. Such a behaviour of \mathcal{E} seems to be quite reasonable for jellium-model lattices, where the two-dimensional density of point charges in a square

basic plane remains unchanged, but a three-dimensional background density changes with varying interplanar distances between square planes mentioned above. As a result, as ξ drops, the tendency towards instability arises due to approaching equal point charges belonging to adjacent square planes in question. On the other hand, in the limit of large ξ , every square plane consisting of point charges can eventually be considered independent of the other ones, but its own instability arises because the background density attributed to this plane appears to be too small to stabilize it.

The bc tetragonal lattices remain stable in a wider interval $0.16981630 < \xi < 7.44895730$. This fact can also be comprehended if we remind ourselves that any bc lattice can be regarded as a combination of two simple tetragonal lattices shifted properly from each other. In such a treatment the potential at a reference point charge is described by the contribution C_1 of the sublattice to which that charge belongs and by the contribution C_2 of the other sublattice. The latter effect leads to attraction and so enhances the overall stability of a system, as will be discussed later on.

Contrary to the absolute boundaries of stability, one more problem shown in table 1 is associated with the fact that the value of ξ at which the energy \mathcal{E} is a minimum strongly depends on the energy units employed in either of the aforementioned cases. It is natural because there are several length parameters typical of the task now. As a result, the energy is a complicated function of those parameters. This circumstance is immaterial if we deal with any fixed lattice. On the other hand, if the lattice stability relative to variations of the lattice parameters is discussed, then an energy unit should be chosen with caution. Indeed, \mathcal{E} measured in units of q^2/r_s attains its minimum value at $\xi = 1$ in both the cases. This result seems to be reasonable, for cubic structures arising at $\xi = 1$ are expected to be the most stable due to their high symmetry. However, in units of q^2/a , a minimum value of $\mathcal{E} = -1.5315068$ takes place at $\xi = 0.65155357$ in simple tetragonal lattices. This fact anyhow resembles the situation in CsCl tetragonal structures [36]. However, the case of bc tetragonal structures turns out to be much more suspicious in this respect.

In order to understand these inferences, we again resort to C_1 in form (55). One can see that the second term on the right-hand side of formula (55) is structureless and so the characteristic length typical of this term is merely $v^{-1/3}$. As far as the first term on the right-hand side of that formula is concerned, this term diverges as $u \rightarrow 0$. This singularity is naturally compensated by the second term. In terms of length units, it seems to be plausible that such a compensation renders the length $v^{-1/3}$ characteristic of both of these terms. It implies that every length parameter proportional to $v^{-1/3}$ is to be suitable as a natural measure of C_1 . The definition of r_s mentioned above apparently agrees with this requirement.

Although the energy contribution of C_1 is intrinsic to every lattice, the explicit energy effect of C_2 is inevitable in lattices with basis. This is the reason why now we consider a jellium model with simple hexagonal (sh) and hexagonal close-packed (hcp) lattices of point charges at various $c/a = \xi$ ratios, where c is the lattice constant along the hexagonal axis and a is the nearest-neighbour distance in the orthogonal plane. Note that at a given ξ the Bravais lattice is common to both of these structures, with $v = a^3\xi\sqrt{3}/2$, and the same is right for the reciprocal lattice specified by \mathbf{h} . Furthermore, if three vectors of elementary translations considered as basic ones are so chosen that the angle between two of these vectors lying in a hexagonal plane is equal to $2\pi/3$, whereas the third vector is normal to this plane, then

$$|\mathbf{R}_i|^2 = a^2(n_1^2 + n_2^2 - n_1n_2 + \xi^2n_3^2), \quad (68)$$

$$|\mathbf{R}_i + \mathbf{b}_1 - \mathbf{b}_2|^2 = a^2\left[\frac{1}{3} + n_1(1 + n_1 - n_2) + n_2^2 + \xi^2\left(\frac{1}{2} + n_3\right)^2\right], \quad (69)$$

Table 2. The jellium-model Coulomb energy \mathcal{E}_{tot} per point charge q that is determined by equations (52)–(71) for simple hexagonal (sh) and hcp lattices, as well as \mathcal{E}_2 contributing to the latter case, at different c/a ratios. For comparison, all the energies are measured in units of q^2/r_s , where $4\pi r_s^3/3 = v/2$ is typical of hcp lattices [25].

c/a	sh lattice		hcp lattice	
	$\mathcal{E}_{\text{tot}} = \mathcal{E}_1$	\mathcal{E}_2	\mathcal{E}_2	$\mathcal{E}_{\text{tot}} = \mathcal{E}_1 + \mathcal{E}_2$
6.969 154 38	1.888 665 36	–1.888 665 36	0	0
3.484 472 47	0	–0.749 483 47	–0.749 483 47	–0.749 483 47
2.00	–0.530 704 41	–0.358 751 47	–0.889 455 88	–0.889 455 88
1.90	–0.556 850 26	–0.335 630 63	–0.892 480 89	–0.892 480 89
1.80	–0.581 417 33	–0.313 127 75	–0.894 545 08	–0.894 545 08
1.70	–0.604 302 23	–0.291 339 25	–0.895 641 48	–0.895 641 48
1.635 639 41	–0.618 086 40	–0.277 752 05	–0.895 838 45 ^{ab}	–0.895 838 45 ^{ab}
1.632 993 16 ^c	–0.618 636 67	–0.277 201 45	–0.895 838 12 ^d	–0.895 838 12 ^d
1.60	–0.625 385 30	–0.270 393 41	–0.895 778 70	–0.895 778 70
1.50	–0.644 525 40	–0.250 460 99	–0.894 986 39	–0.894 986 39
1.40	–0.661 551 91	–0.231 768 49	–0.893 320 40	–0.893 320 40
1.30	–0.676 251 30	–0.214 614 32	–0.890 865 62	–0.890 865 62
1.20	–0.688 343 98	–0.199 387 49	–0.887 731 47	–0.887 731 47
1.10	–0.697 442 80	–0.186 587 21	–0.884 030 01	–0.884 030 01
1.00	–0.702 976 38	–0.176 840 91	–0.879 817 29	–0.879 817 29
0.95	–0.704 143 99	–0.173 347 21	–0.877 491 19	–0.877 491 19
0.928 357 50	–0.704 267 41 ^a	–0.172 157 70	–0.876 425 11	–0.876 425 11
0.90	–0.704 044 52	–0.170 915 95	–0.874 960 47	–0.874 960 47
0.85	–0.702 468 82	–0.169 665 18	–0.872 134 00	–0.872 134 00
0.826 848 52	–0.701 165 20	–0.169 520 77 ^a	–0.870 685 97	–0.870 685 97
0.80	–0.699 139 32	–0.169 721 47	–0.868 860 79	–0.868 860 79
0.75	–0.693 682 98	–0.171 219 88	–0.864 902 86	–0.864 902 86
0.70	–0.685 592 03	–0.174 305 01	–0.859 897 04	–0.859 897 04
0.65	–0.674 166 14	–0.179 134 07	–0.853 300 20	–0.853 300 20
0.60	–0.658 425 03	–0.185 884 26	–0.844 309 29	–0.844 309 29
0.55	–0.636 972 66	–0.194 768 12	–0.831 740 78	–0.831 740 78
0.50	–0.607 778 17	–0.206 062 90	–0.813 841 08	–0.813 841 08
0.221 137 75	0	–0.352 489 97	–0.352 489 97	–0.352 489 97
0.168 028 35	0.423 318 08	–0.423 318 08	0	0

^a This is an extremum value in the corresponding column.

^b This minimum value is discussed in [37, 39].

^c This is an ideal ratio $c/a = \sqrt{8/3}$ for hcp lattices.

^d This value agrees with the results in [25, 37, 39].

$$|\mathbf{h}|^2 = \frac{4\xi^2(n_1^2 + n_2^2 + n_1n_2) + 3n_3^2}{3a^2\xi^2}, \quad (70)$$

$$\mathbf{h}(\mathbf{b}_1 - \mathbf{b}_2) = \frac{4n_1 + 2n_2 + 3n_3}{6}. \quad (71)$$

Here n_1 , n_2 and n_3 are also integers over which the summation in equations (58) and (63) is carried out. Moreover, these parameters are common to equations (70) and (71) upon summation over \mathbf{h} in formula (63). On substituting equations (68)–(71) into formulae (58) and (63), the further numerical calculation based on equations (52), (58), (62) and (63) is straightforward. The results are compiled in table 2.

Note that the peculiar features of table 2 look like those of table 1. A minimum value of \mathcal{E}_1 occurs at $\xi = 0.928\,357\,50$ and this value associated with the stable state of sh lattices can also be expressed as $\tilde{\mathcal{E}}_1 = -0.887\,321\,33q^2/\tilde{r}_s$, where the normalization $4\pi\tilde{r}_s^3/3 = v$ is inherent in the case at hand.

The trend in changing C_1 is similar to that in tetragonal lattices. The opposite trend in changing \mathcal{E}_2 , with a maximum of \mathcal{E}_2 at $\xi = 0.826\,848\,52$, can also be comprehended on the ground of the same arguments as those mentioned above for C_1 . In the limit of small ξ , a drop in C_2 is driven by an increase in the three-dimensional background density, whose contribution to C_2 is stronger here than that of surrounding point charges. This effect correlates with a growth of C_1 due to formula (25). However, in the case of large ξ the influence of a background is predominant again. Although a background density diminishes, this density determines the potential effect at the neighbourhood of reference points specific to C_2 , whereas point charges in hexagonal planes of the other sublattice turn out to be too far from the foregoing reference points. This effect can be understood as a consequence of the negative uniform potential that is necessary to be added so as to make zero value of the mean potential within the plane-wise summation approach [39]. In this case the sublattice potential of interest is originated by hexagonal planes of point charges together with a background contribution, providing that a background is decomposed into portions attributed to every point-charge plane in a symmetric manner. As a result, the negative value of the correcting potential is the only nonzero one surviving on planes situated midway between point-charge hexagonal planes at large ξ . Furthermore, the negative magnitude of that potential increases upon enhancing interplanar distances [39].

Thus, either of the trends is quite typical. The interplay between these trends accounts for a minimum value of \mathcal{E}_{tot} shown in table 2 and corresponding to the stable state of hcp lattices at $\xi = 1.635\,639\,41$ [39, 37]. It is interesting to notice that this minimum appears to be close to the value of ξ characteristic of ideal hcp structures, though extremum values of either of the parameters \mathcal{E}_1 and \mathcal{E}_2 occur in a quite different region of $\xi < 1$. The problem of instability of hcp lattices is also associated with the aforementioned interplay and turns out to be in close connection with the properties of sh lattices. Indeed, on the boundaries of stability of sh lattices, we have $\mathcal{E}_2 < 0$ and so hcp lattices are still stable there. In other words, the interval of stability of hcp lattices includes a narrower interval of stability of sh lattices, by definition.

8. Conclusion

In summary, it is ascertained that the Krazer–Prym theorem described by equation (8)–(11) is governed by local periodic boundary conditions on a unit cell boundaries. As a result, not only does its application enhance the rate of convergence of Coulomb series in accordance with the traditional standpoint addressed to the Poisson summation formula, but also, being a consequence of the translational symmetry of Bravais lattices, this theorem enables one to perform summation of the conditionally convergent Coulomb series in a manner leading to the definite unique result relevant to perfect crystals associated with the thermodynamic limit [11].

As a result, the electrostatic potential subject to translational symmetry has no uniform contribution within every treatment appropriate to the case. This fact follows directly from local electrical neutrality. It is worth noting that this result looks like the case of zero potential in empty space. It is not occasional because, namely, this limiting case appears if we are interested in effects whose scale is large enough with respect to the lattice parameters. Moreover, even if we deal with large, but finite crystals, of all different conditions on their

surfaces, the special ones always exist and warrant the bulk solution discussed here. This issue means that those surfaces are in equilibrium with bulk states, as anticipated in the case of the thermodynamic limit as well.

As for the Coulomb characteristic of a Bravais lattice, it is actually responsible for the inhomogeneous potential effect. This is the reason that a neutralizing uniform background does not contribute to this parameter. On the other hand, this circumstance turns out to be somewhat implicit if we focus our attention on the potential value at a lattice site, providing that this potential is generated by identical point charges located at all other lattice sites. Nevertheless, the application of the Krazer–Prym theorem for calculating the Coulomb characteristic in question takes the foregoing peculiarity into account automatically. Hence, the procedure of numerical calculation discussed here is not only effective, but it resolves some methodical difficulties typical of the task. In particular, it is shown that the inhomogeneous field driven by the Coulomb characteristics accounts for the peculiar features of stability of jellium-model tetragonal and hexagonal lattices, providing that energy units are chosen properly.

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