## Convergence problems of Coulomb and multipole sums in crystals

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**Contents** 

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Abstract. Different ways of calculating Coulomb and dipole sums over crystal lattices are analyzed comparatively. It is shown that the currently alleged disagreement between various approaches originates in ignoring the requirement for the selfconsistency of surface conditions, which are of fundamental importance due to the long-range nature of the bulk interactions that these sums describe. This is especially true of surfaces arising when direct sums for infinite translation-invariant structures are truncated. The charge conditions for actual surfaces being self-consistently adjusted to the bulk state are formally the same as those on the truncation surface, consistent with the concept of the thermodynamic limit for the bulk-state absolute equilibrium and with the fact that the surface energy contribution in this case is, naturally, statistically small compared to the bulk contribution. Two-point multipole expansions are briefly discussed, and the problems associated with the boundary of their convergence circle are pointed out.

### 1. Introduction

In the modern solid-state physics and chemistry, Coulomb sums over a regular lattice are primarily associated with the description of the cohesive energy in ionic crystals [1-6]. The potential fields expressed in terms of such sums are responsible for both the electronegativity [7, 8] and charge transfer in the crystal bulk [6, 7, 9–15]. The effect of bulk potentials on

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Received 30 July 2003, revised 22 December 2003 Uspekhi Fizicheskikh Nauk **174** (10) 1033–1060 (2004) Translated by E Yankovsky; edited by A Radzig the electronic band structure is associated with this [13, 16-24]. Bulk potentials determine the local crystalline fields which split the quantum states of individual ions [25, 26], and are responsible for the manifestations of structural disorder [12, 14, 27]. To describe the various structural and electronic properties of the crystal surface, the knowledge of the electrostatic potentials in the bulk and the procedure of matching with them are required as well [4, 28-38].

The various current methods of summing over the lattice have been described in great detail, for example, in reviews [1, 4, 20, 39]. A distinctive feature of these methods is the fact that they ensure a high rate of the series convergence. However, diverse methods may yield different results. Moreover, conflicting findings may be obtained even within a certain fixed method. These facts go on to originate the discussions about what method is more correct and reliable and also about the understanding of the methods allowing different results upon their various applications argued in every case.

The reason for these difficulties is obvious and lies in the long-range nature of the local potentials being summed. Indeed, the three-dimensional power-law sum over space is absolutely convergent if the terms being summed asymptotically behave as  $R^{-s}$ , where s > 3, and R is the distance. Only in this case will the rate of decrease of the potential prevail over the growth of the volume of the region over which summation is performed, and so the result of summation will be independent of the way in which this summation is done. The Coulomb (s = 1), dipole (s = 2), and even quadrupole (s = 3) potentials do not produce such uniquely determined series. The series that emerge from these potentials may diverge when they are formally summed. Nevertheless, such series belong to the class of conditionally convergent series, provided that they describe parameters with a certain physical meaning, which for this reason assume definite magnitudes. In other words, additional reasonable physical assumptions, which are responsible not for convergence in general but for convergence to the 'necessary' limit, will be required when taking the summation.

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Notice that to justify convergence, as such, only a minimum of necessary arguments is presented. This creates another very important problem, namely, the exceptionally slow convergence of the series, with the result that increasing the rate of convergence becomes the key issue. Just upon solving this problem the main differences between the basic methods of series summation arise, since the approaches applied to accelerate convergence prove to be not so harmless as it would appear and some even violate the requirement that convergence be physically justifiable. Here we deal with the property of uniform convergence of a conditionally convergent series, the property which is violated if the initial series is evaluated by a series whose terms are modified by additional factors strongly decreasing with growing R, so as to render that auxiliary series rapidly convergent. It may seem amazing, but so far this important aspect has not been seriously discussed in the literature concerning the physical applications of conditionally convergent sums over the crystal lattice. One exception that comes to mind is the results describing the spectral features of quasi-particle excitations in the long-wave limit [40], which are mentioned in Section 3.

The present review is a fairly compact and yet full description of the main methods of series summation over the crystal lattice. To our mind, such an organization of the material may be useful for scientists that are only beginning their research and, therefore, need to be introduced to the problem. A fairly exhaustive list of references will enable such researchers to get acquainted with the details of each approach. But it seems to be much more important that such a combined consideration of the different methods of summation enables one to compare those methods from the viewpoint of the general physical concept responsible for the series convergence, a concept that forms the basis of these methods, and to specify the cases where this concept is violated. As a result, on the one hand, it becomes possible to substantiate the existence of a solution that is unique for all approaches and describes the bulk state in an infinite crystal. On the other hand, it appears that other possible solutions also have a certain physical meaning and a general nature, corresponding to metastable states of finite crystals.

For the reader's convenience, we point out the layout of the material presented below. Section 2 is devoted to the discussion of properly Coulomb series. At the beginning, we describe the methods in which a high rate of convergence is achieved by means of functional transformations. Despite the fact that the series representation resulted turns out to be rather cumbersome in those cases, the methods in question are the simplest ones with respect to the treatment of key statements responsible for the convergence of interest.

The Madelung slice-wise summation method is considered first. This method in not only of historical interest, but it has found its modern application in a large number of tasks where the bulk structure is constructed as a slab (stack) of layers convenient for numerical analysis. The peculiar feature of this method is the use of sigh-changing structural fragments. Its classical application to the description of point-charge lattices is the most instructive one. In this case, the natural sequence of summation over structural fragments in order of increasing distances is inherent in this method and implements the electroneutrality condition as a local one. At the same time, if a charge spreading takes place, then it is noted that an ambiguity about the solution is possible. Removing this ambiguity requires using the universal properties of bulk potentials, which are established by other summation procedures.

In this respect, the widely used Ewald method, which is also examined in Section 2 in the original classical interpretation, appears to be completely independent. Here, series convergence again stems from the requirement that the crystal be locally neutral, provided that the initial summation over the charges of the unit cell is carried out. It is significant that the result of such a summation turns out to be independent of the particular choice of a unit-cell volume. The treatment in Section 2 shows that the condition of local neutrality in the same interpretation is also typical of other methods which use either representations in terms of the Fourier integral or expansions over the Brillouin zone in the Born supercell method.

The Ewald solution also reveals that the mean value of the electrostatic potential inside the crystal is always zero. Obviously, this property correlates with the general ideas about mean local electroneutrality and can be considered its second manifestation [27]. As for the high rate of series summation in the Ewald method, it stems from the effect of spreading of point charges, described explicitly in the generalized Bertaut approach which also agrees with the initial summation over the cell charges and the zero mean value of the potential.

There is also another approach to accelerating series convergence (first described by Madelung), related to the introduction of screening potentials. Widely used lately and considered an alternative interpretation of the Ewald method, this approach is capable of reproducing Ewald's result but with one important exception: a finite average potential is added generally to the solution. Mathematically, the reason for this modification is that the emerging series is not uniformly convergent in terms of the screening parameter. Physically, the cause lies in the additional regrouping of the charges under screening, which disturbs the initial translation-invariant sequence of the charge distribution. The discussions that have emerged in the literature are also treated in Section 2, where it is found that the reason for this additional potential effect lies in the appearance of a double layer on the nonequilibrium discontinuity surface of the summation domain.

The problems associated with the effect of a nonequilibrium surface are discussed in Sections 3 and 4. For instance, it is no wonder that an effect similar to allowance for charge screening emerges in direct summation, where convergence is ensured by a particular selection of a fixed charge cell in which the regrouping of charges is assumed by definition. It is shown that simple subtraction of the mean potential from the direct sum is enough for obtaining true bulk solutions. This result is corroborated by symmetry-related arguments and by analyzing the particular solutions existing in the literature, including both the closed summing combinations generated via integration of the Poisson summation formulas and the discussed self-similar approach that uses Padé approximants. Thus, contrary to the ideas common in the scientific literature over the last decades, we substantiate the absolute uniqueness of electrostatic fields in an equilibrium crystal.

Another specific feature of lattice-summed multipole expansions of potential fields, typical of self-consistency problems, is related to the manifestation of the boundary of the convergence circle for the given expansions in the summation of the emerging multiple series in moments. It turns out that, strictly speaking, in the existing systematics of such expansions there are cases where the order of summation may change, and cases where this order is fixed. In view of the latter, we discuss such problems as the nonuniqueness of expansions, the violation of the continuity of the potential description in practical calculations, and aspects of convergence of the respective series.

The uniqueness of bulk potentials is also related to the uniqueness of determining the specific electrostatic energy expressed in terms of bulk potentials. In this connection, I discuss in Section 4 the case where in view of various circumstances unit cells with nonzero dipole moments are examined. The corresponding lattice sums describing the specific energy then again become conditionally convergent. As a result, the direct sum converges to a value that differs from the bulk energy by a correction term whose magnitude depends on the order of summation.

The effect that occurs in the summation over lattices formed by point dipoles is exactly the same. It is shown that the emerging correction term is directly related to the idea of a Lorentz<sup>1</sup> field, which therefore acquires rigorous mathematical meaning. It also becomes clear that the contribution of the Lorentz field is homogeneous in space and refers to a description of the energy of a crystal without boundaries. The effect of the nonequilibrium boundaries of a finite crystal leads to depolarization which depends on the shape of the real boundary and is generally inhomogeneous over the crystal's volume. An exception is ellipsoidal samples, in which the depolarization effect proves to be homogeneous and is described, to within its sign, by the expression identical with that for the Lorentz field in the summation over an expanding ellipsoid.

As noted in this connection with reference to many investigations, the depolarization effect is energetically unfavorable. Hence, achieving thermodynamic equilibrium presupposes a transformation of the surface configuration, so that the surface matches the state of the volume in order to eliminate the depolarization effect. Such a requirement constitutes a marked feature of the thermodynamic limit at which the independence of bulk thermodynamics from surface thermodynamics is retained, despite the long-range nature of the Coulomb and dipole forces. An important conclusion that can be drawn from this is that parallel ordering of dipoles in a crystal is made possible by the action of purely dipole forces, which does not contradict the absence of a dipole order of any kind in polar liquids. The idea of a bulk thermodynamic limit resolves several problems under discussion, problems related to numerical simulation of surface properties.

### 2. Functional transformations

The first detailed discussion of the basic properties of potential solutions with arbitrary three-dimensional translation symmetry can be found in Appell's works [41], where the solution of the Laplace equation in the volume of an elementary parallelepiped is expressed in terms of a twodimensional integral along the parallelepiped's boundaries. A nontrivial solution stems from the assumption that there are singularities in this volume element, whose residues have the meaning of point charges with zero sum. Basing his reasoning on the fact that the potential of a point charge is the Green's function of the problem, Appell [41] was the first to introduce the idea of a bulk potential in the form of a sum of the pointcharge potentials taken over the lattice. It turned out that the series that emerges for charges of each type is divergent.

The interest in point charges also has another basis related to a theorem in electrostatics, which states that the external potentials of local spherically symmetric charge distributions are equivalent to the potentials of point charges placed at the centers of these distributions [42]. Thus, lattices consisting of point charges are classical objects of investigation [2, 4, 43]. In this case, the potential at a point specified by the radius vector **r** is determined by a discrete series of pair Coulomb potentials:

$$U(\mathbf{r}) = \sum_{i,j}^{\prime} \frac{q_j}{|\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|}, \qquad (1)$$

where *i* runs through the sites  $\mathbf{R}_i$  of the Bravais lattice, and *j* runs through the base vectors  $\mathbf{b}_j$  describing the positions of the charges  $q_j$  in the unit cell. They obey the electroneutrality condition

$$\sum_{j} q_j = 0.$$
 (2)

In view of the translation invariance of  $U(\mathbf{r})$ , naturally expected in a perfect infinite crystal, it is sufficient to limit the positions of  $\mathbf{r}$  to the region occupied by a polyhedron of the central unit cell with  $\mathbf{R}_i = 0$ . The prime on the sum in formula (1) means that the particular cases of self-action at  $\mathbf{R}_i = 0$  and  $\mathbf{r} = \mathbf{b}_i$  are excluded. Notice the fact that the real charges are not point-like and this leads to a situation in which the excluded self-action potentials and the respective energies, being the functionals of the local charge distributions, are finite. These terms must be taken into account in studies of the general stability of an ensemble of unlike charged particles [44], a stability achieved through additional allowance for short-range repulsion. All these contributions are important for the overall energy balance in a crystal [45-52], but can be dropped without any consequences in discussions of the features of summation over the already existing lattice. Here, the fundamental problem of conditional convergence of Coulomb and similar sums over the lattice [39, 47, 53] follows from the indeterminateness of the order of series summation in formula (1) [54].

### 2.1 The Madelung slice-wise summation method

In his heuristic sequence of summation based on the vivid feature of the NaCl structure, Madelung [55] isolated the signchanging neutral charge chains from which neutral flat parallel layers constituting the three-dimensional lattice of NaCl are formed [1, 39]. In this model NaCl lattice with a lattice spacing *a* and charges  $\pm q$ , the potential on charge q ( $\mathbf{r} = \mathbf{b}_+$ ) placed for convenience at the origin ( $\mathbf{b}_+ = 0$ ) can be written as follows:

$$U(\mathbf{b}_{+}) = U_{\rm ch}(\mathbf{b}_{+}) + U_{\rm lay}(\mathbf{b}_{+}) + U_{\rm slab}(\mathbf{b}_{+}).$$
(3)

Here, the first term on the right-hand side describes the potential generated by the other charges in the chain containing  $\mathbf{b}_+$  and is equal, with allowance for the fact that  $|\mathbf{b}_-| = a/2$ , to

$$U_{\rm ch}(\mathbf{b}_{+}) = \frac{4q}{a} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} = -\frac{(4\ln 2)q}{a} , \qquad (4)$$

where summation over integers *n* in their increasing order guarantees homogeneity of the results when we go over to the potentials  $U_{ch}(\mathbf{b}_{\pm})$  acting on neighboring charges [56]. The potential contribution from other chains in the layer containing  $\mathbf{b}_{+}$  is described by the second term on the righthand side of equation (3), which is advisable to represent in the form

$$U_{\text{lay}}(\mathbf{b}_{+}) = 2\sum_{n=1}^{\infty} (-1)^{n} \left[ \frac{4q}{a} \sum_{\substack{l=-\infty\\ \{\text{odd}\}}}^{\infty} K_{0}(\pi n l) \right],$$
(5)

where  $K_0(x)$  is the modified cylindrical MacDonald function which rapidly decreases and exhibits the property  $K'_0(x) = -K_1(x) \approx -1/x$  as  $x \to 0$  [57]; the integers *l* describe the reciprocal lattice vectors l/a along the chain. The potential of an individual chain [the expression in square brackets in Eqn (5)] was obtained as translation-invariant solution symmetric in the transverse direction  $\mathbf{r}_{\perp}$ :

$$U(r_{\perp}, z) = \sum_{l=-\infty}^{\infty} f_l(r_{\perp}) \exp\left(\frac{2\pi i l z}{a}\right)$$
(6)

of the boundary-value problem [42]

$$\Delta U(r_{\perp}, z) = 0, \quad -\frac{r_{\perp}}{2} \left. \frac{\partial U(r_{\perp}, z)}{\partial r_{\perp}} \right|_{r_{\perp}=0} = \rho_{\rm lin}(z) , \qquad (7)$$

where the linear charge density along the chain,  $\rho_{\text{lin}}(z)$ , is represented by a series similar to formula (6). The exclusion of even *l*'s in formula (5) emerges because of a coherence effect associated with the local electroneutrality property (2).

The contribution of  $U_{\text{slab}}(\mathbf{b}_+)$  in Eqn (3) is generated by the slab of all other layers parallel to the introduced layer. It is significant that  $U_{\text{slab}}(\mathbf{r})$  specifies the total potential at an arbitrary point of observation  $\mathbf{r}$  between the layers. If we decompose  $\mathbf{r}$  into components along and across the layer,  $\mathbf{r} = (\mathbf{r}_{\parallel}, z)$ , where without loss of generality we can assume that  $0 \le z < a/2$ , the potential  $U_{\text{slab}}(\mathbf{r})$  generated by a slab of layers infinite on both sides assumes the form

$$U_{\text{slab}}(\mathbf{r}) = \sum_{n=-\infty}^{\infty} (-1)^n \left[ \frac{q}{a} \sum_{\substack{l_1=-\infty\\l_2=-\infty}}^{\infty} \frac{F(\mathbf{l})}{|\mathbf{l}|} \times \exp\left( \frac{2\pi \mathbf{i} (\mathbf{lr}_{\parallel})}{a} - \pi |\mathbf{l}| \left| n + \frac{2z}{a} \right| \right) \right],$$
(8)

where the prime on the sum over *n* means that at z = 0 there is no term with n = 0, which formally is divergent in expression (8) but is described by the sum of the contributions (4) and (5). The expression in square brackets on the right-hand side of equation (8) specifies the potential of an individual layer, obtained through an approach similar to that in Eqns (5)– (7). Introduction of the reciprocal lattice vectors  $\mathbf{l}/a = (l_1/a, l_2/a)$  into the layer plane determines a structural factor  $F(\mathbf{l})$  of the form

$$F(\mathbf{l}) = 1 - \exp(-\pi i l_1) - \exp(-\pi i l_2) + \exp\left[-\pi i (l_1 + l_2)\right].$$
(9)

As a result, even  $l_1$ 's and  $l_2$ 's fall out of sum (8).

Summation of the progression in n in formula (8) is the final step that gives the slice-wise summation method its

classical form [55, 58, 59]

$$U_{\text{slab}}(\mathbf{r}) = \frac{4q}{a} \sum_{\substack{l_1, l_2 = -\infty \\ \{\text{odd}\}}}^{\infty} \frac{D_{\mathbf{l}}(z) \exp\left(2\pi i (|\mathbf{l}\mathbf{r}_{\parallel})/a\right)}{|\mathbf{l}| \left[1 + \exp(-\pi |\mathbf{l}|)\right]}, \quad (10)$$

$$D_{\mathbf{l}}(z) = \begin{cases} \exp\left(-\frac{2\pi|\mathbf{l}|z}{a}\right) - \exp\left(\frac{2\pi|\mathbf{l}|z}{a} - \pi|\mathbf{l}|\right) \\ & \text{for } z \neq 0 , \\ -2\exp(-\pi|\mathbf{l}|) & \text{at } z = 0 . \end{cases}$$
(11)

The quantity  $U_{\text{slab}}(\mathbf{b}_+)$  is specified by formulas (10) and (11) in the particular case where  $\mathbf{r}_{\parallel} = 0$  and z = 0.

The high rate of convergence of the series (5) and (10) stems from the passage to the space of reciprocal lattice vectors, which constitutes the main property of the Poisson summation formula [54, 59–61]. The specific energy for the NaCl structure is expressed by Eqn (3) and can be represented in a universal manner as  $(-q^2/a)\alpha_M$ , where  $\alpha_M$  is the Madelung constant.

Direct use of this approach makes it also possible to generalize the results obtained to pair potentials of the central type, which have higher rates of decrease with increasing distance [62]. The simplified formulas due to the cubic symmetry of the NaCl structure in question are not specific to the method which can easily be expanded to encompass the general case of a triclinic system [59, 63]. Partitioning the initial lattice into a set of lattices, each of which contains charges of a single type balanced by a homogeneous charge background to ensure electroneutrality [59], formalizes the calculation of  $\alpha_{\rm M}$  for fairly complex structures [64].

Decomposing the potential into the contributions (4) and (5) of the proper layer, and the contributions (10) and (11) of the other layers is typical of slice-wise summation [65] and means that formula (10) does not give a full description of the ionic potential (3) [58]. It is interesting to note, however, that the ionic potential can be obtained directly by employing the passage to the limit  $\mathbf{r} \rightarrow 0$  based on formula (8). Indeed, basing our reasoning on the relationship  $\partial |\mathbf{r}|/\partial r_{\mu} = r_{\mu}/|\mathbf{r}|$ , where  $r_{\mu}$  is an arbitrary projection of vector  $\mathbf{r}$  with an Euclidean metric, we can represent series (1) at  $\mathbf{r} = \mathbf{b}_{+}$  in a form proposed by Mackenzie [66]:

$$U(\mathbf{b}_{+}) = \sum_{i,j}' \frac{q_{j}}{|\mathbf{Q}_{(ij)}|} = \left[\frac{\partial}{\partial r_{\mu}} \sum_{i,j} \frac{q_{j} Q_{(ij)\mu}}{|\mathbf{Q}_{(ij)} - \mathbf{r}|}\right]_{\mathbf{r}=0}, \quad (12)$$

where  $\mathbf{Q}_{(ij)} = \mathbf{R}_i + \mathbf{b}_j - \mathbf{b}_+$ ; the equalities  $Q_{(0+)\mu} = 0$  exclude the limiting contribution of the point of observation from the sums on the right-hand side. We assume that the summation rule for the repeating index holds for orthogonal projections, while for nonorthogonal projections the given convolution is modified by allowing for the metric tensor. This is important, since the convergence of the series on the right-hand side is guaranteed upon slice-wise summation if all three projections are orthogonal to the layers, with the result that their proper orthogonality may be violated. As a result, differentiation under the summation sign is admissible, and this corroborates the matching of the right- and left-hand sides in formula (12) upon slice-wise summation as long as each of the three selected plane orientations is equivalent in the description of potential (10) [67]. On the other hand, calculating each righthand-side sum for each fixed  $\mu$  prior to differentiation, we can immediately apply expansion (8), where the allowance for  $Q_{(ij)\mu}$  trivially modifies only the sum of the progression. In the particular case of NaCl, subsequent differentiations are identical and lead to Benson's result [4, 58] for the limiting sum (as  $\mathbf{r} \rightarrow 0$ ):

$$U(\mathbf{b}_{+}) = -\frac{96\pi q}{a} \sum_{\substack{l_{1}, l_{2}=1\\ \{\text{odd}\}}}^{\infty} \frac{\exp(-\pi|\mathbf{l}|)}{\left[1 + \exp(-\pi|\mathbf{l}|)\right]^{2}}.$$
 (13)

Similar formulas have been derived for cases of an orthorhombic ( $a_1 \neq a_2 \neq a_3$ ) NaCl structure [68], and the CsCl structure [69]. The reader will note the common energy interpretation of potential (12), where the sum on the righthand side specifies the double specific interaction energy of the two crystal half-spaces on a per-area basis of a unit cell in the plane that separates these half-spaces [4, 58, 62, 66, 68 – 72], while differentiation can be related to the minimization of this energy, which stresses the inner relationship between the absolute value of the potential and the interaction energy [55]. The resulting series prove to converge very rapidly, which made it possible to calculate the values of  $\alpha_M$  with extreme accuracy [69].

Notice that at l = 0 in formula (5), as at l = 0 in formula (8), there is an indeterminacy of the 0/0 type, which is removed by first summing over the charges of the neutral cell, a procedure specific both to a chain and to an individual, flat, neutral, and infinitely thin layer [55]. But if the translationally repetitive layers possess a certain charge distribution over their thickness, the existence of a transverse dipole moment of this distribution leads to a double-layer effect [42], thus generating gradients in the bulk potential as an artifact [72]. But even when there is no transverse dipole moment in a layer, the nonzero second moment of the transverse charge distribution in such a layer generates within the volume a potential shift which depends on the orientation of the layers [63, 67], so that the results of other calculation methods [59] are needed if we want to clarify the situation.

### 2.2 The Ewald method and its generalizations

A powerful alternative approach to the problem of summation of Coulomb series consists in the use of integral transformations. Here, the most general subject of investigation, which incorporates all the main cases of lattice sums, is the Z-function introduced by Epstein [39, 53, 73, 74]:

$$Z \left| \begin{array}{c} g_1 \dots g_p \\ k_1 \dots k_p \end{array} \right| (s)_{\varphi} = \sum_{\substack{m_1 = -\infty \\ m_p \equiv -\infty}}^{\infty} ' \frac{\exp\left[2\pi i (m_1 k_1 + \dots + m_p k_p)\right]}{\varphi \langle\!\langle m + g \rangle\!\rangle^{s/2}},$$
(14)

where  $m_1, \ldots, m_p$  are integers, and  $k_1, \ldots, k_p, g_1, \ldots, g_p$  are real-valued parameters; the denominator contains a power of the metric form of a general type in a *p*-dimensional space:

$$\varphi \langle\!\langle m+g \rangle\!\rangle = \sum_{\mu,\nu=1}^{p} d_{\mu\nu} (m_{\mu} + g_{\mu}) (m_{\nu} + g_{\nu}) > 0 , \qquad (15)$$

and the prime on the sum in formula (14) indicates that the contribution of  $\varphi \langle \langle m + g \rangle \rangle = 0$  is excluded. The procedure of calculating the series (14), proposed by Epstein [53], consists of two stages: transforming the denominator through the use of an integral representation of the gamma function (as a particular case of the Mellin transformation [39, 75]), and then applying the Poisson summation formula.

Limiting ourselves to the series (1) as an important particular case of expression (14) [73], we can easily reduce the representation of the denominator in terms of the gamma function to a simpler form [4, 39, 76]

$$\frac{1}{|\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp\left(-t^2 |\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|^2\right) \mathrm{d}t.$$
(16)

Now, if we substitute Eqn (16) into formula (1), we arrive at a series that can be transformed, according to the Krazer – Prym theorem [53, 77, 78], into a series in the reciprocal lattice vectors **h**:

$$\sum_{i} \exp\left(-t^{2} |\mathbf{R}_{i} + \mathbf{b}_{j} - \mathbf{r}|^{2}\right)$$
$$= \frac{\pi^{3/2}}{vt^{3}} \sum_{\mathbf{h}} \exp\left[-\frac{\pi^{2} |\mathbf{h}|^{2}}{t^{2}} + 2\pi i \mathbf{h} (\mathbf{b}_{j} - \mathbf{r})\right], \quad (17)$$

where v is the unit-cell volume. Note that if the transformation (17) is carried out over all the coordinates except one, we obtain rapidly convergent series with MacDonald functions for the potentials with different rates of decrease [79]. Such series are extremely effective both in three-dimensional summation [80-83] and in problems with two-dimensional geometry [84], resulting, in particular, in formula (5). What is more, the use of a two-dimensional analog of expansion (17) in the sum on the right-hand side of Eqn (12) [71] immediately leads to solution (13) [62, 68]. Here, we do not discuss alternative ways of obtaining series involving MacDonald functions as applied to the problem of lattice summation of Coulomb potentials, alternatives based on the use of Schlömilch series [85] (progressions augmented by Bessel functions, whose very appearance in the given problem is closely related to the Poisson summation formula [86]).

A special feature of expansion (17) is that for large t's the sum on the left-hand side rapidly converges, while for small t's the sum in h rapidly converges. This property of relationship (17), which was first obtained in the one-dimensional case by Poisson [87] and corresponds to the imaginary Jacobi transformation [4, 54, 88], is well known in the theory of Jacobi's theta functions (progressions with members whose exponents are quadratic in the summation parameter) and is used for their effective numerical calculation [89]. It was exactly this approach combined with a decomposition of the integration domain in t on the right-hand side of formula (16) at point t = 1 that Epstein used. What Ewald introduced in Ref. [76] (and this made his method highly successful) was a variable decomposition boundary of the integration domain, which made it possible to achieve equal convergence rates of both sums. Substituting Eqn (16) into formula (1) and using both representations of Eqn (17), with the boundary parameter  $\eta$  in integrating with respect to t we arrive at Ewald's formula for the bulk potential  $U_{\rm b}(\mathbf{r})$  [1, 20]:

$$U_{\rm b}(\mathbf{r}) = \frac{1}{\pi v} \sum_{\mathbf{h},j}' \frac{q_j}{|\mathbf{h}|^2} \exp\left[-\frac{\pi^2 |\mathbf{h}|^2}{\eta^2} + 2\pi i \mathbf{h}(\mathbf{b}_j - \mathbf{r})\right] + \sum_{i,j}' q_j \frac{\operatorname{erfc}(\eta |\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|)}{|\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|} - \left\{\frac{2\eta q_j}{\sqrt{\pi}}\right\}_{\mathbf{r} = \mathbf{b}_j}, \quad (18)$$

where the prime on the sum with respect to **h** means that the term with  $\mathbf{h} = 0$  is absent as a result of allowing for condition (2) in the summation with respect to *j* on the right-hand side of expression (17) multiplied by  $q_j$ ; the term in braces is

facultative and is present only in the potential acting on the charge  $q_i$ ; by definition, it follows that

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} \exp(-y^2) \,\mathrm{d}y \,. \tag{19}$$

The optimum value of  $\eta$  depends on the lattice structure [4, 9, 90, 91]; for the NaCl lattice, one finds  $\eta = 2\sqrt{\pi}$  [76, 92]. Notice also that the potential averaged over the unit-cell volume is given by

$$\bar{U}_{\rm b} = \frac{1}{v} \int_{\rm cell} U_{\rm b}(\mathbf{r}) \,\mathrm{d}\mathbf{r} = 0\,, \qquad (20)$$

with each of the three contributions to potential (18) vanishing independently. This can easily be verified if we account for condition (2) and for the fact that integration over the cell, combined with summation over the Bravais lattice, is equivalent to integration over the entire space [16, 93].

The physical meaning of this result is that the spreading of the point charges accelerates the convergence of the series [55, 76]. Following Bertaut [94], we can describe the effect of isotropic charge spreading in the crystal by a charge distribution of the form

$$\rho_{\rm c}(\mathbf{r}) = \sum_{i,j} q_j \sigma \left( |\mathbf{r} - \mathbf{R}_i - \mathbf{b}_j| \right) = \frac{1}{v} \sum_{\mathbf{h}}' F(\mathbf{h}) \exp(2\pi i \mathbf{h} \mathbf{r}) ,$$
(21)

$$\int \sigma(|\mathbf{r}|) \, \mathrm{d}\mathbf{r} = 1 \,, \tag{22}$$

$$F(\mathbf{h}) = \sum_{j} q_{j} \exp(-2\pi i \mathbf{h} \mathbf{b}_{j}) \int \sigma(|\mathbf{r}|) \exp(-2\pi i \mathbf{h} \mathbf{r}) \, \mathrm{d}\mathbf{r} \,. \tag{23}$$

The absence of a term with  $\mathbf{h} = 0$  in Eqn (21) is caused by the vanishing of  $F(\mathbf{h} = 0)$  in view of condition (2). Here, the specific interaction energy in the point-charge lattice and the potential on the *j*th charge are given by the expressions

$$\mathcal{E}_{\text{int}}^{\text{point}} = \mathcal{E}_{\text{tot}} - \mathcal{E}_{\text{over}} - \mathcal{E}_{\text{self}}, \quad U_{\text{b}}(\mathbf{b}_{j}) = \frac{\partial \mathcal{E}_{\text{int}}^{\text{point}}}{\partial q_{j}}, \quad (24)$$

where

$$\mathcal{E}_{\text{tot}} = \frac{1}{2N} \int \frac{\rho_{\text{c}}(\mathbf{r}_{1})\rho_{\text{c}}(\mathbf{r}_{2})\,\mathrm{d}\mathbf{r}_{1}\,\mathrm{d}\mathbf{r}_{2}}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} = \frac{1}{2\pi\nu} \sum_{\mathbf{h}}' \frac{|F(\mathbf{h})|^{2}}{|\mathbf{h}|^{2}}\,,\quad(25)$$

$$\mathcal{E}_{\text{over}} = \frac{1}{2} \sum_{i, j_1, j_2}' q_{j_1} q_{j_2} \left[ \int \frac{\sigma(|\mathbf{r}_1 - \mathbf{b}_{j_1}|) \sigma(|\mathbf{r}_2 - \mathbf{b}_{j_2}|) \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2}{|\mathbf{R}_i + \mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{R}_i + \mathbf{b}_{i_1} - \mathbf{b}_{i_1}|} \right],$$
(26)

$$\mathcal{E}_{\text{self}} = \frac{1}{2} \sum_{j} q_{j}^{2} \int \frac{\sigma(|\mathbf{r}_{1}|) \sigma(|\mathbf{r}_{2}|) \, \mathrm{d}\mathbf{r}_{1} \, \mathrm{d}\mathbf{r}_{2}}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} \,.$$
(27)

Here,  $\mathcal{E}_{tot}$ , also specified by the term with the integral in Eqn (26), is the total specific energy of a lattice containing an infinite number N of unit cells. The priority of summation with respect to *j*, inherent in Eqn (21), excludes the term with  $\mathbf{h} = 0$  from formula (25). The quantity  $\mathcal{E}_{over}$  describes the part of  $\mathcal{E}_{tot}$  related to the charge overlapping which rapidly decreases with increasing distance, so that direct summation in expression (26) proves effective. Finally,  $\mathcal{E}_{self}$  represents the contribution of self-action of the charges  $q_j$ , which is present in Eqn (25).

In the particular case of a Gaussian distribution normalized by condition (22) [95-98], one finds

$$\sigma(r) = \left(\frac{2}{\pi}\right)^{3/2} \eta^3 \exp\left(-2\eta^2 r^2\right), \qquad (28)$$

and equations (23)-(27) lead to formula (18) with term-byterm correspondence of each of the three contributions, in accordance with Ewald's original idea [76]. The extremely high effectiveness of Gaussian smearing explains the wide application of the Ewald method in cases of complex crystal structures [9, 51, 91] and more complicated constructions being summed, typical of multipole expansions [19, 99] and the indirect RKKY (Ruderman-Kittel-Kasuya-Yoshida) interaction [100]. This explains why Ewald's method has been used to develop the powerful computational algorithms of today [101-103].

At the same time, form (28) is not the only possible one. A general approach based on results (21)–(27) makes it possible to study other types of charge spreading [98, 104–109], which have proved to be effective in calculating the Madelung constant  $\alpha_M$  [110]. This approach is also useful in studying the effects of real charge overlapping [97, 111, 112] and charge transfer, including the analysis of stability of competing crystal structures [113] and the description of complex anions [114]. A two-dimensional modification of the structural factor (9) following the pattern seen in Eqn (23) is also meaningful upon slice-wise summation [32, 33], which with Gaussian smearing corresponds to the use of a two-dimensional analog of expression (17) [115].

Generally, the given approach has two important features. As noted by F Bertaut, the case of nonoverlapping distributions  $\sigma(r)$  is exceptional. Term (26) then vanishes, with the result that only rapidly convergent sums over the reciprocal lattice contribute to Eqn (24) [94]. Moreover, the existence of two representations of the potential with different meanings has become a subject of discussion (see Refs [105, 106, 116]). On the one hand, the Poisson equation for the charge distribution (21)–(23) generates local potentials of the form

$$U_{\rm loc}(\mathbf{r}) = U_0 + \mathbf{r}\mathbf{E} + \frac{1}{\pi v} \sum_{\mathbf{h}}' \frac{F(\mathbf{h})}{|\mathbf{h}|^2} \exp(2\pi i\mathbf{h}\mathbf{r}), \qquad (29)$$

where the constants of integration  $U_0$  and  $\mathbf{E}$  can be found from the boundary conditions. It is obvious that  $\mathbf{E} = 0$  for translation-invariant solutions and, as will be shown in Sections 2.3 and 3,  $U_0 = 0$ , too. As for the total potential acting on the *j*th charge from the side of all other charges and determined by expression (24), it can be found by subtracting from  $U_{\text{loc}}(\mathbf{r})$  its own potential field and subsequent integrating with a weight  $\sigma(|\mathbf{r} - \mathbf{b}_j|)$  [105, 117]. Nonoverlapping spherical distributions constitute an exception: the local potential generated by the surrounding charges at the center of the given charge distribution directly describes the interaction energy of this charge with the lattice.

Furthermore, comparison of potentials (18) and (29) shows that in the case of a point-charge lattice the smearing effect of type (21)-(23) is homogeneous and extends to all points of space. Such a feature of the solution makes it possible to restore the potential in approach (24) at any intermediate point **r** via the formal passage

$$U_{\mathbf{b}}(\mathbf{r}) = \lim_{q_{a} \to 0} U_{\mathbf{b}}(\mathbf{b}_{q_{a}} = \mathbf{r})$$
(30)

by placing the auxiliary charges  $q_a$  at the given point and at all points that are translation-conjugate to that point. Result (20) is retained in the process.

## 2.3 The Bethe potential effect upon changing the order of summation

The absence of the term with  $\mathbf{h} = 0$  in formulas (18) and (25) is the consequence of a definite order of summation and is the reflection of the fact that the charge distribution acts as the initial reason for the generation of the potential field [76]. The delicacy of this peculiar fact becomes obvious if, taking into account the difference nature of the interaction energy (26) and of the potential generated by it, we express, following Nijboer and De Wette [118], the partition of sum (1) in a more formalized form

$$U(\mathbf{r}) = \sum_{i,j}' \frac{q_j}{Q_{ij}} = \sum_{i,j}' \frac{q_j g(Q_{ij})}{Q_{ij}} + \sum_{i,j} \frac{q_j \left[1 - g(Q_{ij})\right]}{Q_{ij}} - \left\{q_j \lim_{Q \to 0} \frac{1 - g(Q)}{Q}\right\}_{\mathbf{r} = \mathbf{b}_j},$$

and perform summation over the reciprocal lattice in the second term under the summation sign with respect to *j*:

$$U(\mathbf{r}) = \sum_{i,j}' \frac{q_j g(Q_{ij})}{Q_{ij}} + \frac{1}{v} \sum_{j,\mathbf{h}} P_j(\mathbf{h}) G(-\mathbf{h}) - \left\{ q_j \lim_{Q \to 0} \frac{1 - g(Q)}{Q} \right\}_{\mathbf{r} = \mathbf{b}_j},$$
(31)

where  $Q_{ij} = |\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|$ ; the auxiliary function g(Q) rapidly decreases as Q increases, and g(0) = 1 (in the case of Eqn (18), this is the erfc(x) function), and  $P_j(\mathbf{h})$  and  $G(\mathbf{h})$  are the Fourier transforms of the charge distribution  $q_j \sum_i \delta(\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}')$  with the Dirac delta functions and the interaction kernel  $[1 - g(|\mathbf{r}' - \mathbf{r}|)]/|\mathbf{r}' - \mathbf{r}|$ , respectively. In addition to the convergence rate being studied now in relation to the choice of g(Q) [118–122], result (31), in contrast to Eqns (18)–(27), now contains a term with  $\mathbf{h} = 0$ possessing an indeterminacy of the 0/0 type, thus reflecting the contemporary state of the exciting intrigue in the problem of lattice summation, which has been going on for more than seventy years [123].

It should be emphasized that approach (31) is universal for accelerating the convergence of lattice sums, although the exclusion of the contribution from the zero **h**, typical of bulk solutions, can be based on different arguments. For instance, to describe neutron scattering, when the charge aspect of the problem is unessential, the contribution from the nonscattered neutron flux is excluded, by definition, from the expression for the scattering cross section [124].

The nontrivial nature of the case of a charged system becomes apparent if to substantiate relationship (31) we complete the definition of series (1) with the passage to the limit [55, 125, 126]

$$U(\mathbf{r}) = \lim_{\varepsilon(\hat{\mathbf{R}}_i) \to 0} \sum_{i,j}' \frac{q_j \exp\left[-\varepsilon(\hat{\mathbf{R}}_i)|\mathbf{R}_i|^2\right]}{|\mathbf{R}_i + \mathbf{b}_j - \mathbf{r}|},$$
(32)

where  $\hat{\mathbf{R}}_i = \mathbf{R}_i / |\mathbf{R}_i|$ . The absolute convergence of the series for  $\varepsilon(\hat{\mathbf{R}}_i) > 0$  allows for arbitrary permutations of the summation operations, including the functional transformations of type (31). The use of a simple exponential function describing the

screening of the Coulomb potential is also justified in this sense [43, 76, 125, 127, 128]. The point is that, according to condition (2), series (1) is an alternating one and inner summation with respect to *j* ensures homogeneous signalternation in summation with respect to *i*, just as in the case of potential (4). As for the illusion of the universal nature of the result of absolute convergence in series (32), the reader will recall that the presence of the exponential factor  $\exp(-\varepsilon |\mathbf{R}_i^2|)$  under the summation sign leads to a discontinuity in the magnitude of the series as  $\varepsilon \to 0$ , which serves as a classical example of violation of uniform convergence of a series in the theory of functional series [54].

The presence of this singularity in solution (31) [128] means that one should be very careful when dealing with a passage to the limit (often used in physics), when it comes to the conditional convergence. The new limiting contribution arose as  $\mathbf{h} \rightarrow 0$  has its own independent physical meaning [129], which manifests itself in both the potential and the energy. It has proven convenient to discuss this contribution on the basis of general solution (29), where it corresponds to the constants of integration described by the first two terms on the right-hand side [130]. Leaving the discussion of the energy aspect related to the field **E** to Section 4, we here focus on the meaning of  $U_0$ , which emerges in the passage to the limit in question. To this end, we write down the translationally repetitive charge distribution of type (21) in the crystal in the general form

$$\rho_{\rm c}(\mathbf{r}) = \sum_{i} \rho(\mathbf{r} - \mathbf{R}_{i}), \qquad (33)$$

where an arbitrary charge distribution  $\rho(\mathbf{r})$  in the unit cell meets the conditions that incorporate the case of point charges:

$$\int_{V} \rho(\mathbf{r}) \, \mathrm{d}\mathbf{r} = 0 \,, \quad \rho(\mathbf{r}) \Rightarrow \sum_{j} q_{j} \delta(\mathbf{r} - \mathbf{b}_{j}) \,, \tag{34}$$

and integration is done over the region of the distribution  $\rho(\mathbf{r})$ . Combining this with formulas (23) and (29), we get

$$U_{0} = \lim_{\substack{\mathbf{h}_{1} \to 0\\\mathbf{h}_{2} \to 0\\\mathbf{h}_{3} \to 0}} \frac{\exp(2\pi i \mathbf{h}_{2} \mathbf{r})}{\pi v |\mathbf{h}_{3}|^{2}} \int_{V} \rho(\mathbf{r}') \exp(-2\pi i \mathbf{h}_{1} \mathbf{r}') \, d\mathbf{r}' \,.$$
(35)

Solutions (18)–(27) follow from Eqn (35) if the limit in  $\mathbf{h}_1$  is taken first [125, 128]. This requirement, however, is not contained in expression (35) explicitly. Hence, it is quite natural that a different case is described in the literature:  $\mathbf{h}_1 = \mathbf{h}_2 = \mathbf{h}_3 = \mathbf{h}$  [13, 17, 35, 123, 131–134]. When the exponentials are expanded in a series in small  $\mathbf{h}$ , the first terms of the general expansion are determined by the lower moments of  $\rho(\mathbf{r})$ :

$$M_{\mu} = \int_{V} r_{\mu} \rho(\mathbf{r}) \,\mathrm{d}\mathbf{r} \,, \quad G_{\mu\nu} = \int_{V} r_{\mu} r_{\nu} \rho(\mathbf{r}) \,\mathrm{d}\mathbf{r} \,, \tag{36}$$

where  $r_{\mu}$  are the Cartesian components of **r**. As a result, the finite limit in Eqn (35), which does not depend on the direction of **h**, emerges under the additional conditions [13, 131, 135]

$$M_{\mu} = 0, \qquad G_{\mu\nu} = H\delta_{\mu\nu}, \qquad (37)$$

where  $\delta_{\mu\nu}$  is the Kroneker delta, and the value of *H*, related to the trace of the tensor  $G_{\mu\nu}$ , remains arbitrary. Averaging over

the orientations of **h** [35, 123, 132, 134], which replaces conditions (37) [131], also follows from Eqn (32) with an isotropic  $\varepsilon$ . As a result, we arrive at the following quantity

$$U_0 = -\frac{2\pi H}{v} = -\frac{2\pi}{3v} \int_V |\mathbf{r}|^2 \rho(\mathbf{r}) \,\mathrm{d}\mathbf{r} = \bar{U}_{\mathrm{Cd}} \,, \tag{38}$$

where the first equality also emerges upon slice-wise summation with a symmetric transverse distribution of charges in the layer [59, 125, 136].

The last equality in relationship (38) is a reflection of Bethe's well-known result [93], which states that a zero Fourier harmonic of the potential is obtained by using formula (20) to average the potential  $U_{\rm Cd}(\mathbf{r})$  which is defined by a direct sum of the form

$$U_{\rm Cd}(\mathbf{r}) = \sum_{i}' \int_{V} \frac{\rho(\mathbf{r}') \, \mathrm{d}\mathbf{r}'}{|\mathbf{R}_{i} + \mathbf{r}' - \mathbf{r}|} \,. \tag{39}$$

Expanding the denominator of the integrand in Legendre polynomials [42], we readily see that conditions (34) and (37) with an arbitrary H are necessary and sufficient for absolute convergence of series (39) [137–139], as expected. If formula (39) is substituted into Eqn (20), a passage to the limit in the following form is admissible [93]:

$$\bar{U}_{Cd} = \frac{1}{v} \int_{cell} d\mathbf{r} \sum_{i}' \int_{V} \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{R}_{i} + \mathbf{r}' - \mathbf{r}|}$$
  
$$\Rightarrow \lim_{R \to \infty} \left[ \frac{1}{v} \int_{V} \rho(\mathbf{r}') d\mathbf{r}' \int_{|\mathbf{r}| < R} \frac{d\mathbf{r}}{|\mathbf{r}' - \mathbf{r}|} \right].$$
(40)

The integral over the cell in the first row, combined with the sum over the Bravais lattice, is transformed into an integral over the entire space. Since the crystal, no matter what its symmetry, is placed in homogeneous isotropic space, integration with respect to **r** in an expanding spherical region reflects the properties of this space. Further changes in the order of integration with respect to  $\mathbf{r}$  and  $\mathbf{r}'$  lead to an angular averaging of the properties of  $\rho(\mathbf{r})$  and finally yield formula (38). Thus, the angular averaging procedure, mentioned earlier in connection with the derivation of formula (38) as a limit in **h**, is a consequence of conditions (34) and (37) of absolute convergence of series (39), guaranteeing that for a given  $\rho(\mathbf{r})$  series (38) is uniquely defined [123, 140]. Note that in the particular case of spherical nonoverlapping atoms of a single kind,  $\bar{U}_{Cd} > 0$  is specified by the total moment of inertia of the electrons in the atom [93]. Then, result (38) emerges immediately if, following Frenkel [141], we interpret such atoms as spherical capacitors. The presence of the function g(Q) in potential (31) does not affect the derivation of formula (38).

The existence of the introduced potential correction [17, 130, 140] means matching the value of quantity (38) describing the solution inside a finite crystal to the zero value of the potential at infinity, because the potential undergoes a compensating jump at the surface even if quantity (38) does not depend on the shape of the surface [136, 142]. When the second condition in Eqn (37) is not met, the emerging potential effect depends on the shape of the surface, and this dependence is retained in the passage to the limit of an infinite crystal [135, 136]. This has led to the idea (a paradoxical one) [125] that for an infinite crustal (i.e., without boundaries) there is no way in which the average potential can be uniquely defined [131]. Obviously, this point of view,

which gained wide support (e.g., see Refs [123, 133, 134]), contradicts the results of a consistent analysis of the singularities being mutually compensated as  $\mathbf{h} \rightarrow 0$  [54, 90, 143], which was clearly demonstrated in the review by Bagno et al. [133]. In turn, the proof of the uniqueness of a nonzero average potential in a crystal with boundaries, based on the study of a slab of infinite layers [131], was refuted by obvious counterexamples [144].

The reasons for these differences in opinion are obvious just look at how the statement of the initial problem has changed! While before we analyzed a volume translationally symmetric solution in an infinite crystal without boundaries, now we are discussing the situation with infinitely distant boundaries. This agrees with the intuitively clear idea that all real crystals have boundaries but a thermodynamically equilibrium bulk solution should not depend on these boundaries, provided that the real boundary acts as an independent self-adjusting physical object [145]. Then, Ewald's result (18) corresponding to the first statement of the problem must also describe an equilibrium solution within the second statement [65, 125, 136]. (The existence of an equilibrium solution for systems with Coulomb long-range interactions in the context of homogeneous electric fields will be considered in Section 4.) However, in parallel with such an equilibrium solution there may be a multitude of metastable solutions which depend on the nonequilibrium configurations of charge distribution over the surface. This follows from the classical Picard theorem [146] which states that any constant potential matching the boundary conditions is always an admissible bulk periodic solution of the Laplace equation. Actually, this fact was discussed many times in connection with Eqn (31), when in the bulk potential we isolated the bulk potential contribution in the form (18) and the spatially permanent part depended on the surface configuration [20, 125, 136, 142, 147] and incorporated into modern computational algorithms [83, 148]. Nevertheless, the scientific literature contains no clear indication that an arbitrarily formulated boundary-value problem must generally be a nonequilibrium one. This explains why Ewald's equilibrium solution is not believed by somebody to be a true one [20, 123, 133, 134, 142, 149, 150].

From this stems the inconsistency in modeling the physical situation, which is the reason for numerous discussions. In particular, it comes as no surprise that using a nonzero average potential [93, 123] for describing equilibrium electronic properties, such as the work function [30, 151], led to certain problems. For instance, the calculated value of  $\bar{U}_{Cd}$ proved to be unreasonably large due to the total contribution of all the atomic orbitals, a fact that has been repeatedly discussed in order to determine the contribution from valence orbitals more accurately [93, 123, 136, 152]. The unquestionable nonuniqueness of  $U_{Cd}$  can be related to the arbitrariness in specifying  $\rho(\mathbf{r})$  in a particular crystal structure [123]. If, in addition, the second condition in Eqn (37) is not met, the value of  $U_0$  proves to be dependent on the shape of the sample, thus contradicting the results of experiments [136, 151], since this would mean that the work function for a face of arbitrary but fixed orientation must change as the size and orientation of other faces vary. Without going into details about this effect, we only note that the conventional potential approach to its description presupposes, provided that we have proved the uniqueness of the bulk potential, the independence of the work function from direction, which is always the case in the leading order of magnitude [353], thus bringing us back to the consideration of the potential features of the boundaries [125]. On the other hand, the observed dependence of the effect on the orientation of the surface may still be an indication of the inelastic nature of electron emission accompanied by surface excitation.

The diversified opinions concerning the problem of the bulk potential manifest themselves most vividly in studies of the classical jellium model, where one of the charged subsystems involving ions or conduction electrons is considered an auxiliary one, the subsystem that ensures the overall electroneutrality, and is represented in a simplified way by a homogeneously charged background [16, 93, 153– 158]. One feature of the jellium model, first mentioned by Fuchs [16], is that, in view of condition (20), the interaction of the homogeneous background with the resulting bulk potential contributes nothing to energy deposition. Hence, the energy of the charged lattice immersed in the compensating background is reduced to the energy of point charges in the field  $U_{\rm b}(\mathbf{r}_0)/2$ , where  $\mathbf{r}_0$  specifies the position of a point charge in the cell [78]. This led to a conclusion that later was substantiated many times over, namely, that in the limit of low electron density, where the potential energy contribution is predominant [153, 159], the bcc structure, i.e., a typical structure of alkali metals [160], is most stable in the jellium model [16, 143, 161, 162]. Note that, in this approach, allowing for the Debye screening of point charges as their number density grows makes it also possible to explain the emergence of an fcc structure [90].

A heuristic substantiation of Fuchs's result follows from the fact [163] that the interaction of the Bravais lattice of point charges q with the compensating charge background per unit cell can be consistently represented in the form

$$\frac{q^2}{v} \int_{\text{cell}} d\mathbf{r} \sum_{i} \frac{1}{|\mathbf{R}_i - \mathbf{r}|} = \frac{q^2}{v^2} \int_{\text{cell}} d\mathbf{r}' \int \frac{d\mathbf{r}}{|\mathbf{r}|} , \qquad (41)$$

where on the right-hand side we have formally added the integral with respect to  $\mathbf{r}'$ , which cancels an extra v in the denominator, while the integral with respect to **r** is evaluated over the entire space as result of a combination of the sum and integral on the left-hand side. A subsequent shift of the integration variable,  $\mathbf{r} \rightarrow \mathbf{r} - \mathbf{r}'$ , transforms the right-hand side of Eqn (41) into an expression compensating for the background-background interaction. It should be noted, however, that the sum on the left-hand side of Eqn (41) diverges, while the passage to the integral with respect to r on the right-hand side (also divergent) presupposes a change in the order of summation. The rightfulness of the independent interpretations of the vanishing and remaining energy contributions stems from the fact that the same interaction between point charges and background describes both contributions and therefore serves as a common basis for excluding the singularities in each contribution. Such rightfulness was substantiated by Coldwell-Horsfall and Maradudin [143], who used a transformation of the theta functions in partitioning the integral representation of the Coulomb denominators in the remaining part of the interaction, without, however, going over to the momentum representation [88]. Here, the cancellation of the singular contributions follows directly from the electroneutrality of the cell.

On the other hand, direct summation of the expression for the energy, truncated according to Eqn (41) [143, 163], leads in a natural way to an energy correction term related to the potential (38) [135]. The existence of a nonzero average potential was acknowledged in the discussion that emerged in Refs [130, 131, 149, 164, 165]. However, it was noted that the homogeneous background also interacts with this potential, so that the resulting energy of the electroneutral lattice is independent of the average potential [130, 149]. In this way, Fuchs's result was found to be justified only from the viewpoint of the obtained energy values but not in its essence [59, 164].

Thus, the absence of a clear understanding of how longrange forces can generate metastable states in addition to a stable state led to two concepts of summation [140] based on Eqns (18) and (31), with the second approach being not a generalization of the first to nonequilibrium cases but a competitor [20]. The universality of Bethe's result (38), which is independent of the surface shape, is used here as the chief argument. However, in Section 3 we will show that the fundamental value of Bethe's result amounts to just the opposite, i.e., with it we are able to match all existing schemes of lattice summation, in contrast to their traditional opposition [74, 138, 166].

### 2.4 The use of Fourier transformations

Since the effect that emerged in Eqn (31) is related to the nonpermutability of inner summation over the electroneutral cell in the equilibrium case, it is worth demonstrating that this circumstance manifests itself in approaches that are directly based on the integral Fourier representation of the type [20, 167, 168]

$$\frac{1}{\left|\mathbf{r}\right|} = \frac{1}{2\pi^2} \int \frac{\exp(i\mathbf{p}\mathbf{r}) \,\mathrm{d}\mathbf{p}}{\left|\mathbf{p}\right|^2} \,. \tag{42}$$

Considering the potential  $U_{\rm b}(\mathbf{b}_{j_0})$  on the  $j_0$ th charge placed, for convenience, at the origin and substituting formula (42) into Eqn (1), Harris and Monkhorst [167] found that

$$U_{\rm b}(\mathbf{b}_{j_0}=0) = \frac{q_{j_0}C}{2\pi^2} + \frac{1}{\pi v} \sum_{j \neq j_0} q_j \sum_{\mathbf{h}}' \frac{\exp(2\pi i\mathbf{h}\mathbf{b}_j)}{|\mathbf{h}|^2} , \quad (43)$$

$$C = \lim_{\mathcal{P} \to \infty} \left\{ \frac{2\pi}{v} \sum_{2\pi \mathbf{h} \in \mathcal{P}}' \frac{1}{|\mathbf{h}|^2} - \int_{\mathbf{p} \in \mathcal{P}} \frac{d\mathbf{p}}{|\mathbf{p}|^2} \right\},\tag{44}$$

where the contribution from the neighborhood of  $\mathbf{h} = 0$  is again excluded according to arguments based on the necessity of primary summing over all *j*, and *C* is a universal Coulomb characteristic of the Bravais lattice.

The definiteness of the limit and the rapid convergence of series (44) is achieved by integrating with respect to **p** over a certain region  $\mathcal{P}$  (say, over the volume of a sphere of radius P), summing over  $2\pi \mathbf{h} \in \mathcal{P}$ , and then setting the size of  $\mathcal{P}$  to infinity. The second term on the right-hand side of Eqn (43) describes the structural factor, and the rate of convergence of this term is determined by the oscillatory contribution of the exponential. In the case of the jellium model, in which the lattice consisting of the charges  $q_{j_0}$  of a single kind is immersed in a homogeneous compensating charge background [76, 169], the sum over j in Eqn (43) is transformed into an integral taken over the unit cell. As a result, this term vanishes, thus reflecting the limiting effect of the charge spreading [16]. Notice that the given integration is again used as an inner procedure. Here, C determines the ionic potential, in accordance with Fuchs's result [16, 167]. In particular, for a simple cubic lattice with a lattice constant a, the value of C in units of  $2\pi/a$  amounts to -8.913633. In Section 3.2 we discuss an elegant way of obtaining this value.

The structure of expression (44) makes it possible, via step-by-step calculations, to estimate the remainder term by the Euler – Maclaurin formula and in this way increase the effectiveness of numerical computations [54, 167]. Notice that in the cases of absolutely convergent lattice sums, when the rate of decrease of the potentials being summed with increasing distance is high, replacing the 'far-off' part of the sum with an integral [70, 74, 88, 170, 171] implements the idea of Born and Bormann [45]. In other cases, however, such a procedure requires a careful approach [127, 172].

In connection with classical approaches, one should mention the Born formalism [173], which demonstrates a quite different type of the Fourier transformation [1, 39]. This approach, related to the problem of establishing structural configurations that are optimal in energy [15, 27, 51, 59, 174-177], precedes, in its ideas, the modern description of aperiodic systems modelled by large supercells with periodic boundary conditions [133, 134, 178, 179]. It is assumed that different point charges (among which there may be zero charges) are arranged regularly at the sites of a simple lattice of a given symmetry. Here, to be more graphic, we limit ourselves to orthorhombic lattices with the parameters  $a_1, a_2$ , and  $a_3$  along the principal orthogonal directions. The charges  $q_{\mathbf{R}_i}$  are grouped into translationally repetitive rectangular blocks with the sides  $a_1N_1$ ,  $a_2N_2$ , and  $a_3N_3$  on the assumption that the charges  $q_{\mathbf{R}_i}$  belonging to a separate cell of this kind meet condition (2). The cell energy is given by

$$\mathcal{E}_{\text{cell}} = \frac{1}{2} \sum_{i,j}' \frac{q_{\mathbf{R}_i} q_{\mathbf{R}_j}}{|\mathbf{R}_i - \mathbf{R}_j|} = \frac{1}{2} \sum_i' \frac{w(\mathbf{R}_i)}{|\mathbf{R}_i|}, \qquad (45)$$

where, in view of the periodicity of  $q_{\mathbf{R}_i}$  with respect to  $q_{\mathbf{R}_j}$ , the point set

$$w(\mathbf{R}_i) = \sum_j q_{\mathbf{R}_j} q_{\mathbf{R}_j + \mathbf{R}_i} = \sum_{\mathbf{k}}' w(\mathbf{k}) \cos(\mathbf{k}\mathbf{R}_i)$$
(46)

possesses the same periodicity and, quite obviously,  $w(\mathbf{R}_i) = w(-\mathbf{R}_i)$ . Hence, this point set can be represented as an indicated sum over  $\mathbf{k}$ , with

$$w(\mathbf{k}) = \frac{1}{N_1 N_2 N_3} \sum_{j} w(\mathbf{R}_j) \cos\left(\mathbf{k}\mathbf{R}_j\right), \qquad (47)$$

$$\mathbf{k} = 2\pi \left( \frac{m_1}{a_1 N_1}, \ \frac{m_2}{a_2 N_2}, \ \frac{m_3}{a_3 N_3} \right), \quad 0 \le m_p < N_p \,. \tag{48}$$

Here,  $m_p$  are the integers, and the set of points **k** comprises the first Brillouin zone [129, 180], being a corollary of the Born– von Kármán periodic boundary conditions [181]. According to Eqns (2) and (47),  $w(\mathbf{k} = 0) = 0$ , which explains the absence of this term in sum (46); summation over *j* is again inner in relation to formula (46). Substituting Eqn (46) into Eqn (45) yields

$$\mathcal{E}_{\text{cell}} = \frac{1}{2} \sum_{\mathbf{k}}' w(\mathbf{k}) \Pi(\mathbf{k}), \quad \Pi(\mathbf{k}) = \sum_{i}' \frac{\cos(\mathbf{k}\mathbf{R}_{i})}{|\mathbf{R}_{i}|}.$$
 (49)

For small  $N_p$ , the number of terms in the sum over **k** is small, too, and becomes even smaller if we fall back on the symmetry properties of the Brillouin zone. Thus, the problem of summation is reduced to calculating the 'basic Born potentials'  $\Pi(\mathbf{k})$  at the points of the reduced subset of the Brillouin zone. An effective method of calculating  $\Pi(\mathbf{k})$  is based on the use of Ewald's approach [73, 173].

A specific feature of this formalism, related to transformations (46) and (47) of one point set to another point set with the same dimension, presupposes that in describing the nonlinear convolution (49) we must consider all points of the initial set (46) simultaneously, i.e., the additivity is excluded of sums (49) with respect to the decomposition of the initial set into parts, with the contribution of each part being described within the given approach independently. Hund [169] was the one who restored this additivity in its rights by establishing that a lattice consisting of Born cells with the sides  $N_p a_p$  can be broken down into  $N_1 \times N_2 \times N_3$ *j*-sublattices in such a way that each sublattice will contain only one charge  $(q_i)$  in a Born cell; this charge is located at one of the cell's apices and is balanced by a homogeneous charge background. Each sublattice determines (to within a common factor  $q_i$  inherent in it) the universal potentials

$$\psi\left(\frac{a_1m_1}{N_1}, \, \frac{a_2m_2}{N_2}, \, \frac{a_3m_3}{N_3}\right),\tag{50}$$

where the integers  $0 \le m_p < N_p$  specify all equidistant points **b**<sub>j</sub> at which other charges emerge when all the sublattices are added. Thus, knowing the Hund potentials, which are calculated by Ewald's method [169], is sufficient for calculating the energy of a point-charge cell [4, 169], which is given by the formula

$$\mathcal{E}_{\text{cell}} = \sum_{j,j'} \frac{q_j q_{j'}}{2} \psi\left(\frac{b_{j1} - b_{j'1}}{N_1}, \frac{b_{j2} - b_{j'2}}{N_2}, \frac{b_{j3} - b_{j'3}}{N_3}\right), (51)$$

where in summation the indices *j* and *j'* run through the Born cell, with the case j = j' not excluded. If we go over to representation (46) in formula (51) and compare the result with expression (49), we find that for orthorhombic lattices [39, 169]

$$\Pi(\mathbf{k}) = \sum_{j} \psi\left(\frac{b_{j1}}{N_1}, \frac{b_{j2}}{N_2}, \frac{b_{j3}}{N_3}\right) \cos(\mathbf{k}\mathbf{b}_j) \,. \tag{52}$$

Representation (51) makes it possible to describe complex lattices as combinations of simpler lattices of the same crystal system [4, 39, 97, 169, 182, 183]. At the base of all this lie the recurrent relations between the Born potentials at different points of the lattice [56] and similar relations, in view of relationship (52), between the Hund potentials [4].

For oblique lattices, all the exponentials in formulas (46)-(52) still contain bilinear forms of the type  $(k_1b_1 + k_2b_2 + k_3b_3)$  with projections of the vectors along the axes of the parallelepiped of the Born cell, as a consequence of the fact that the translation group is Abelian [184]. Thus, such a bilinear form, which agrees in appearance with the exponent in the numerator of expression (14), can no more be reduced to the invariant scalar product  $\mathbf{k} \cdot \mathbf{b}$ described by formula (15) and depends on the shape of the cell. Remember that for the reciprocal lattice vectors h the possibility of an invariant convolution with vectors of a direct lattice of any symmetry is inherent, by definition. This is one of the main features that sets the Born-von Kármán periodic boundary conditions apart from the periodicity conditions in an infinite crystal. The attendant violation of the symmetry of description emerges as a general topological property of the Born supercell formalism, which leads to an overestimate in the physical correlations [185, 186]. The fact that the nonorthogonality of the base components of k, typical in the general case, does not manifest itself in orthorhombic lattices is occasional because the axes of a rectilinear parallelepiped form a Cartesian coordinate system underlying the definition of the Euclidean metric used here.

Since the presence of a surface effect is quite evident in the Born supercell formalism, we note that the potential inside a cell, which is determined by the Ewald potential generated by the surrounding lattice [187], can be modelled by a proper selection of the charge distribution on the cell surface [188, 189]. Refocusing the problem on the description of the properties of a real surface, we arrive at the conditions needed for its reconstruction [29, 32-34, 36, 190, 191]. What is more important for translational systems, however, is that the same potential effect occurs when on the surface we directly impose potential conditions that reflect the structural features of the inner distribution of charges in the form of a potential field acting on the same charges [192], as a result of applying the electrostatic image method [42]. Here, an interference effect, which manifests itself in the structure of solutions (49) and (52), is inevitable.

As for practical applications of the method, many tabulated data have been gathered for  $\Pi(\mathbf{k})$  and the Hund potentials  $\psi$  [39, 193, 194]. These have been utilized to calculate, with an extremely high degree of accuracy, the values of the Madelung constant  $\alpha_M$  for a number of basic crystal structures [195]. Many of the interpolation formulas for the Madelung constant of hexagonal crystals were proposed by Hund [169].

In computer simulation of thermodynamic problems by the Monte Carlo method [196], the Coulomb interaction in a translational cell is also taken into account by formula (51) with potentials calculated by the Ewald method [185, 197]. The use of interpolation procedure accelerates series convergence [185, 198-200]. This makes it possible to obtain, with high effectiveness of computations, results that well agree with the experimental data within a broad range of values of the thermodynamic parameters [185, 186, 199, 201] and, for instance, to develop an interpretation (based on the longrange nature of the interaction) of the non-Debye relaxation of the dielectric response [202]. Here, the emerging screening effect, which forms the basis of the dielectric formalism for describing condensed media, ensures the possibility of replacing the original Coulomb interaction with an effective short-range interaction that reproduces the peculiarities of the pair radial distribution function [198, 200, 203].

The evaluation of integrals over the Brillouin zone constitutes a fairly independent problem of numerical simulation. Here, the integrals of periodic functions can be effectively expressed in terms of finite sums, when the summation points are specially selected under the natural condition that the larger the number of such points the higher the accuracy of the result [204, 205]. The algorithm of 'fast Fourier transforms' [206] is left over as a more general approach in calculating arbitrary sums. In this algorithm the number of partition nodes of the Brillouin zone along each independent direction is represented in the form of a product, which substantially increases the computational speed as the number of particles in the cell grows.

This advantage of the algorithm of fast Fourier transforms becomes especially important in numerical simulations by the methods of molecular dynamics [198, 207], since it speeds up the calculation of Coulomb sums by application of the Ewald method [102, 103, 208, 209]. The increase in the number of particles examined in the model volume reveals the obvious tendency of the optimal value of the Ewald parameter  $\eta$  to grow [198, 210, 211]. Furthermore, what has proved to be really effective in this case is a variation of the Ewald method, in which instead of sum (25) one first considers the sum (which converges much more rapidly) of forces acting on the spreaded charges in the cell, which is followed by integration of the sum [212-214]. Ewald's method retains its effectiveness even if it is only partially used to describe the long-range part of the Coulomb interaction in crystals consisting of macromolecules, where the arrangement of charges is irregular within large cells, so that it is more convenient to describe their interaction at the cell scale by direct summation [215]. As for the special features of band calculations, the search for solutions in the form of Bloch functions (products of harmonics, as in the case of formula (47), over the Brillouin zone and translation-invariant functions expanded in the vectors h) leads to additional problems associated with the diagonalization of the equations of motion, where the expansions in k and h are combined and the completeness of the set of base harmonics becomes important [216].

### **3.** Summations in the problem space

On the basis of the above material we conclude that when the Poisson summation formula is employed for the equilibrium case, it is assumed that summation over *j* constitutes an inner procedure which excludes the homogeneous potential contribution. The assumption is corroborated by the obvious example of diatomic symmetric lattices of the *AB* type with point charges, where the potentials on the unlike charges, being opposite in sign, must be equal in value by symmetry [9, 28, 97, 139, 217]. Here, the bulk potentials are uniquely defined, so that the specific Coulomb energy is given by the value of the potential on a positive charge [9, 43, 56, 76, 116, 118, 137, 167, 217–222]. In the case at hand, condition (20) also holds by symmetry [125]. The condition of unit-cell electroneutrality turns out to be sufficient for characterizing an equilibrium bulk state [76].

The situation loses its definiteness in the case of series with MacDonald functions, mentioned in Sections 2.1 and 2.2, where summation over one of the three independent directions is done exclusively in the direct space and there is certain arbitrariness in the choice of the cross section of the charge layers employed [59]. Here again, the computation can be accelerated if first we sum the forces. However, the integration that follows anew generates an arbitrary potential shift which requires further definition [81, 223]. When the correct values of the equilibrium bulk potentials are restored in the case of two point-charge sublattices, additional information about Madelung constants, corresponding to the foregoing symmetry of the potentials, can be invoked [81].

The indefiniteness of the potential values is also a distinguishing feature of direct three-dimensional summation, where knowledge about the higher multipoles of an arbitrarily specified unit cell is needed to concretize the procedure. The additional information provided in this connection by the Bethe average potential (38) is just what is in great request.

#### 3.1 Absolute convergence of potentials

Let us again turn to direct sum (39), where integration corresponds to summation over j and is initially defined as an inner procedure. Nevertheless, absolute convergence of series (39) is achieved only if the additional conditions (34) and (37) are satisfied. It is in this case that solution (38) is also uniquely defined. Thus, for condition (20) to be met it is sufficient to consider, for instance, the difference between two consistently determined quantities:

$$U_{\rm b}(\mathbf{r}) = U_{\rm Cd}(\mathbf{r}) - \bar{U}_{\rm Cd} \,. \tag{53}$$

By its very meaning, relationship (53) corresponds to the matching of Eqns (31) and (18) [140], since it directly describes the correction of the potential  $U_{Cd}(\mathbf{r})$  in a bounded volume to remove the potential boundary effect. However, in contrast to the existing interpretation of the above relationship as linking the potentials on the two sides of the crystal boundary [142], here both the potentials  $U_{b}(\mathbf{r})$  and  $U_{Cd}(\mathbf{r})$  refer to the same volume, but only  $U_{b}(\mathbf{r})$  corresponds to the bulk crystal equilibrium reflecting the crystal symmetry.

Since the derivation of formula (53) is based on absolute convergence conditions (39), which by themselves are ambiguous and are met through a local redistribution of charges when determining  $\rho(\mathbf{r})$  [20, 137, 138], we dwell on two approaches that connect  $\rho(\mathbf{r})$  to the complete charge distribution  $\rho_{\rm c}(\mathbf{r})$  in the crystal [123]. In the first approach,  $\rho(\mathbf{r})$  is defined as the total charge inside the elementary crystallographic polyhedron [128]. Obviously, by appropriately shifting this polyhedron in relation to  $\rho_c(\mathbf{r})$  we can send the dipole moment of  $\rho(\mathbf{r})$  to zero [36, 130, 133, 134, 137]. This is also true of a  $\rho(\mathbf{r})$  that extends beyond the elementary polyhedron but is obtained by virtue of the functional localization of  $\rho_{\rm c}(\mathbf{r})$ , as is the case of Wannier functions [224, 225] under a proper general shift of their 'centers of gravity' [226, 227]. Within the second approach, the cell consists of a discrete number of ionic distributions [123, 228–231]. Here, it constitutes a closed neutral system whose dipole moment cannot be changed by shifting the origin as long as the given ion composition is conserved [132]. But when the ionic configuration changes due to a shift in the boundaries of the cell, the dipole moment changes in a jumplike manner.

Thus, there is a limited possibility that the dipole moment can be made to vanish through a shift in the second approach and, what is more, neither approach makes it possible, because of a lack of degrees of freedom, to send the quadrupole moment to zero via a shift, so as to sustain the second condition in Eqn (37). This means that with the above definitions of  $\rho(\mathbf{r})$ , all conditions (37) can be satisfied only due to an additional inner symmetry in this charge distribution [17, 133, 135, 137, 232]. In this respect, the NaCl structure again appears to be quite unique. The choice of a cell consisting of the eight nearest neighbors, which form a cube, ensures absolute convergence of series (39) with a high rate and, at the same time, guarantees that  $\overline{U}_{Cd} = 0$  [36, 216, 233].

A regular way of reducing direct lattice summation to computation of the absolutely convergent series of  $U_{Cd}(\mathbf{r})$ defined by formulas (39), (34), and (37) was put forth by Evjen [137], who proposed the idea of fictitious fractional charges and applied it to calculating the Madelung constant for the cubic NaCl, CsCl, and ZnS structures with point charges. To satisfy conditions (34) and (37), the charge cell was again chosen in the form of a cube, but with a charge at its center, while all the other original point charges, which by the construction find themselves on the surface of the cell, are evenly distributed among all the cells touching each other at the point occupied by the given charge. The idea of fictitious fractional charges proved to be extremely productive, since it

makes also possible to send to zero the lower multipoles that follow the quadrupole moment, which increases the rate of convergence of the series enormously [234]. Here, the choice of linear charge fragments as cells substantially reduces the number of nontrivial conditions imposed on the multipoles [139], although it also excludes the possibility of taking into account useful symmetry features in transverse directions. On the other hand, it is also desirable that the symmetry in the arrangement of the fictitious charges in a cell be high, so that the number of conditions imposed on the multipoles be small. By increasing the number of introduced types of fictitious charges and basing one's reasoning on a specific type of invariants for different crystal groups [235], one can nullify a sufficiently large number of the lower multipoles for a lattice of arbitrary symmetry [234]. Notice that the employment of Evjen cells also accelerates convergence in Ewald's approach [9]. The possibility of partitioning the crystal into simpler sublattices is retained in this approach as well [65].

The general problem of direct summation is related to the limit to which the lattice sums  $U_{\rm Cd}(\mathbf{r})$  converge. Lattices of the AB type with point charges exhibit a typical breaking of symmetry of the ionic potentials [137, 234]. The cause of this phenomenon becomes obvious when we realize that as long as the integrity of the contributions of  $\rho(\mathbf{r})$  into Eqn (39) is not violated, the result is independent of the way we sum over *i*, in view of the absolute convergence of  $U_{Cd}(\mathbf{r})$  [20, 32, 33, 133, 136, 138]. In this case, it is convenient, without loss of generality, to do summation in an isotropic way in relation to the lattice — that is, summation should be done over a sequence of closed shells, each of which consists of flat monolayers of unit cells and encompasses the previous one. The central cell is interpreted as an independent shell. Then, by definition, inside the summation volume the fictitious charges add up to real charges. However, the individual nature of the fictitious charges is retained on every intermediate surface that bounds the next shell in turn, where the fictitious charges form charged planes. As a result, a doublelayer effect manifests itself on the surface, with a dipole parameter that is constant in the limit, which leads to stability of the limit [137, 217]. At the same time, a variation in the choice of  $\rho(\mathbf{r})$  alternates the parameters of this double layer and, accordingly, the magnitude of the potential generated by this layer [137, 139, 234]. This sets the surface of the summation domain as a strictly auxiliary object [66] differing fundamentally from real surfaces [191].

For point *AB* lattices, the correction of the potentials on oppositely charged ions, obtained with a fixed  $\rho(\mathbf{r})$ , is achieved very simply via direct symmetrization of the type

$$U_{b}(A) = U_{Cd}(A) - \frac{1}{2} \left[ U_{Cd}(A) + U_{Cd}(B) \right]$$
  
=  $\frac{1}{2} \left[ U_{Cd}(A) - U_{Cd}(B) \right],$  (54)

which resembles formula (53) and coincides in form with the formula for calculating the Madelung energy, which in the case of an electroneutral cell is independent of homogeneous potential shifts [33, 130, 132-134, 236]. Since relationship (54) can be represented as the arithmetic mean of two sums with cells defined identically but oppositely charged [139], the complete exclusion of the contribution from the surface double layer from formula (54) becomes obvious.

Such a compensation effect for AB lattices appears automatically when the fictitious charges are introduced in an entirely different way. According to Frank [237], these charges are located at the apices of the polyhedrons that surround each real charge and are built by the Wigner – Seitz cell rules [238], but in relation to all neighbors. As neighboring polyhedrons with opposite signs of charges touch each other, these fictitious charges cancel out as the homogeneous background of *j*-sublattices [239], and as the results of two rapidly convergent sums for lattices consisting of charges of each sign are added, the surface effects cancel out. The introduction of additional fictitious charges at other symmetric points of the polyhedrons increases the convergence rate even more [234].

Returning to the problem of sums with Evjen's fictitious charges, we note that although the Bethe result (38) has been known for a long time, equation (53) has never directly been applied to such objects. It is significant that the local relationships (34), which lead to the compact form (38), are violated when we go over to the double-layer representation. As a result, surface effects can be excluded by the introduction of additional corrective charge distributions over the surface [240]. On the other hand, in the simplest cases expression (53) with a correction term in the form specified precisely by formula (38) is obtained directly from symmetrization of the potential effect for the double layer, described by the Gauss integral theorem [219] without, however, any association with the moments of the local distribution  $\rho(\mathbf{r})$ . In the same approach to more complex cells, when condition (20) is taken as the boundary condition, in relationship (53) there appears a cumbersome construction with a structural factor (23) at  $\sigma(\mathbf{r}) = \delta(\mathbf{r})$ , instead of a corrective term described by formula (38) [232].

Thus, when summing absolutely convergent series (39), we can, nevertheless, still speak of the contribution from the surface of the summation domain [136, 142], which in turn is fully described by the trace of the tensor of the second moment of the distribution  $\rho(\mathbf{r})$  in accordance with formula (38), thus reflecting the random nature of the selection of  $\rho(\mathbf{r})$ in the translationally repetitive structure of the crystal. Such an effect is not present in potential (20), where, in contrast to Eqn (40), a change in order of integration with respect to  $\mathbf{r}$  is not critical, since in the first term on the right-hand side of expression (18) the required order of summation has already been taken into account (the absence of a contribution from  $\mathbf{h} = 0$ ), and the other two terms have no problems with convergence. An important point is that the correction in the form (38) is appropriate precisely in relationship (53), i.e., in connection with absolutely convergent direct sums  $U_{\rm Cd}(\mathbf{r})$ . Since the use of fictitious charges to ensure that conditions (37) are met is universal and agrees well with the simplicity of the computational algorithms [138, 241], equation (53) proves an effective way of directly restoring the bulk potential fields in any crystals, contrary to the commonly accepted idea about the limited possibilities presented by Evjen's approach [4, 166, 239-241].

## 3.2 Regroupings, Padé approximants, and generating integrals

The restrictions (37), which make it possible to describe the procedure of direct summation in terms of the well-defined infinite series  $U_{Cd}(\mathbf{r})$ , are, undoubtedly, of an auxiliary nature. This circumstance manifested itself in the derivation of relationship (40), as well as in all the approaches considered earlier, which allow for inner summation over the cell under Fourier transformations, where the condition that the cell be electroneutral is sufficient. If in determining  $\rho(\mathbf{r})$  directly on

the base of the distribution  $\rho_c(\mathbf{r})$  we exclude, either completely or partially, conditions (37), then, in summation over *i* inside a bounded, simply connected domain incorporating the origin, quantity (39) will always be finite and may serve as a basis for defining infinite series (39) as a limit of the form

$$U_{\rm Cd}(\mathbf{r}) = U_{\rm b}(\mathbf{r}) + \lim_{S \to \infty} U_{\{S\}}(\mathbf{r}), \qquad (55)$$

where  $U_{\rm b}(\mathbf{r})$  is singled out against the background of the surface contribution  $U_{\{S\}}(\mathbf{r})$ , which is a functional of the shape of the boundary of the summation domain as the size of this domain tends to infinity [20, 33, 36, 76, 123, 133, 138, 139, 166, 217, 236, 239, 240]. Equation (53) becomes a particular case of Eqn (55), when the surface-shape effect disappears but its presence as a topological violation of the spatial homogeneity in direct summation is still felt. The loss of the individuality of  $\rho(\mathbf{r})$  inside the summation domain and the preservation of this individuality on its surface are also true for relationship (55) [108, 131, 219]. Moreover, the meaning of the potential term with  $\mathbf{h} = 0$  of type (38) as the surface contribution to Eqn (55) becomes obvious and is retained in the general case of any closed, piecewise smooth surface of the summation domain. This is true both in summation over the crystalline shells as in the case of potential (54) and in using a limit relation of type (32) as the right-hand side of expression (55).

There are two fundamental problems that arise in connection with the representation of the direct sum in the form of Eqn (55). First, is there a finite limit in general? Second, what is the correct way to single out  $U_{\rm b}(\mathbf{r})$  against the background of such a finite limit [127, 222]? The first problem has been studied in the simplest case of a lattice consisting of point charges. A rigorous proof of the formal convergence of sum (55), based on the theorems of one-parameter alternating series, has so far been presented only for the case of summation over crystalline (cubic) shells but not over spherical shells [127, 242]. It has also been proven that there is no such a shape of the boundary for which the result of summation is independent of the choice of a cell, but that conditions (37) and the vanishing of potential (38) guarantee that the sum is independent of boundary effects [166]. As shown in Section 3.1, these conditions are exhaustive, but their meaning is different: conditions (37) ensure that the sum is independent of the shape of the boundary [20], while the vanishing of potential (38) removes the topological contribution due to the presence of such a boundary [243].

The classical example of the CsCl structure with summation over monatomic shells shows that there can be several limits. The arithmetic mean of these limits is employed for obtaining the correct values of the bulk potentials [91, 217, 233]. This means that the potentials  $U_m(\mathbf{r})$ , each of which corresponds to the sum over *m* shells, form a sequence  $\{U_m(\mathbf{r})\}$  whose limit points in total determine  $U_b(\mathbf{r})$  even if the method of summation is not optimal. The limiting values of  $\{U_m(\mathbf{r})\}$  can be obtained based on a difference estimate of the remainder term in this sequence [244]. More effective, however, is the Padé approach [245] specified by the following equalities

$$U_{\rm b}(\mathbf{r}) = \mathcal{U}(\mathbf{r}, 1) \,, \tag{56}$$

$$\mathcal{U}(\mathbf{r},\xi) = \sum_{m=0}^{\infty} \left[ U_m(\mathbf{r}) - U_{m-1}(\mathbf{r}) \right] \xi^m, \qquad (57)$$

where  $U_{-1}(\mathbf{r}) = 0$ , and  $0 < \xi \leq 1$ . By forming a Padé approximant of the form [246]

$$[p/q]\mathcal{U}(\mathbf{r},\xi) \equiv \frac{P(\mathbf{r},\xi)}{Q(\mathbf{r},\xi)} = \mathcal{U}(\mathbf{r},\xi) + \mathcal{O}(\xi^{p+q+1}), \qquad (58)$$

$$P(\mathbf{r},\xi) = \sum_{m=0}^{p} P_m(\mathbf{r})\xi^m, \quad Q(\mathbf{r},\xi) = \sum_{m=0}^{q} Q_m(\mathbf{r})\xi^m$$
(59)

with  $Q_0 = 1$ , we can use the set of values  $U_0(\mathbf{r}), \ldots, U_{2m}(\mathbf{r})$  to find  $[m/m]\mathcal{U}(\mathbf{r},\xi)$ . These values can be used in subsequent iterations in m in sum (57). If in the first iteration we allow for  $m \leq 12$  monatomic shells, the second iteration yields the ionic potentials for NaCl and CsCl to within the eighth decimal point [245], while if we take  $m \leq 31$  the accuracy is to within the 20th decimal point [247], with the first 16 points corresponding to Sakamoto's results [195]. Here, the initial partial sums in some cases have been found to form sets of divergent sequences.

Also note the effectiveness of applying Padé approximants to various difference-estimate schemes in self-consistent descriptions of defective structures, which are more complicated from the viewpoint of convergence conditions [247]. The general conclusion is that when Padé approximants are used, the absolute bulk potentials are obtained as a selfsimilar solution independent of the distant boundaries. Naturally, no metastable states, which are manifestations of boundary effects, appear in this approach.

Generally, the appearance of metastable states is the physical consequence of the conditional convergence of Coulomb series. An instructive example of how the metastability effect is excluded from the bulk solution emerges from the calculation of a certain class of lattice sums that follow from Poisson's summation formula

$$\sum_{n=-\infty}^{\infty} \exp(-\alpha n^2) = \sqrt{\frac{\pi}{\alpha}} \sum_{n=-\infty}^{\infty} \exp\left(-\frac{\pi^2 n^2}{\alpha}\right),$$
 (60)

where n are the integers. It is advisable to represent the generalization of formula (60) for the case of m dimensions as follows:

$$\sum_{\mathbf{N}}' \left[ \exp\left(-\alpha |\mathbf{N}|^2\right) - \left(\frac{\pi}{\alpha}\right)^{m/2} \exp\left(-\frac{\pi^2 |\mathbf{N}|^2}{\alpha}\right) \right] = \left(\frac{\pi}{\alpha}\right)^{m/2} - 1,$$
(61)

where  $|\mathbf{N}|^2 = n_1^2 + \ldots + n_m^2$  and the prime on the summation sign indicates the absence of a term with  $\mathbf{N} = 0$ , which is specified explicitly on the right-hand side. Within the interval  $0 < \alpha < \infty$ , the convergence of the series in Eqn (61) is uniform, so that both sides of relationship (61) can be integrated with respect to  $\alpha$  for any *m*. In the process there appears an integration constant  $\tilde{C}_m$ , which is independent of  $\alpha$ [248]. In the particular case of m = 3, we obtain

$$\sum_{\mathbf{N}}' \left[ \frac{\exp(-\alpha |\mathbf{N}|^2)}{|\mathbf{N}|^2} + \frac{\sqrt{\pi}}{|\mathbf{N}|} \Gamma\left(\frac{1}{2}, \frac{\pi^2 |\mathbf{N}|^2}{\alpha}\right) \right] = \frac{2\pi^{3/2}}{\alpha^{1/2}} + \alpha + \tilde{C}_3,$$
(62)

where we have introduced the incomplete gamma function

$$\Gamma(x, y) = \int_{y}^{\infty} t^{x-1} \exp(-t) dt.$$
 (63)

According to the right-hand side of formula (61), the righthand side of Eqn (62) and, hence, the left-hand side have a minimum at  $\alpha = \pi$ . This value corresponds to a certain optimum, at which the series in Eqn (62) can be effectively calculated and thus the value of  $\tilde{C}_3$  can be found. On the other hand, one finds

$$\tilde{C}_{3} = \lim_{\alpha \to 0} \left[ \sum_{\mathbf{N}}' \frac{\exp(-\alpha |\mathbf{N}|^{2})}{|\mathbf{N}|^{2}} - \frac{2\pi^{3/2}}{\alpha^{1/2}} \right],$$
(64)

as an obvious corollary of relationship (62). Note that each of the terms in the square brackets in expression (64) diverge in the limit, while their difference can assume any value as  $\alpha$ tends to zero in an arbitrary manner in each of these terms, since at point  $\alpha = 0$  the condition of uniform convergence of series (61) and (62) is violated, just as in the case of series (32). The fact that  $\tilde{C}_3$  exists and is constant in the entire domain of variability of  $\alpha$ , when the boundaries are unimportant, determines the preference of the limit solution (64) over all other possibilities in describing equilibrium bulk properties. This conclusion is quite obvious if we compare Eqn (64) with expression (44) for C in the case of a simple cubic lattice with a lattice spacing a. Introducing the proper exponential factors under the summation and integration signs in expression (44) to ensure a single integration and summation domain, and integrating, we get  $C = 2\pi \tilde{C}_3/a$ . Here, the numerical estimate  $\tilde{C}_3 = -8.913633$  [248], naturally, agrees with the result mentioned in Section 2.4.

Varying relation (60) by incorporating cosine-like dependences into it makes possible the extension of the given approach with integration of Poisson's formulas to more complicated lattices sums that determine the potentials of point-charge lattices [39, 220].

Of course, summation over shells consisting of cells with zero lower multipoles is sure to be more universal in formula (55). Here, following Hajj [239], we can exclude the surface effect geometrically by taking  $\rho(\mathbf{r})$  in the form of a parallelepiped comprised of charges and considering six additional charge distributions  $\rho_p(\mathbf{r})$  obtained from  $\rho(\mathbf{r})$  via a general deformation of the parallelepiped, deformation corresponding to a shift of one face in each pair of the parallel faces by its length along each major axis parallel to it (in the process, the acute dihedral angles become obtuse, and vice versa). Potential effect (55), related to  $\rho(\mathbf{r})$ , is further averaged arithmetically with each similar contribution  $\rho_n(\mathbf{r})$ . The final result is the arithmetic mean of these six intermediate averages. Clearly, the emerging effect is related to the inversion of the moments of  $\rho_p(\mathbf{r})$  with respect to the moments of  $\rho(\mathbf{r})$ , a process that leads to their mutual compensation. Hence, under such averaging, the contribution of the last term on the right-hand side of formula (55) is indeed excluded.

Within the procedure of summation over shells consisting of neutral cells, a study of the potential effect generated by Evjen and Frank's fractional charges that are uncompensated for at the crystal's boundary makes it possible to single out the surface contributions in relationship (55) in the general case [240]. Similar results are obtained if one employs the fictitious dipole approach [63]. The possibility of representing all these results in the form of Eqn (53) can be rigorously proved on the basis of a detailed study of the periodic boundary conditions in an infinite crystal [249].

The limiting nature of relationship (55) also manifests itself in slice-wise summation as the number of parallel layers forming a slab increases, with each layer being infinite in the plane and electroneutral on the average. The result for a limit slab converges only in the absence of an uncompensated perpendicular dipole moment of the infinitely thin layers [31, 33]. If each translation layer consists of a set of charged layers, bulk potential characteristics appear under surface charge reconstruction [31, 190], which can be related to partial compensation for Evjen's fractional charges, similar to the above-mentioned case of summation over shells [29, 32, 139]. Here, the contribution from the nonzero second transverse moment of the charge of the translation layer in the general case of an arbitrary orientation of the slab differs from Eqn (38) [63]. As in the case of relationship (53), this contribution is excluded when  $U_{\rm b}(\mathbf{r})$  is isolated either on a heuristic basis as the uncompensated dipole contribution of the surface [63, 67] or by allowing for Ewald's result (20) [32, 33, 59]. Obviously, this effect is absent in the case of neutral Madelung monolayers consisting of point charges [166]. Thus, the potential effects of point charges and spherical charge local distributions in the crystal's bulk differ [83, 117, 249].

# **3.3** Green's function methods and spherical harmonics in the self-consistency problem

Additional specific features in the description of potentials emerge when the equilibrium state is determined as a result of mutual matching of the charge and potential distributions [20-22, 250]. This means, among other things, the simultaneous solution of the Poisson and Schrödinger equations describing the electronic configurations, which in turn awakens the interest in local expansions on the basis of spherical harmonics whose application is typical in electron calculations [19, 43, 83, 128, 251, 252].

It is advisable to begin the discussion of the pertinent problems with Slater's well-known augmented plane wave method [253], in which the local solutions in spherically symmetric potentials with centers at the nuclei are matched to the plane waves beyond the spherical regions that enclose these nuclei [19, 254]. Then, the electron dispersion law may be deduced either by directly examining the time-independent Korringa states [255] or by using an equivalent Kohn-Rostoker variational approach [256]. An important point is that the wave zone then corresponds to a certain constant potential  $U_0$  and that the particular case of  $U_0 = 0$  is a prime consideration, since in this case the hybridization of local states, caused by the off-diagonal matrix elements of the potential in the wave zone, disappears [253]. As a result, the condition  $U_0 = 0$  is adopted in the given approach as a convention [19].

Two remarks are in order at this point. First, the specified condition corresponds to a metastable state. This is obvious in the case of a simple metal, since the condition  $\overline{U} > 0$  then directly follows from the fact that the potential is positive in nonwave zones. Second, the fact that the potential vanishes on the spherical boundary of each inner region may reflect the overall neutrality of the inner charge distribution, when the nature of the simplifying conditions imposed on the electronic spectrum becomes trivial.

While examining only the potential aspect of the problem, Weinert [221] suggested an opposite approach, in which the method of the boundary-value problem is applied when calculating bulk potentials. Remember that the ordinary Coulomb potential is only a particular solution for the Green function, describing the solution of the Poisson equation in a volume without boundaries, while the general solution for the Green function in the case of a boundaryvalue problem allows for an addition to the Coulomb potential of an arbitrary solution of the Laplace equation [42]. Thus, the problem of the potential distribution inside a sphere of radius  $\mathcal{R}_i$ , where there is a charge distribution  $\rho(\mathbf{r})$  and the Dirichlet boundary conditions are imposed, i.e., a potential is specified at the boundary of this sphere, is determined by a Green function whose expansion in terms of the normalized spherical harmonics  $Y_{lm}$  takes the form [42]

$$G(\mathbf{r},\mathbf{r}') = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{Y_{lm}^{*}(\hat{\mathbf{r}}')Y_{lm}(\hat{\mathbf{r}})}{2l+1} \left[\frac{r_{<}^{l}}{r_{>}^{l+1}} - \frac{(rr')^{l}}{\mathcal{R}_{i}^{2l+1}}\right], (65)$$

where the vectors  $\mathbf{r}$  and  $\mathbf{r}'$  are inside the sphere of radius  $\mathcal{R}_i$ and originate at its center, while  $\hat{\mathbf{r}}$  and  $\hat{\mathbf{r}}'$  denote the set of spherical angles for  $\mathbf{r}$  and  $\mathbf{r}'$ , respectively, with  $r = |\mathbf{r}|$ ,  $r' = |\mathbf{r}'|$ ,  $r_{<} = \min\{r, r'\}$ , and  $r_{>} = \max\{r, r'\}$ . Here, the potential inside the given sphere is given by the formula

$$U_{i}(\mathbf{r}) = \int_{\mathcal{V}_{i}} \rho(\mathbf{r}') G(\mathbf{r}, \mathbf{r}') \, \mathrm{d}\mathbf{r}' - \frac{\mathcal{R}_{i}^{2}}{4\pi} \oint_{\mathcal{S}_{i}} U_{\mathcal{S}_{i}}(\mathbf{r}') \frac{\partial G}{\partial n'} \, \mathrm{d}\Omega_{i} \,,$$
(66)

where in the first term on the right-hand side integration is taken over the sphere's volume, while in the second term integration is carried out with respect to angular variables over the sphere's surface;  $U_{S_i}(\mathbf{r}')$  is the fixed value of the potential at the boundary; the partial derivative of the Green function vanishes on this surface and is taken along the outward normal to the given boundary with respect to the variable  $\mathbf{r}'$  [42].

Applying results (66) to each spherical region in Slater's construction, Weinert restored the potentials inside these ordered spheres by defining  $U_{S_i}(\mathbf{r}')$  in terms of the potentials in the wave zone, which are expanded in the reciprocal lattice vectors with the zero component excluded. Here, however, there arises the problem of a discontinuity in the potential at the sphere boundaries, a discontinuity that emerges because in the wave zone the summation over the reciprocal lattice vectors is extended to infinity and, in turn, the expansion in spherical harmonics for each such a vector also extends to infinity, while inside the spheres the matched solution is limited for practical calculations to a finite (in *l*) set of harmonics [19, 43, 221]. In this connection, there is the need to develop additional approximate procedures of interpolation smoothing at the matching boundaries [257, 258].

An alternative description consists in directly examining cells that fill an entire space. The Green function corresponds in this case to an unbounded region and is described by formula (65) with  $\mathcal{R}_i \to \infty$ . Here, its actual expansion is done over the complete basis set of solid harmonics:

$$J_{lm}(\mathbf{r}) = r^l Y_{lm}(\hat{\mathbf{r}}), \quad H_{lm}(\mathbf{r}) = r^{-l-1} Y_{lm}(\hat{\mathbf{r}}), \quad (67)$$

which are regular and irregular, respectively, at  $\mathbf{r} = 0$ . Then the expansion of the potential  $U(\mathbf{r})$  generated by a charge distribution  $\rho_0(\mathbf{r})$  assumes the form [42, 43, 128]

$$U(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left[ A_{lm}(\mathbf{r}) J_{lm}(\mathbf{r}) + B_{lm}(\mathbf{r}) H_{lm}(\mathbf{r}) \right], \qquad (68)$$

$$A_{lm}(\mathbf{r}) = \frac{4\pi}{2l+1} \int_{V_0(r'>r)} \rho_0(\mathbf{r}') H_{lm}^*(\mathbf{r}') \,\mathrm{d}\mathbf{r}', \qquad (69)$$

$$B_{lm}(\mathbf{r}) = \frac{4\pi}{2l+1} \int_{V_0(r' < r)} \rho_0(\mathbf{r}') J_{lm}^*(\mathbf{r}') \,\mathrm{d}\mathbf{r}', \tag{70}$$

where the vectors  $\mathbf{r}$  and  $\mathbf{r}'$  are defined with respect to the common expansion center, and integration is performed over the volume  $V_0$  occupied by  $\rho_0(\mathbf{r}')$ .

Two important features of using multipole expansions when describing the properties of a crystal should be mentioned here. The first is that equilibrium charge and potential distributions are characterized by an identical representation of the point group belonging to the crystal's symmetry group [235, 259], so that the spherical harmonics are combined here into invariant lattice harmonics

$$W_{l,n}(\hat{\mathbf{r}}) = \sum_{m=-l}^{l} w_m(l,n) Y_{lm}(\hat{\mathbf{r}}), \qquad (71)$$

which modify the contribution of harmonics (67) both in the case of Eqns (68) - (70) and in other similar cases [19, 43, 221].

The other feature lies in the fact that it is expedient to define expansions in harmonics with respect to the centers of different cells with a separation vector  $\mathbf{R}_i$ . This brings up the problem of two-center expansions. Typical cases that lead to the appearance of powers of  $\mathbf{R}_i$  in the denominator of expansions correspond to the conditions

$$|\mathbf{r} - \mathbf{r}'| < |\mathbf{R}_i|, \tag{72}$$

 $|\mathbf{r}| < |\mathbf{R}_i + \mathbf{r}'|, \quad |\mathbf{r}'| < |\mathbf{R}_i|, \tag{73}$ 

$$|\mathbf{r}'| < |\mathbf{r} - \mathbf{R}_i|, \quad |\mathbf{r}| < |\mathbf{R}_i|. \tag{74}$$

Obviously, conditions (72)-(74) are not of equal status. Furthermore, there may be six other conditions involving variations of reverse inequalities, which lead to the presence of powers of  $\mathbf{R}_i$  in the numerator.

Expansions of the first level, corresponding to inequality (72) and the first condition in Eqn (73), follow from the first term on the right-hand side of formula (65) and, respectively, are of the form

$$\frac{1}{|\mathbf{R}_{i} + \mathbf{r}' - \mathbf{r}|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{J_{lm}^{*}(\mathbf{r} - \mathbf{r}')H_{lm}(\mathbf{R}_{i})}{(2l+1)}, \qquad (75)$$

$$\frac{1}{|\mathbf{R}_{i} + \mathbf{r}' - \mathbf{r}|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{J_{lm}^{*}(\mathbf{r})H_{lm}(\mathbf{R}_{i} + \mathbf{r}')}{(2l+1)} .$$
 (76)

In the case of inequality (74), the expansion can be derived from Eqn (76) by replacing  $\mathbf{r}$  with  $\mathbf{r}'$  and  $\mathbf{R}_i + \mathbf{r}'$  with  $\mathbf{r} - \mathbf{R}_i$ .

Expansions of the second level, which lead to complete separation of variables, are, naturally, performed within the already noted sums and, according to formula (67), are described by a finite sum in the case of Eqn (75) or by an infinite series in the case of Eqn (76) and its analog corresponding to inequality (74). Here, the addition theorem for spatial harmonics is employed [260, 261], in view of which the expansion coefficients are expressed, depending on the normalization conditions used, either in terms of the Gaunt numbers [262] defined by integrals of the product of three associated Legendre functions with varying indices, but the same argument, the integrals which are taken from -1 to 1 [19, 128, 252, 263, 264], or in terms of the related Wigner 3*j*-symbols (Clebsch–Gordan coefficients) [19, 261, 263–265].

It should be emphasized that an arbitrary function expanded in an infinite series is specified by this series only within its circle of convergence [54]. Hence, two-center expansions have unpleasant singularities near the boundary of the convergence circle for the first-level expansion, singularities related to the above-noted order of summation [128, 251, 266]. The reason is that the quantity expanded under the summation sign on the right-hand side of Eqn (75) or Eqn (76) enters into the definition of the circle of convergence for the outer expansion, so that its own expansion must not take the outer expansion (the first-level expansion) outside its convergence circle.

This problem is refined via a systematization in which, in contrast to systematizations defined by conditions (72)–(74) and similar conditions [252], four regions  $S_j$  are specified for a fixed  $|\mathbf{R}_j|$ :

$$S_{0}: \begin{cases} ||\mathbf{R}_{i}| - |\mathbf{r}'|| \leq |\mathbf{r}| \leq |\mathbf{R}_{i}| + |\mathbf{r}'| & \text{or} \\ ||\mathbf{R}_{i}| - |\mathbf{r}|| \leq |\mathbf{r}'| \leq |\mathbf{R}_{i}| + |\mathbf{r}| & \text{or} \\ ||\mathbf{r}| - |\mathbf{r}'|| \leq |\mathbf{R}_{i}| \leq |\mathbf{r}| + |\mathbf{r}'|; \end{cases}$$

$$S_{1}: |\mathbf{r}| > |\mathbf{R}_{i}| + |\mathbf{r}'|; \quad S_{2}: |\mathbf{r}'| > |\mathbf{r}| + |\mathbf{R}_{i}|;$$

$$S_{3}: |\mathbf{R}_{i}| > |\mathbf{r}| + |\mathbf{r}'|. \qquad (77)$$

These regions, not overlapping each other completely, cover the entire range of values of  $|\mathbf{r}|$  and  $|\mathbf{r}'|$  [260, 264], with all three above definitions of  $S_0$  being identical. For instance, in this case in the region  $S_3$  there appears a first-level expansion (75). However, the conditions in the region  $S_3$  are more stringent than conditions (72) and guarantee that conditions (73) and (74) are fulfilled simultaneously. Hence, in  $S_3$  there appears a two-center expansion that is totally symmetric in both  $\mathbf{r}$  and  $\mathbf{r}'$  [260, 263–265], a representation that allows for a change in the order of summation that transforms Eqn (76) into Eqn (75) with a finite inner sum. The independence of the result from the order of summation in regions  $S_1$  and  $S_2$  can be proved in a similar manner [263].

As a result, the region  $S_0$  is the only one where the order of summation is determined by the requirement of convergence, which, therefore, solves the general problem of convergence of multiple series in question [252, 260, 264]. It is significant that the region  $S_0$  partially encompasses expansions (75) and (76) and similar expansions corresponding to the reverse inequalities with respect to those in Eqns (72)–(74) [261].

Substituting formulas (68) - (70) and (76) with the secondlevel expansion into formula (39) generates a typical threeterm formula for local potentials [251]:

$$U(\mathbf{r}) = U_{\text{cell}}(\mathbf{r}) + U'_{\text{latt}}(\mathbf{r}) + U_{\text{corr}}(\mathbf{r}).$$
(78)

Here,  $U_{\text{cell}}(\mathbf{r})$  is described by formulas (68)–(70), where  $V_0$  is the volume of the cell in which the point of observation  $\mathbf{r}$  is located [128]. The contribution of  $U'_{\text{latt}}(\mathbf{r})$  to Eqn (78) corresponds to summation over all the other cells, provided that the spheres around these cells do not, according to condition (73), encompass the point of observation  $\mathbf{r}$ . The prime indicates the exclusion of the nearest cells from the given sum, i.e., the cells for which the first condition in Eqn (73) is violated for a given  $\mathbf{r}$  [128, 251].

These irregular contributions of the neighboring cells are specified by the correction term  $U_{\text{corr}}(\mathbf{r})$ . Of course, such cases may be embraced by relationships (68)–(70) if these neighbors are included in the integration volume  $V_0$ . What is more, the existence of at least one point  $\mathbf{r}$  in the elementary polyhedron, for which condition (73) is met in relation to all neighboring polyhedrons, makes it also possible to remove all irregular contributions through a proper shift of the system of elementary polyhedrons in relation to the crystal's structure as applied to each point of observation  $\mathbf{r}$  [128]. The same effect in terms of the multipoles of a given cell can be achieved via an identical representation of the Coulomb denominator:

$$\mathbf{R}_{i} + \mathbf{r}' - \mathbf{r} \equiv |\mathbf{r}' + (\mathbf{R}_{i} - \mathbf{r} - \mathbf{b}) + \mathbf{b}|, \qquad (79)$$

with the vector **b** selected in such a way that the following conditions are met:

$$|\mathbf{b}| < |\mathbf{r}' + (\mathbf{R}_i - \mathbf{r} - \mathbf{b})|, |\mathbf{r}'| < |\mathbf{R}_i - \mathbf{r} - \mathbf{b}|;$$
 (80)

these conditions form the basis for a further two-center expansion, just as conditions (73) and (74) do [251].

Characteristically, the quantity  $U_{corr}(\mathbf{r})$  is determined primarily by the contribution from  $S_0$ , although additional contributions from the regions  $S_1$  and  $S_2$  are also possible as the anisotropy of the crystal increases [252]. Note that cases where the powers of  $\mathbf{R}_i$  prove to be in the numerator of the multipole expansions may be inherent in  $S_0$ , although their fraction is small, at least for highly symmetric lattices, with the result that usually such contributions are simply ignored in the regular constructions of self-consistent solutions [128, 265, 267].

In considering  $U_{\rm corr}(\mathbf{r})$  there appears also a second unpleasant property of two-center expansions, related to each level of expansion and consisting of a drastic slowingdown of the convergence of the series in the corresponding *l* as we get closer to the boundary of its circle of convergence [128]. From the practical angle of summing  $U_{\rm corr}(\mathbf{r})$  this means that the inner sums must be limited to larger values of *l* than the outer sum [128, 251, 252, 266, 268], and for a given computational accuracy the minimum limiting values of the boundary moments strongly depend on the position of the point of observation r [128, 266]. In this connection, the ambiguity in determining the parameter **b** in approaches (79), (80) proves to be useful for optimizing the calculations [251, 268]. However, a general property here is that with limitations imposed on the inner sums in *l* a first-level series transforms from an absolutely convergent one to an asymptotic series, so that the accuracy of the result lowers in outer summation up to the values of *l* that exceed a certain limit [128, 251, 268].

Multipole expansions also exhibit specific features in another classical problem involving the interaction of crystal fields with multipole moments of atomic nuclei. Such interaction is described by the first term in expansion (68) centered at the given nucleus, provided that integration in formula (69) is extended over the entire crystal [254, 269– 272]. Here, as in the previous problem, when the interest is limited to a finite number of lower local multipoles [128, 264], a practical approach is to directly expand the root describing the denominator of the Coulomb potential in a Taylor series:

$$\frac{1}{|\mathbf{R}_i + \mathbf{r}' - \mathbf{r}|} = \frac{1}{|\mathbf{R}_i|} \left[ 1 + \sum_{n=1}^{\infty} \frac{(-1)^n (2n-1)!}{2^{2n-1} (n-1)! n!} X^n \right], \quad (81)$$

$$X = \frac{2[(\mathbf{R}_{i}\mathbf{r}') - (\mathbf{R}_{i}\mathbf{r})] + |\mathbf{r}' - \mathbf{r}|^{2}}{|\mathbf{R}_{i}|^{2}}, \quad |X| < 1,$$
(82)

and then factorize the dependences of  $X^n$  on  $\mathbf{r}$ ,  $\mathbf{r}'$ , and  $\mathbf{R}_i$  by using binomial expansions [250]. Note, however, that applying the condition specified in Eqn (82) for the convergence of the series (81) to a case where the directions of the vectors  $\mathbf{r}$ ,  $\mathbf{r}'$ , and  $\mathbf{R}_i$  are uncorrelated corresponds to the following inequality [263]:

$$|\mathbf{r}| + |\mathbf{r}'| < (\sqrt{2} - 1)|\mathbf{R}_i|, \qquad (83)$$

which is much stronger than condition (77) imposed on the region  $S_3$ , although a two-center expansion in  $S_3$  [265] can, naturally, be obtained by regrouping the terms in formula

(81). In other words, the convergence circle proves to be dependent on the type of expansion.

As for the practical aspects of calculating multipole sums over lattices in both problems at hand, according to Eqn (75) a characteristic feature of these problems is the factorization of the dependence on  $\mathbf{R}_i$  in the denominator, which, isolating lattice summation over  $\mathbf{R}_i$  against the background of selected multipole values, is retained in the entire region where there are problems in the convergence of the given lattice series [128, 250]. In this case, in calculating lattice series we can use either the Bertaut method for nonoverlapping charge distributions [221, 269] or direct summation [250, 269-271]. In Section 4, we will discuss the features of dipole sums that emerge in the latter case; here, we only note that the magnitude of the gradient of the electric field interacting with the quadrupole nuclear moment [273] also depends on the order of summation [138, 254, 270]. Here, too, summation over the crystalline shells produces a surface-independent bulk solution [138, 243], while summation over expanding spherical regions that ignores the topology of the crystal structure is sure to be one of the reasons why the results of calculations in this approach differ from the experimental data [270, 271, 274]. Note that, notwithstanding the high effectiveness of calculations, the slice-wise summation method [272, 275] does not monitor the degree of metastability of the obtained solution either. So far, only Ewald's method extended to multipole sums remains universal [19, 257]; in the limit of large values of  $\eta$  it again corresponds to the case of nonoverlapping charge distributions. Moreover, as the order of multipoles increases, the convergence of direct sums is accelerated, while the passage to summation in the reciprocal space becomes less and less effective [257].

In connection with the formalism of Green's functions in the space of an infinite crystal, we note that if we combine Eqns (33) and (39) with Eqn (66), we get

$$U_{\rm b}(\mathbf{r}) = \int G(\mathbf{r} - \mathbf{r}') \,\rho_{\rm c}(\mathbf{r}') \,\mathrm{d}\mathbf{r}',\tag{84}$$

where  $G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r} - \mathbf{r}')$  describes the Coulomb potential. The representation of  $G(\mathbf{r} - \mathbf{r}')$  in the form of an expansion in **h**, governed by the last term either in formula (29) or in formula (43), namely

$$G(\mathbf{r} - \mathbf{r}') = \frac{1}{\pi v} \sum_{\mathbf{h}}' \frac{\exp[2\pi i\mathbf{h}(\mathbf{r} - \mathbf{r}')]}{|\mathbf{h}|^2}, \qquad (85)$$

guarantees the periodicity of this Green's function, which is not, however, an intrinsic property of  $G(\mathbf{r} - \mathbf{r}')$  requiring a nonspecific extension of its definition [83] but only reflects the link between the periodicities of  $\rho_c(\mathbf{r})$  and  $U_b(\mathbf{r})$  inherent in Eqn (84) [43, 254]. Naturally, the term with  $\mathbf{h} = 0$  is absent from formula (85), since the discreteness of the vectors  $\mathbf{h}$ excludes the possibility of examining such a limit as a function of the translation-invariant charge distribution  $\rho_c(\mathbf{r})$ , which by definition is unrelated to the cases of metastability. It is interesting that the convergence of the series in formula (85) can be accelerated by directly introducing auxiliary acceleration functions of the type (31) under the sign of summation in formula (85). Naturally, when the accelerating function is of the Gaussian type, Ewald's result (18) is reproduced [43].

Also note that a representation of the potential at a certain point  $\mathbf{r}$  in the form of a sum of contributions from the local multipoles of the enclosing charge distributions can be obtained directly by applying multipole expansion of each sum in Eqn (18) [83], although such expansion is not of the multipole–multipole nature. Of course, the dependence of the form of contributions from the nearest cells on the ratio of mutual distances is retained in the process.

Note that in itself direct summation is substantially accelerated when multipole expansions are employed [271], expansions which effectively represent the spatial charge distributions in unit cells [221]. The algorithm of rapid multipole summation based on this property [276], which also takes into account the problems of falling outside the boundaries of the region  $S_3$ , is applied in the molecular dynamics method and in the Monte Carlo method. Here, the sought quantity is described by the multipole contributions of the cells that follow those nearest to the given cell. At each iteration step, the 'central' cell and nearest cells that were not taken into account in the previous steps are partitioned into smaller cells [269], and the procedure is repeated, with the inner boundary of summation moving closer to the point of observation with each step. The method's specific feature involving the use of iterations ensures the effectiveness in the parallel processing mode, when structures with complex molecules are calculated [277]. However, this method has proven less effective than Ewald's approach in solving problems of molecular dynamics for simpler systems [214].

### 4. Direct summation and the Lorentz field

An important subject of research that presupposes lattice summation is the crystal's specific Coulomb energy which can be represented in many ways, including a representation in terms of multipoles [251, 268]. If the bulk potentials  $U_{\rm b}(\mathbf{r})$  are known, this energy can be written down as follows:

$$\mathcal{E}_{\rm b} = \frac{1}{2} \int_{V} \rho(\mathbf{r}) \ U_{\rm b}(\mathbf{r}) \ \mathrm{d}\mathbf{r} \Rightarrow \frac{1}{2} \sum_{j} q_{j} \ U_{\rm b}(\mathbf{b}_{j}) \,. \tag{86}$$

The last relation describes the energy of a point-charge lattice and corresponds to relationship (51), which is also equivalent to substituting the potentials in the forms (18), (24), or (43) into the integrand in Eqn (86). Formula (86) can also be obtained by using approach (31) if, following Williams [278], we apply this approach directly to the Patterson function of the form [94]

$$\mathcal{W}(\mathbf{R}) = \int_{V_1} \rho_1(\mathbf{r}) \,\rho_2(\mathbf{r} + \mathbf{R}) \,\mathrm{d}\mathbf{r} \,. \tag{87}$$

Here, in the definition of  $W(\mathbf{R})$ , summation over *j* is already incorporated as an inner summation. The function  $W(\mathbf{R})$  is an analog of expression (46) and, in addition, describes the charge overlapping effect [97]. The local distributions  $\rho_1(\mathbf{r})$ and  $\rho_2(\mathbf{r})$  correspond to  $\rho_c(\mathbf{r})$ , provided that conditions (34) are met, but may differ [106]. The latter property follows from the universality of the bulk potential field  $U_b(\mathbf{r})$  related to  $\rho_c(\mathbf{r})$  and is retained in the general case of relationship (86) [9, 249], where  $U_b(\mathbf{r})$  is also given by formula (53). As an example of how  $\mathcal{E}_b$  can be used we will mention the optimization of configurations in the Born cell, which corroborates the energetic preference of a bcc lattice for electron distributions [175].

### 4.1 The Coulomb and dipole interaction energies

The functional of the energy per unit cell can be constructed directly from first principles. Within this approach, the pair nature of Coulomb interaction between distant charges is taken into account. Here, we are immediately confronted with the problem of direct summation. If we allow for relationships (39) and (55), such a functional assumes the form

$$\mathcal{E} = \lim_{\mathcal{I} \to \infty} \frac{1}{2} \sum_{i \in \mathcal{I}}' \int_{V} \frac{\rho(\mathbf{r}_{1})\rho(\mathbf{r}_{2}) \, \mathrm{d}\mathbf{r}_{1} \, \mathrm{d}\mathbf{r}_{2}}{|\mathbf{R}_{i} + \mathbf{r}_{1} - \mathbf{r}_{2}|}$$
$$\Rightarrow \mathcal{E}_{\mathrm{b}} + \left\{ \frac{2\pi |\mathbf{M}|^{2}}{3v} \right\}_{\mathrm{cubic}}, \tag{88}$$

where M is the dipole moment vector of the unit cell, described by the first relation in Eqn (36);  $\mathcal{I}$  is the bounded region of the Bravais lattice points, similar to  $\mathcal{P}$  in formula (44), and passage to the limit in the first relation, which extends  $\mathcal{I}$  to the entire infinite lattice, is caused by assuming conditions (37) are completely violated [36, 126, 150, 279]. The second relation in Eqn (88) is justified by the use of formula (55) with a surface term in the form (35). Because of substituting this term into the first relation in Eqn (88), the contribution of  $U_{\rm b}(\mathbf{r})$  leads to the separation of bulk term (86), while the expansion of the exponents in the remainder term in h with allowance for Eqn (36) and subsequent spherical averaging of h yields the second term [126, 134]. Such a form of the term with M, corresponding to spherical summation (with an isotropic  $\varepsilon$ ), implies indirectly that the structure is cubic; it is valid also for summation over cubic shells, but is different for other shapes of the surface [279, 280]. Note that the energy contribution of the surface to the bulk energy appears because of the effect of the zeroth Fourier harmonic of the potential in the bulk, which is clear from the procedure for deriving formula (88). The meaning of this relationship is also obvious since for  $\mathbf{M} \neq 0$  the limit  $\mathbf{h} \rightarrow 0$  in Eqn (29) also generates, in addition to  $U_0$ , a gradient term with the field E, which is excluded from the translationinvariant solution [150, 281].

If we set the size of the region V occupied by  $\rho(\mathbf{r})$  to zero in Eqns (34) and (36), the first relation in formulas (88) describes, in the multipole expansion of the denominator, the specific interaction energy of point multipoles. Here, beginning with the quadrupole–quadrupole interaction, there is no problem with the limit of sums for the interaction of the higher multipoles [53, 73, 74, 127, 170], although here, too, resorting to momentum representations [62, 278] could be useful in optimizing the rate of convergence. Naturally, the respective acceleration of series convergence can also be achieved by directly using theta-function transformations in the partition of the integration domain in the integral representation of the power-like denominators [88, 282, 283].

However the second relation in Eqn (88) is still valid in the case of a purely dipole system, so that the bulk energy of the dipole interaction of parallel dipoles equals

$$\mathcal{E}_{b} = \mathcal{E}_{Md}^{\circ} - \frac{1}{2} \mathbf{ML}^{\circ}(\mathbf{M}), \qquad (89)$$

where

$$\mathcal{E}_{\mathrm{Md}}^{\mathrm{o}} = -\frac{1}{2} \sum_{\langle i \rangle}' D_{\mu\nu}(\mathbf{R}_i) M_{\mu} M_{\nu} , \qquad (90)$$

$$D_{\mu\nu}(\mathbf{R}_{i}) = \nabla_{\mu}^{i} \nabla_{\nu}^{i} \frac{1}{|\mathbf{R}_{i}|} = \frac{3R_{i\mu}R_{i\nu}}{|\mathbf{R}_{i}|^{5}} - \frac{\delta_{\mu\nu}}{|\mathbf{R}_{i}|^{3}}, \qquad (91)$$

$$L^{\circ}_{\mu}(\mathbf{M}) = \mathcal{L}^{\circ}_{\mu\nu}M_{\nu} \Rightarrow \begin{cases} \frac{4\pi(\mathbf{M}\mathbf{e}_{\perp})e_{\perp\mu}}{v} \\ \frac{4\pi(\mathbf{M}_{\mu})}{3v} \end{cases}_{\text{sphere}} \qquad (92)$$

Here, the prime on the summation sign in formula (90) again indicates that the contribution from  $\mathbf{R}_i = 0$ , which is the energy of self-action (per unit cell), is unessential for the problem of lattice summation and is excluded. This contribution diverges in the point-dipole limit but remains finite when the point dipoles are spreaded [44, 284]. The first equality in Eqn (91), expressed in terms of operators of the gradient  $\nabla^i$ acting on  $\mathbf{R}_i$ , determines the relation between dipole sums and Coulomb sums [126, 127, 186, 269, 285-289], which forms the basis for the agreement between relations (89) and (88). The quantity  $L^{\circ}(M)$  describes the Lorentz field [290] with the tensor  $\mathcal{L}_{\mu\nu}^{\circ}$  [52, 281, 291–293], so that the related contribution in formula (89) is a topological addition to the direct sum  $\mathcal{E}_{Md}^{\circ}$ (this relationship is indicated by the superscript in the form of a small circle), thus ensuring the invariance of  $\mathcal{E}_{b}$  for any choice (no matter how extravagant this choice may be) of a finite set  $\{i\}$  of summation points in  $\mathcal{E}_{Md}^{\circ}$ . If the total volume of the unit cells corresponding to the set  $\{i\}$  is a simply connected region bounded by a piecewise smooth surface, the Lorentz field acquires its classical meaning of a surface imitation of the contribution from the other regularly arranged dipoles [42]. This fact is directly related to the formalism of supercells with periodic boundary conditions [134, 179, 294], where allowing for the Lorentz field eliminates an overestimate of the correlation effect [186, 295]. Note that the factors 1/2 in Eqns (89) and (90) are of a common nature [50, 286, 296-298].

The case of spherical summation over a cubic lattice leads, in natural agreement with Eqn (88), to a result noted in Eqn (92). Here, as noted by Lorentz [42, 299], the direct sum  $\mathcal{E}_{Md}^{\circ}$  with parallel dipoles vanishes under spherical summation [138, 296, 297, 300–303], so that the specific bulk energy is determined solely by the contribution of the Lorentz field [47]:

$$\mathcal{E}_{b} = -\frac{\mathbf{M}\mathbf{L}^{\text{sphere}}(\mathbf{M})}{2} = -\frac{2\pi|\mathbf{M}|^{2}}{3v}.$$
(93)

Kornfeld [304] arrived at this result by numerical means, directly calculating  $\mathcal{E}_{b}$  by Ewald's method he extended to dipole sums [301], where in view of the complexity of the resulting expressions the factor  $2\pi/3$  was represented only by five decimal digits. In the given special case, one should note the fact that invariance of formula (93) with respect to the shape of the domain of direct summation and vanishing of  $\mathcal{E}_{Md}^{cubic}$  in summation over cubic shells lead to a situation in which the Lorentz fields are the same for spherical and cubic summations [297]. In other words, the direct summation method uniquely determines the Lorentz field, while the inverse problem [301] does not provide for such uniqueness.

The nontrivial topological nature of the result obtained becomes obvious if we rewrite formula (89) in the generalized form as follows:

$$\mathcal{E}_{\rm b} = -\frac{1}{2} \, \mathcal{D}_{\mu\nu}^{\rm dip} M_{\mu} \, M_{\nu} = -\frac{1}{2} \, (\mathcal{K}_{\mu\nu}^{\rm o} + \mathcal{L}_{\mu\nu}^{\rm o}) \, M_{\mu} M_{\nu} \,, \qquad (94)$$

where the meaning and form of the direct-sum tensor  $\mathcal{K}_{\mu\nu}^{\circ}$ immediately follow from formula (90). From the property of the local dipole tensor  $D_{\mu\mu}(\mathbf{R}_i) = 0$  and finiteness of the sum over *i* determining  $\mathcal{K}_{\mu\nu}^{\circ}$ , it follows that  $\mathcal{K}_{\mu\mu}^{\circ} = 0$  [286]. On the other hand, the components of the tensor  $\mathcal{D}_{\mu\nu}^{\text{dip}}$  are structural parameters, which do not depend on the boundaries. Here, from formula (94) we get

$$\mathcal{D}_{\mu\mu}^{\rm dip} = \mathcal{L}_{\mu\mu}^{\rm o} = \mathcal{T}_{\rm struc} = \frac{4\pi}{v} \,, \tag{95}$$

i.e., the trace of the Lorentz tensor also proves to be independent of the boundary shape and is determined solely by the lattice structure [291]. Formula (95), which is quite obvious in the particular case of orthorhombic lattices [291, 292], remains valid in the general case, at least for any simply connected summation domain, and, naturally, agrees well with formulas (92) and (93). Thus, the nonzero value of  $T_{\text{struc}}$ violates the tensor nature of the local characteristics  $D_{\mu\mu}(\mathbf{R}_i)$ in the passage to the translation-invariant solution  $\mathcal{D}_{u\mu}^{\text{dip}}$ .

Note that such a structural peculiarity is just inherent in the kernel  $\mathcal{D}_{\mu\mu}^{dip}$ , whose symmetry reflects the action of regularly arranged dipoles in a translation-invariant closure of space on the same dipole construction far from the boundary of such a closure. In this connection, it is interesting that a quite different result emerges when one calculates the electric field gradient described by the kernel  $\mathcal{D}_{\mu\nu}^{EFG}$ , which formally is similar to  $\mathcal{D}_{\mu\nu}^{dip}$  [272, 273, 275]. Provided that inner summation over the charges of the unit cell has been carried out, the lattice sum determining this gradient proves to be absolutely convergent and contains no topological contribution that would correspond to the Lorentz field [243].<sup>2</sup>

Solution (93) allows one more interpretation (possibly, a partial one) reflecting the internal symmetry of  $\mathcal{D}_{\mu\nu}^{dip}$  and the relation between the Lorentz field and the spatial homogeneity. To this end, one needs only to develop what is known as Griffiths's concept one step forward [284], in which the result of dipole summation is not changed by spreading the charge that forms the local dipole over a small sphere of radius  $r_0$  that surrounds the dipole and does not intersect the neighboring spheres. Then the energy of the dipole interaction with its own field  $\mathbf{E}_{self}(\mathbf{r})$  assumes the form

$$\mathcal{E}_{\text{self}} = \frac{1}{8\pi} \int \left| \mathbf{E}_{\text{self}}(\mathbf{r}) \right|^2 d\mathbf{r} = \frac{|\mathbf{M}|^2}{2r_0^3} \Rightarrow \frac{2\pi |\mathbf{M}|^2}{3\upsilon} \,. \tag{96}$$

However, the last transformation in Eqn (96) introduces a sphere whose volume is that occupied by a unit cell:  $4\pi r_0^3/3 = v$ , so that  $\mathcal{E}_{self}$  acquires an effective meaning not related to the crystalline order proper. This, in turn, may explain the interest in a structureless description in terms of uniform polarization  $\mathbf{m} = \mathbf{M}/v$ , when the total energy of a macroscopically large spherical sample of radius  $R_s$  is given by the formula

$$\mathcal{E}_{S} = -\frac{m_{\mu}m_{\nu}}{2} \int_{|\mathbf{r}_{1}|, |\mathbf{r}_{2}| \leq R_{S}} D_{\mu\nu}(\mathbf{r}_{1} - \mathbf{r}_{2}) \,\mathrm{d}\mathbf{r}_{1} \,\mathrm{d}\mathbf{r}_{2} = 0 \,.$$
(97)

<sup>2</sup> This result for  $\mathcal{D}_{\mu\nu}^{\text{EFG}}$  has been discussed in detail in my recent paper [354]. There I also study more comprehensively the internal relationship between the average potential (38) and the specific energy (88), which in Sections 2.3 and 4.1 were derived on the basis of general expansion (35) in the formally small parameter h. It turns out that at the base of this relationship lies the Lorentz tensor  $\mathcal{L}^{\circ}_{\mu\nu}$  which is the only universal functional in the lattice summation method. As a result, just as the topological contribution to the energy is determined, according to Eqns (89) and (92), by a convolution of  $\mathcal{L}_{\mu\nu}^{\circ}$  with the dipole moments of the unit cell, we can introduce a topological potential of the form  $\Phi_{top} = \mathcal{L}^{\circ}_{\mu\nu} G_{\nu\mu}/2$ , where  $G_{\nu\mu}$ is the quadrupole moment described by the second relation in formulas (36). The addition of  $\Phi_{top}$  to the direct sum in Eqn (53) or Eqn (55) generates  $U_{\rm b}(\mathbf{r})$ . This result lies at the base of the general conclusion [354] that any method of direct summation over the lattice turns out to be convergent if it leads to matrix elements  $\mathcal{L}_{\mu\nu}^{\circ}$  that are limited in absolute value. The corresponding procedure of direct summation also proves to be valid in relation to any charge distribution  $\rho(\mathbf{r})$  limited by the sole condition (34). (Note added in proof.)

Here,  $D_{\mu\nu}$  is specified by expression (91). Note that the integral in relationship (97) is an improper one, so that its value depends on the way we integrate [272]. If, following the idea that space is homogeneous and isotropic, we define the spherical angles of  $\mathbf{r}_2$  in relation to  $\mathbf{r}_1$ , then the immediate integration over the spherical angles of  $\mathbf{r}_1$  nullify the entire expression. This agrees with the zero discrete direct sum in formula (93). Thus, result (93), which corresponds to the combination of Eqns (96) and (97), can be considered the exclusion from the specific dipole energy of self-action normalized to a unit cell. At the same time, it is obvious that here we are speaking about the description of the logarithmic singularity in expression (97), having in mind that singular contributions as  $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$  and  $|\mathbf{r}_1 - \mathbf{r}_2| \to -\infty$  are related by a transformation of the r' = 1/r type. This means, in the spirit of Appell's approach [41], that subtracting self-action is similar to allowing for the contribution of a residue at infinity. However, this problem requires additional investigations.

In describing fluctuations in a crystal, it is important to also allow for dipole sums with modulation [40, 78, 289, 305, 306]:

$$\mathcal{D}_{\mu\nu}^{\rm dip}(\mathbf{k}) = \sum_{i}^{\prime} D_{\mu\nu}(\mathbf{R}_{i}) \exp(\mathrm{i}\mathbf{k}\mathbf{R}_{i}) , \qquad (98)$$

which specify the electrostatic or magnetostatic part of the dynamic matrix [129, 296], responsible for the dispersion of phonons [45, 285] or magnons [307–309], respectively, and appear also in the description of dipole ordering phase transitions [287, 310, 311]. If in expression (98) we pass to the limit  $\mathbf{k} \rightarrow 0$ , we again have a limit jump in the sum to the value  $\mathcal{D}_{\mu\nu}^{dip}$  determined, according to formula (92), by the quantity  $\mathcal{L}_{\mu\nu}^{\circ}$  [281]. Thus, we are again confronted with the property of nonuniform convergence of the sum (98) in  $\mathbf{k}$  [40], which is similar to property (32). As a result, the dispersion of the excitation energy in the limit  $\mathbf{k} \rightarrow 0$  proves to be dependent on the direction of  $\mathbf{k}$  [306], while the case where  $\mathbf{k} = 0$  drops out of the overall spectrum [307].

As for direct calculations of dipole sums, both the Ewald–Kornfeld method [40, 286, 289, 304, 312] and direct summation, beginning with isotropic summation [297], are applied. To these methods we must add the decomposition of complex lattices into combinations of simple lattices [286, 289, 292, 298], where, as in the case of Hund potentials, there is a relationship between dipole fields at different symmetric points of the unit cell [286, 298]. In connection with the use of gradient representation (90), we should bear in mind, however, that the operations of differentiation and summation are commutative only in the region of uniform convergence of the sums [54]. Hence, one should be careful when introducing differentiation procedures [286, 289, 304] into the methods of summation described above [40, 127, 286].

There is still some interest in the classical Madelung method of slice-wise summation [45, 47]. The use in this method of representations of both type (16) [275, 288, 292, 308] and type (42) [285] makes it possible to increase the rate of convergence of the emerging sums. Note that, in view of the particular property (93), the tensor  $\mathcal{D}_{\mu\nu}^{dip}$  is sometimes called the Lorentz factor in the literature. This factor describes the bulk properties of crystals that are surface-independent [275, 288]. Here, when the components of  $\mathcal{D}_{\mu\nu}^{dip}$  are numerically calculated, it is advisable to take into account the upper equality in Eqn (92). For instance, it has proven convenient to calculate the off-diagonal components in a geometry in which

the appropriate axes are oriented in the plane of the slab, provided that the third crystallographic direction is orthogonal to these axes. In this case, the absence of a dipole contribution that is perpendicular to the slab leads to the absence of the respective Lorentz field [288, 308]. On the other hand, when calculating each diagonal component of  $\mathcal{D}_{\mu\nu}^{dip}(0)$ , it is advisable to employ a cylindrical geometry, when the thickness of a slab of layers with its normal directed along the component under investigation tends to infinity faster than the transverse dimensions of these layers. Then, the corresponding Lorentz field vanishes again, and the result is reduced to a direct sum [288, 293].

#### 4.2 The thermodynamic limit

It is only natural to assume that the configurations of the ground state and the related quasi-particle excitations essentially describe the bulk properties of crystals [129, 180]. Such ideas of classical bulk thermodynamics, which is independent of the boundaries, emerge naturally when the lattice sums determining the dynamic matrix converge absolutely and uniformly [313]. The existence of a certain thermodynamic limit as the dimensions of the system tend to infinity follows here from the additivity of the free energy as a function of the volume [284].

The dipole interaction destroys these ideas and generates a dependence in the thermodynamic limit of homogeneously polarized media on the limit shape of the boundary [314], notwithstanding the nature of the dipoles [286, 315, 316], which may be either magnetic [296] or electric, when dipoles appear as a result of the existence of peculiarities in defining the unit cell. The contribution of dipoles induced by an external or internal crystal field manifests itself in addition to a permanent dipole component [52, 305, 317]. We include an external field  $\mathbf{E}_{ext}$  generated by extraneous sources, which is especially important since in this case the existence of real boundaries of the dipole systems is assumed explicitly. The internal local field acting on an individual dipole parallel to all other dipoles can then be written as follows [275, 286, 296, 298, 301, 305, 310]:

$$\mathbf{E}_{\text{loc}} = \mathbf{E}_{\text{m}} + \mathbf{E}_{\text{dip}}, \quad \mathbf{E}_{\text{m}} = \mathbf{E}_{\text{ext}} - \mathbf{E}_{\text{D}}^{S}, \quad (99)$$

$$\mathbf{E}_{\rm dip} = -\frac{\partial \mathcal{E}_{\rm b}}{\partial \mathbf{M}} = \mathbf{E}_{\rm Md}^{\circ} + \mathbf{L}^{\circ}(\mathbf{M}) \Rightarrow \frac{4\pi}{3}\mathbf{m}\,,\tag{100}$$

where the field  $\mathbf{E}_{dip}$  is structured according to formula (89) and in the symmetric case (93) is reduced to the classical expression in terms of the mean polarization  $\mathbf{m} = \mathbf{M}/v$  [129, 186, 310]. The external field  $\mathbf{E}_{ext}$  is assumed uniform. The formula for the macroscopic field  $\mathbf{E}_{m}$  in the sample incorporates the depolarizing field  $\mathbf{E}_{\mathrm{D}}^{\mathrm{S}}$  generated by the last term on the right-hand side of equation (88) in the case of a real surface S. In contrast to the field  $\mathbf{E}_{dip}$ , which without loss of generality can be calculated at the center of the summation domain,  $\mathbf{E}_{\mathbf{D}}^{S}$  depends on the coordinates  $\mathbf{R}_{i}$  of the point of observation in relation to the boundary, so that only the value of  $\mathbf{E}_{D}^{S}$  averaged over the sites  $\mathbf{R}_{i}$  carries information in formula (99) [318]. An exception is presented by ellipsoidal boundaries [296, 301, 318, 319], when the field  $\mathbf{E}_{D}^{\text{ell}}$  is uniform and is specified by the components of the tensor  $\mathcal{L}_{uv}^{\text{ell}}$ . According to expression (89), this corresponds to a description of the farther part of the dipole sum by an integral. Thus, the depolarizing field and the Lorentz field considered together describe the contributions of the outer and inner boundaries of the domain of such integration [286, 296, 301].

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The dependence of the tensor  $\mathcal{L}_{\mu\nu}^{\text{ell}}$  on the shape of a uniformly polarized ellipsoid with axes  $a_1, a_2$ , and  $a_3$  is determined by its eigenvalues [286, 319, 320]

$$\mathcal{L}_{j} = \frac{2\pi a_{1}a_{2}a_{3}}{v} \int_{0}^{\infty} \frac{\mathrm{d}\lambda}{(a_{j}^{2}+\lambda)\sqrt{(a_{1}^{2}+\lambda)(a_{2}^{2}+\lambda)(a_{3}^{2}+\lambda)}}$$
(101)

and has been thoroughly tabulated [320, 321]. The sum  $\mathcal{L}_1 + \mathcal{L}_2 + \mathcal{L}_3$  agrees in a natural manner with the last equality in Eqn (95) [275], and the limit forms  $\mathcal{L}_j$  [301] follow from Eqn (101) and lead, in particular, to relationships (92) when  $a_1 \rightarrow \infty$ ,  $a_2 \rightarrow \infty$ , or  $a_1 = a_2 = a_3$ , respectively.

It is significant that the thermodynamic description of an ellipsoidal sample does not claim to be a strictly unique bulk solution; such a description only imitates its possible homogeneity. Here, the thermodynamic functions expressed in the dependence on  $\mathbf{E}_{m}$  do not contain the shape effect explicitly. This property, obtained for the susceptibility within the scope of high-temperature expansions [322] and in the spherical model [305], proves to be quite general for the free energy treated in the classical as well as in the quantum cases [323, 324]. The passage via thermodynamic identities [323, 324] to the field  $\mathbf{E}_{ext}$  as a controllable external field parameter [296] restores the shape effect in the thermodynamic derivatives. Here, the dependence of  $\mathbf{E}_{D}^{S}$  on uniform polarization that is the thermodynamic conjugate of  $\mathbf{E}_{m}$  presupposes the existence of additional self-consistency [52, 310].

A description specifically in terms of  $E_{loc}$ , without specifying  $E_m$ , is also justified if we want to exclude the shape effect, which stresses the typical nature of the combination of depolarization and the Lorentz field in  $E_{loc}$  [323]. This peculiarity is retained even when  $E_{ext} = 0$ , i.e., when the effective field formalism loses its universality in view of the nonuniform convergence of the thermodynamic expansions that form the basis of this formalism [323].

In view of the apparent nonuniqueness of the thermodynamic description in relation to the sample's shape [126, 134, 150, 279, 280, 286, 302, 314, 318], Griffiths's remark in Ref. [284] that the concept of a thermodynamic limit is welldefined only for an absolutely equilibrium volume configuration becomes extremely important. However, such a definition does not exclude the possibility of existence of metastable states; it only characterizes the energy of an equilibrium state as the lower limit of admissible values of the energy of a thermodynamic system [44, 47]. Actually, we are speaking here of the removal of the depolarization effect related to a loss in bulk energy in the process of relaxation of the surface of the confined thermodynamic system to equilibrium [295, 310]. For Coulomb systems this means that generally an equilibrium surface is not reduced to a model breaking of the bulk structure along a certain plane; such a surface is characterized by certain 'fractional' charges generated by the condition of minimization of the bulk energy of the system [47, 280, 325]. In other words, a passage to volume summation over the unpolarized unit cells, which exclude the depolarization effect, is assumed. The charge transformation of the surface is unavoidable when the structure of the initial surface contradicts the given volume requirement [326]. Thus, with arbitrarily shaped real crystals it is always possible to achieve a thermodynamic limit. As noted by J Larmor in 1921 (see Refs [327, 328]), insulators that are in equilibrium exhibit no homogeneous bulk dipole properties, so no depolarization effect can be associated with them [285, 297].

Still, it should be noted that Coulomb 'tuning' of the surface configuration in metals occurs almost immediately [49, 319, 328, 329], while for insulators the characteristic times of formation of a free equilibrium surface may be long enough [330] for an alternative mechanism to come into play. This mechanism, which lowers the extent to which the bulk of the crystal resides in a nonequilibrium state, amounts to spontaneous 'domenization' of the crystal, although the nature of this phenomenon is different and is related to the suppression of the energy of the field induced by a dipoleordered crystal beyond the crystal boundaries [328, 330-332]. In this connection, an interesting case is that of an interface acting as a 'tunable' surface and leading, among other things, to an instantaneous relaxation at the boundary between the crystal and a liquid electrolyte. Obviously, such 'tuning' in directions that are perpendicular to the elements of the nonequilibrium surface differs from the fluctuating polarization of the electrolyte along the equilibrium surface of an ionic crystal [333].

Another case, which is important for practical purposes, is similar in meaning to the previous case and is related to the participation of external charges in balancing the surface. It has to do with the special features of the experimental facility for measuring polarization effects, a facility in which the sample shaped as a flat plate is firmly held between the plates of a plane capacitor, which are then short-circuited [326, 328, 329, 332, 334, 335]. The charges induced on the plates of the capacitor effectively participate in the relaxation of the metastable state of the sample with incomplete inherent surface relaxation, thus finalizing it.

The fact that there are no magnetic monopoles in nature essentially reduces the reconstruction ability of the surface of magnetic samples, although here, too, there may be (at least theoretically) a powerful magnetic polarization of the surface atoms, caused by the effect of the sample bulk. Nevertheless, in a more common approach the passage to the thermo-dynamic limit for ferromagnetic materials is based on the allowance for the dependence of the depolarization effect on the external shape of the crystal and is realized in needlelike samples with the axis along the magnetization vector [296–298]. Another possibility, related to twinning [47, 284] (as in Coulomb systems), only weakens the depolarization effect and is limited from below by the size of crystals, since in small enough samples spontaneous 'domenization' turns out to be energetically unprofitable [300].

Thus, despite the existence of very different ways of achieving equilibrium in electric and magnetic substances, it can be stated that the thermodynamic limit of dipole systems is well-defined in principle, at least in a zero external field, and is described by the specific bulk energy  $\mathcal{E}_{b}$  specified by formulas (88), (89), and (93), which for Coulomb systems are equivalent to formula (86).

### 4.3 Equilibrium and metastability

By no means can the metastable states under discussion always be linked to absolutely equilibrium states via a continuous adiabatic transformation of some sort. This feature manifests itself most vividly in the topological differences of the dipole configurations of the ground state, configurations that emerge in all such cases as a result of the dipole interaction.

First, it must be noted that the analysis of the dipole ordering within the group-theoretical approach [298] predicts that the ground state of simple cubic lattices has antiferromagnetic order. Usually, the discussion of this problem is limited to the classical Sauer configuration [297], in which the dipoles are directed along a four-fold axis and are ordered parallel to this axis, while in the perpendicular plane the orientations of neighboring dipoles are opposite. Such a configuration is also typical of simple tetragonal structures [289, 307, 316], but in triclinic lattices the nature of antiferromagnetic ordering may be more complicated [316]. A different case of equilibrium antiferromagnetic ordering in crystals with cubic symmetry is characteristic of dipoles packed in a diamond structure [336]. Note that, as in the case of a simple cubic lattice, the collinear orientation of dipoles in the ordered phase [336] is not here the only one possible. On the contrary, there is complete spherical degeneracy in the orientation angles of an arbitrarily selected dipole, provided that the orientations of the neighboring dipoles are 'tuned' to that of the given dipole in a way in which the mean dipole moment of the unit cell is zero [337]. It must also be noted that an antiferromagnetically ordered ground state is also typical of all types of hexagonal lattices, at least when the ratio of their structural parameters is close to the respective ideal values [286, 292]. It is significant that in all the above cases the gain in the energy of the antiferromagnetically ordered state compared to that of a parallel one excludes depolarization problems related to the thermodynamic limit [286, 297, 316].

A quite different basic situation may occur in complex Bravais lattices [243, 297, 298, 307, 316]. For instance, for fcc and bcc lattices in the case of bulk equilibrium, the effect of the Lorentz field (93) is predominant and leads to parallel ordering of dipoles in a direction determined by the effects that are next-in-order infinitesimal [307]. The effect of metastability related to depolarization counteracts the Lorentz field, fully neutralizing it in spherical samples, provided that the surface parallel configuration of dipoles coincides with the bulk configuration. It is for such nonequilibrium configurations of surface dipoles that the depolarization effect is at its maximum in the case of a flat plate with transverse polarization [293]. As a result, the ground state of fcc and bcc lattices shaped as such plates is predicted to be antiferromagnetically ordered [297]. In the intermediate case of an ellipsoid of revolution (a spheroid) with nonequilibrium boundaries, the transition of the ground state from ferromagnetically ordered to antiferromagnetically ordered occurs when the ratio of the spheroid axes is of order six [298]. As for the equilibrium bulk configuration in lattices with a basis that specifies the arrangement of several dipoles in the unit cell, it is determined by the parallel [281, 306, 338] or antiferromagnetically ordered [250] configuration of local dipoles, depending on the extent to which the situation is close to one of the situations described above.

The dependence of the energy of dipole ordering on the depolarization contribution to the metastable state also has a natural effect on the critical thermodynamics of ordering. Here, the Lorentz field reduced by the depolarization contribution acts as Weiss's molecular field [339], retaining its self-consistent nature even against the background of the short-range exchange interaction in magnetic substances [296, 307, 310]. As a result, the temperature of parallel ordering of dipoles in the metastable state depends on the sample's shape (this temperature is predicted in mean-field theory) [316]. The concept of a phase transition as a bifurcation point at which the thermodynamic solution splits necessarily presupposes the existence of a singularity in the

susceptibility at the phase transition point [296, 305, 310, 311, 318]. In this connection, the unusual possibility of depolarization manifestation has been noted in renormalization-group analysis, when, in addition to the variable critical temperature as a function of the sample's shape, susceptibility may remain finite in a phase transition [287].

The complexity of the question of whether dipole forces alone can lead to ordering [296, 315, 318] follows from Onsager's construction [317], within which a dipole  $\mathbf{M}_i$  is surrounded by a hollow spherical cavity of a small volume  $v_s$ , so that the field  $\mathbf{E}_{loc}^{(i)}$  acting on  $\mathbf{M}_i$  is given by the formula

$$\mathbf{E}_{\text{loc}}^{(i)} = \frac{3\epsilon}{2\epsilon + 1} \mathbf{E}_{\text{m}} + \frac{8\pi(\epsilon - 1)}{3v_{\text{s}}(2\epsilon + 1)} \mathbf{M}_{i}, \qquad (102)$$

where both fields outside the sphere contribute to the righthand side of expression (102):  $\epsilon \mathbf{E}_{m}$  with the dielectric constant  $\epsilon$  and the polarizing field from  $\mathbf{M}_{i}$ , but the resulting fields are the solutions of the boundary-value problem of electrostatics inside the given sphere [42]. When all the  $\mathbf{M}_{i}$  are parallel to  $\mathbf{E}_{m}$ , and  $v_{s}$  is the volume per dipole ( $\mathbf{M}_{i}/v_{s} = \mathbf{m}$ ), the general equality ( $\epsilon - 1$ ) $\mathbf{E}_{m} = 4\pi\mathbf{m}$  transforms formula (102) into formula (99) with the cubic variant (100) [296]. If we perform averaging over the orientations of the  $\mathbf{M}_{i}$  in field (102), then, in view of the obvious absence of correlations [305, 315], the thermodynamics that emerges is one without a phase transition [296, 302, 317].

As applied to polar liquids [301, 317], this result provides a meaningful explanation of the absence in such liquids of a long-range structural order, with the result that there are strong local fluctuations in these liquids. Indeed, the fluctuation effect by itself, considered against the background of the molecular field related to uniform polarization, explains only the tendency of the Curie temperature to lower [315]. At the same time, the above-noted possibility of a dramatic change in the ordered configuration of the ground state, even if the lattice crystal system is retained, is an indication that there is no preferred dipole order in structurally disordered media. This suggests a limited applicability of structurally concretized lattice models for describing the dipole properties of such objects.

As for the manifestation of the dipole interaction in magnetic substances, it should be noted that the contribution of such interaction is usually small compared to the exchange energy, so that the features of critical behavior associated with this contribution manifest themselves only in a narrow region around the phase transition point [340]. This does not exclude, however, the effect of anisotropic ordering under isotropic exchange [289, 309], an effect generated by this interaction. In addition to the classical situation with diluted magnetic substances [296], the cases of low-temperature ordering of the dipole nature include, for instance, the ferromagnetism of LiTbF<sub>4</sub> ( $T_c = 2.86$  K), in which dipole interaction exceeds the exchange energy [306]. A substantial contribution of the dipole energy is a characteristic feature of the cerium-magnesium nitrate ( $T_c \approx 0.019$  K). Another possibility of the ordering dipole interaction manifesting itself emerges when direct exchange of the antiferromagnetic type is modified by a frustration effect, as occurs in Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>  $(T_{\rm c} = 0.97 \text{ K})$ . The common tendency in the last two cases is related to an increase in the ratio of the strength of the dipole interaction to the exchange energy and corresponds to a transition from antiferromagnetic order to ferromagnetic order through an intermediate phase of a layered antiferromagnet [341], which may manifest itself as an incommensurate phase [309, 342].

Knowing  $\mathcal{E}_b$  makes it possible to use the thermodynamic definition of the specific surface energy  $\mathcal{E}_{surf}$  of a real surface for a Coulomb system [4, 31, 56]. Such a definition is formulated most simply for a slab of parallel translationally repetitive layers:

$$\mathcal{E}_{\text{surf}} = \lim_{N_{\text{slab}} \to \infty} \left[ \min_{\{g\}} \left( \frac{\mathcal{E}_{\text{slab}}\{N_{\text{slab}}, g\} - N_{\text{slab}}\mathcal{E}_{\text{b}}}{2} \right) \right], \quad (103)$$

where  $\mathcal{E}_{slab}\{N_{slab}, g\}$  is the energy of a column with the section of a unit cell in the plane of the layer cutting through the slab of  $N_{\text{slab}}$  layers transversely. The magnitude of  $\mathcal{E}_{\text{slab}}\{N_{\text{slab}}, g\}$  is a functional not only of  $N_{\text{slab}}$  but also of the configurational variations  $\{g\}$  in the subsurface layers over which minimization is carried out in order to achieve thermodynamic equilibrium in formula (103) [28, 125]. Here, the neutral Madelung layers prove to be more optimal than combinations of charged layers [71]. Generally, we have a typically overdetermined boundary-value problem, where  $\mathcal{E}_b$  and  $U_{\rm b}({\bf r})$  specify the solution in the bulk of the crystal [29, 32, 37] with a zero potential at points located at an infinite distance from the crystal [125]. The resulting surface transformation [125, 136] includes its relaxation (adiabatic shifts of ions with allowance for their polarizability [37, 70, 149, 343, 344]) and reconstruction (a change in composition in relation to the ideal composition in the bulk [29, 31, 36, 190, 345]), including the formation of surface vacancies [326]. In the latter case, an effect associated with charge transfer along covalent bonds may also emerge [12, 50, 346]. In such an effect the breaking of some of the bonds of this type in the surface formation process changes the value of the local charges on this surface [329]. As a result, beginning with the deep layers in the slab, the solution can be constructed on the basis of formula (18) by isolating the components of all vectors perpendicular to the surface  $(r_{\perp}, R_{i\perp}, b_{j\perp}, \text{ and } h_{\perp})$  and then integrating with respect to  $h_{\perp}$  from  $-\infty$  to  $\infty$  [72, 345].

On the other hand, the surface solution can be formed on the basis of the fact that the potential is zero at infinity. In such cases as the study of the work function on surfaces of various orientations [30, 37, 156],  $U_{\rm b}({\bf r})$  is not specified, and its bulk nature manifests itself indirectly in the position of the Fermi level as a reference point in the bulk [18, 28]. Here, the effects of surface relaxation and reconstruction can be compared by calculating them independently [347]. Such an approach, however, allows for the possibility of a nonequilibrium state. This is obvious, since the exclusion or even a simple limitation of the optimization procedure in expression (103) leads to a mismatch in the values of  $\mathcal{E}_{slab}\{N_{slab},g\}$  and  $\mathcal{E}_{b}$ , which manifests itself in the divergence of energy (103) in  $N_{\text{slab}}$  [348]. A simple (but not really justified) way out of this difficult situation is to replace in formula (103) the independent quantity  $\mathcal{E}_b$  with a parameter  $\mathcal{E}_{b}^{slab}$  similar in dimensional structure (this parameter is the linear in  $N_{\text{slab}}$ 's contribution to the slab energy) [37, 348-351]. The fact that the quantities  $\mathcal{E}_{slab}\{N_{slab}, g\}, \mathcal{E}_{b}^{slab}$ , and  $\mathcal{E}_{surf}^{slab}$ are in this case nonequilibrium follows from the statistical feature of pair interaction (action equals counteraction), since the effect of volume elements on each surface element leads to a loss in energy proportional to  $N_{\rm slab}$ , thus promoting relaxation tendencies on the surface [349]. In other words, the specific nature of the Coulomb interaction also stems from the fact that the possible metastability of bulk states, while corresponding to deviations from the equilibrium

thermodynamic limit, is always equivalent to the instability of surface configurations. Thus, the unquestionable equality of  $\mathcal{E}_{b}^{\text{slab}}$  to  $\mathcal{E}_{b}$  is the necessary condition for an equilibrium of the modelled surface with respect to the volume that this surface bounds [36, 37, 125, 128, 349].

### 5. Conclusions

Summing up, we can argue that the condition of thermodynamic equilibrium is a delicate feature of physical systems with long-range interaction. Allowing for this feature in a meaningful way makes it possible to consider the above summation methods as being equal from the point of view of the final result, so that the choice of a particular method can be dictated only by the specific features of the problem being solved and the related way in which the charge distribution is described. For instance, in calculating Bloch electron functions, methods that involve the use of structural factors seem to be the most appropriate ones. On the other hand, in examining ionic crystals in terms of spherical charge distributions restricted by ionic radiuses, direct summation is sure to be more effective. This approach also directly encompasses the description of dipole systems, reducing it in crystals without boundaries to the Coulomb case of excluding depolarization in view of the topological identity of dipole sums

A special feature of functional transformations, which is very important in obtaining truly bulk solutions, amounts to separating charge summation over the Bravais lattice from summation over the basis, which eliminates the arbitrariness in selecting the unit cell. Here, inner summation over the basis vectors acquires the meaning of a self-consistent link between the independent (within the volume) Fourier transforms of different charge components via common boundary conditions, which are invariant in the case of an equilibrium surface. Then and only then are the energy contributions of the volume and the bounding real surface statistically separated.

In the direct-summation approach, inner summation over the basis is represented somewhat differently, since it forms the ground for determining the local multipoles responsible for the series convergence. As a result, the values of the emerging sums may be related to both equilibrium and metastable systems. The fact that in order to find surfaceindependent bulk potentials one must subtract from the direct sum the cell average of the potential in the compact Bethe form may be considered as a convenient formal technique that matches the results of direct summation to equilibrium bulk solutions based on functional transformations. At the same time, this result is a direct consequence of periodic boundary conditions in an infinite crystal that differ from Born – von Kármán periodic boundary conditions in that the position of the matching boundaries can in no way be fixed [249], so that in this sense a crystal cannot be reduced to a supercell.

As for using multipole expansions in locally orthogonal bases, the main problems here are related to the difficulties in describing such expansions near the boundary of the convergence circle. As a result, in numerical simulations one is sure to be confronted with asymptotic series whose properties, in the final analysis, form the basis of interpolation methods being developed in self-consistency problems.

It should be emphasized that although the present review is devoted primarily to methodical questions of excluding metastable states, as states that not agree with the thermodynamic limit in problems with Coulomb long-range interaction, examining such states consistently, step by step, with allowance for their subsequent relaxation may constitute a research problem of its own right in describing pyro-, piezo-, and ferroelectric properties as manifestations of the polarity of the crystal structure [352].

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