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A new approach for modelling lattice energy in finite crystal domains

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Abstract. Evaluation of internal energy in a crystal lattice requires precise calculation of lattice sums. Such evaluation is a problem in the case of small (nano) particles because the traditional methods are usually effective only for infinite lattices and are adapted to certain specific potentials. In this work, a new method has been developed for calculation of lattice energy. The method is a generalisation of conventional geometric probability techniques for arbitrary fixed lattices in a finite crystal domain. In our model, the lattice energy for wide range of two-body central interaction potentials (including long-range Coulomb potential) has been constructed using absolutely convergent sums. No artificial cut-off potential or periodical extension of the domain (which usually involved for such calculations) have been made for calculation of the lattice energy under this approach. To exemplify the applications of these techniques, the energy of Coulomb potential has been plotted as the function of the domain size.

1. Introduction

We recently developed a new method for evaluation of the lattice energy in finite crystals [1]. This method initially was created for the medium with continuous distributed mass. The central idea of this method is an adaptation of the geometric probability approach [2] for the lattices in finite domain. We applied the above mentioned method for calculation of long-range Coulomb interaction between lattice nodes (point charges) and continually distributed charge density (jellium). The Coulomb interaction, which has been intensively discussed in the literature from the end of nineteenth century, plays a central role in condensed matter crystals systems [3]. We assumed that the domain is neutral (the number of positive and negative charges is equal) and it has zero dipole moment. Our final result made under this assumption has been expressed in terms of unconditionally convergent sums. In real crystals negative and positive charges on the surface usually separated, and they form the surface dipole moment. For example, the electron gas above the surface of the metals together with positive charges of the ions on the metal surface creates the dipole moment. In presence of the dipole moment some sums do not converge absolutely for Coulomb potential. The problem has been solved by considering the finite size of the lattice nodes (ions or molecules). This leads to the expressions of the lattice energy in the form of absolutely convergent sums. We derived the expression for interaction energy in lattices domains by using this method. The interaction energy included node-node, jellium-jellium and node-jellium components. This method is applicable for any two-body central potential. Essentially, that we do not use periodic boundary conditions or vanishing exponential method [4] in

our approach. Moreover, all kinds of interactions: lattice-lattice, lattice-jellium and jellium-jellium can be evaluated separately.

2. Geometric probability techniques for crystals lattice

The common expression for the self-energy of two-body potential

$$\langle U(R)\rangle \equiv \int\int d\vec{r}_1 d\vec{r}_2 \rho(\vec{r}_1) U(|\vec{r}_1 - \vec{r}_2|)\rho(\vec{r}_2), \tag{2.1}$$

where $\rho(\vec{r})$ is a density of the particles, has been written by Schleef et al. [2] in very useful form

$$\langle U(R)\rangle = \int_{r_0}^{2R} G(r_{12};\rho_1,\rho_2) U(|\vec{r}_{12}|) dr_{12}, \tag{2.2}$$

with r_0 being the minimum possible distance between the points. Inside the jellium, we assume that $r_0 = 0$ due to contiunuum. The radial density distribution function (RDF) $G(r_{12};\rho_1,\rho_2)$ for the number of points of the pairs inside the sphere can be written [2] as

$$G(r_{12},R) = r_{12}^2 \int_0^R 4\pi r_1 \rho(r_1) \left[\int_0^\pi 2\pi \sin\theta_{12} \rho\left(|\vec{r}_{12} + \vec{r}_1|\right) d\theta_{12} \right] dr_1 = 16\pi^2 r_{12} \int_{r_{12}/2}^R r_1 \rho(r_1) \left(\int_{|r_{12}-r_1|}^{r_1} r_2 \rho(r_2) dr_2 \right) dr_1. \tag{2.3}$$

The normalized probability density for finding two points in the sphere to be a distance r_{12} apart, is simply normalized RDF

$$P(r_{12}) = \frac{G(r_{12};\rho_1,\rho_2)}{N}, \; N = \int_{r_0}^{2R} G(r_{12};\rho_1,\rho_2) dr_{12}\,. \tag{2.4}$$

Therefore, using these expressions, the problem of self-energy of two-body potential can be considered with the probability theory. The advantage of this approach is in separation of purely geometrical factor (in the function $G(r_{12},R)$), from the interaction potential $U(|\vec{r}_{12}|)$. For that reason, when RDF solution was obtained once, it can be used for calculation of the self-energy for the different central two-body potentials by simple integration in (2.2). In our recent publication1 [1] this technique has been extended for crystals systems, by using the set of Dirac delta-functions as a microscopic density distribution function.

The interaction energy (self-energy) of N particles set

$$H = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} U(|\vec{r}_i - \vec{r}_j|) \tag{2.5}$$

may be written in the continuous form as

$$H = \frac{1}{2} \int_V \int_V \rho(\vec{r}_1) U(|\vec{r}_1 - \vec{r}_2|) \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \tag{2.6}$$

with the microscopic density distribution function [5]

$$\rho(\vec{r}) = \sum_{\vec{n}\in\inf} \delta\left(\vec{r} - n_1 \cdot \vec{a}_1 - n_2 \cdot \vec{a}_2 - n_3 \cdot \vec{a}_3\right), \tag{2.7}$$

where δ being the Dirac delta-function, $\vec{a}_i$ is the basis vectors of the 3-D lattice, n_i - integers. The Eq. (2.3) is applicable only for a spherical-symmetric density $\rho(r)$, which depends only on the distance $|\vec{r}|$ (scalar). In our case the density function in (2.7) depends on the vector $\vec{r}$. Therefore, the approach has to be modified. By repeating steps leading to (2.3), but without initial integrations over azimuthal angles φ_1 and φ_2, we came to the expression

$$G(r_{12},R) = 2r_{12}^2 \int_{\frac{r_{12}}{2}}^R r_1 \int_{\theta_1=0}^{\pi} \left(\int_{\varphi_1=0}^{2\pi} \rho(\vec{r}_1) d\varphi_1 \right) d\theta_1 \left\{ \int_{|r_1-r_{12}|}^{r_1} \left(\int_{\varphi_2=0}^{2\pi} \rho(\vec{r}_2) d\varphi_2 \right) r_2 dr_2 \right\} dr_1. \tag{2.8}$$

3. A new model

In the conventional model of lattice crystal described above, the real charges (which occupy some finite volume) are substituted by the infinite small charged nodes (points). The advantage of this discretization method is its relative simplicity, but the main disadvantage is the problem with convergence of the lattice sums, especially for spherical lattice domain [3]. Many publications, starting from early Ewald's article [5] have considered the solution to this problem for infinite lattice domain by using a lattice assembled from finite size objects rather than point nodes. Under this approach, atoms or ions in the lattice are represented as smeared-out 3D density distribution of lattice nodes [7]. This method also describes lattice vibrations.

In our new model, explicitly distribution has been used due to the specifics of the geometric probability method. The integrals in (2.8) for point charges (atoms) of the lattice model now are generalized for smeared-out spatially-distributed objects with the distribution function $f_d(\chi)$. It means that while the integration over r_1 gives the contribution for counting the number of the centers of the charges on the spherical surface, the integration over χ corrects this expression for smeared-out objects by integration over the spherical surface layer. The distribution function can also involve effects of thermal vibrations, lattice imperfections and the uncertainty principle. Here we are using 1D Gaussian

$$f_g(\chi, r_g) = \frac{1}{r_g\sqrt{\pi}} e^{-\frac{\chi^2}{r_g^2}} \tag{3.1}$$

as the distribution function. Generalizing the Eq. (2.8) with this distribution function (3.1) we receive RDF as

$$G(r_{12}, R) = G_{jj}(r_{12}, R) + G_{jl}(r_{12}, R) + G_{ll}(r_{12}, R) \tag{3.2}$$

with jellium-like component

$$G_{jj}(r_{12}, R) = \frac{16\pi^2 r_{12}}{v^2 N} \int_{r_{12}/2}^{R} r_1 dr_1 \int_{|r_{12}-r_1|}^{r_1} r_2 dr_2, \tag{3.3}$$

jellium-lattice correction

$$\begin{aligned} G_{jl}(r_{12}, R) \simeq \frac{16\pi^2 r_{12}}{v^2 N} \Bigg[& \int_{r_{12}/2}^{R} r_1 dr_1 {\sum_{\vec{\gamma}\in\inf}}' \frac{1}{2\pi\gamma} \int_{|r_{12}-r_1|}^{r_1} \int_{-\infty}^{\infty} \frac{1}{r_g\sqrt{\pi}} e^{-\frac{\chi^2}{r_g^2}} \cdot \sin(2\pi\gamma \cdot r_2 + 2\pi\gamma \cdot \chi) dr_2 + \\ & + {\sum_{\vec{\gamma}\in\inf}}' \frac{1}{2\pi\gamma} \int_{r_{12}/2}^{R} \int_{-\infty}^{\infty} \frac{1}{r_g\sqrt{\pi}} e^{-\frac{\chi^2}{r_g^2}} \cdot \sin(2\pi\gamma \cdot r_1 + 2\pi\gamma \cdot \chi) dr_1 \int_{|r_{12}-r_1|}^{r_1} r_2 dr_2 \end{aligned} \tag{3.4}$$

and lattice-lattice correction

$$\begin{aligned} G_{ll}(r_{12}, R) \simeq \frac{16\pi^2 r_{12}}{v^2 N} \Bigg[& {\sum_{\vec{\gamma}\in\inf}}' \frac{1}{2\pi\gamma} \int_{r_{12}/2}^{R} \int_{-\infty}^{\infty} \frac{1}{r_g\sqrt{\pi}} e^{-\frac{\chi_1^2}{r_g^2}} \cdot \sin(2\pi\gamma \cdot r_1 + 2\pi\gamma \cdot \chi_1) d\chi_1 dr_1 \times \\ & \times {\sum_{\vec{\gamma}\in\inf}}' \frac{1}{2\pi\gamma} \int_{|r_{12}-r_1|}^{r_1} \int_{-\infty}^{\infty} \frac{1}{r_g\sqrt{\pi}} e^{-\frac{\chi_2^2}{r_g^2}} \cdot \sin(2\pi\gamma \cdot r_2 + 2\pi\gamma \cdot \chi_2) d\chi_2 dr_2 \Bigg] \end{aligned} \tag{3.5}$$

components. Here the Poisson summation and the Rayleigh expansion formulas (up to second order) similar to Ref. [1] have been used.

4. Discussion

The part of the whole lattice energy, which corresponds the uniform charge distribution, is contained within the term:

$$H_{jj}(R,r_g)=\frac{1}{2}\int_{r_0}^{2R} G_{jj}(r_{12},R)U(|\vec{r}_{12}|)r_{12}dr_{12}. \quad (4.1)$$

This energy is compensated by the background energy of the opposite charge in the Wigner model. Such compensation eliminates the lattice Coulomb energy from divergence in infinite crystal. Other parts of lattice energy contain only absolutely convergent sums, even for Coulomb energy. RDF $G_{jl}(r_{12},R)$ can be interpreted as the number pairs of points with one point belongs to continuum distributed matter and another - to the lattice nodes. Therefore, the corresponding $H_{jl}(R,r_g)$ contribution to the whole lattice energy is equal to background-lattice interaction energy. Last energy component H_{ll} (with RDF $G_{ll}(r_{12},R)$) has exclusively discrete lattice origin.

As an example of application of this theory we calculate jellium-lattice contribution $H_{jl}(R)$

$$H_{jl}(R,r_g)=\frac{e^2}{v}\sum_{\vec{\gamma}\in\inf}{}'\left\{R^{-1}\frac{\sin(2\pi\gamma R)}{2\pi^2\gamma^3}-R^{-2}\frac{3}{4\pi^3}\frac{\cos(2\pi\gamma R)}{\gamma^4}-R^{-3}\frac{3\sin^2(2\pi\gamma R)}{8\pi^4\gamma^5}\right\}\exp\left(-\pi\gamma r_g\right) \quad (4.2)$$

for Coulomb potential in the spherical domain with zero total charge. The result is shown in the Figure 1.

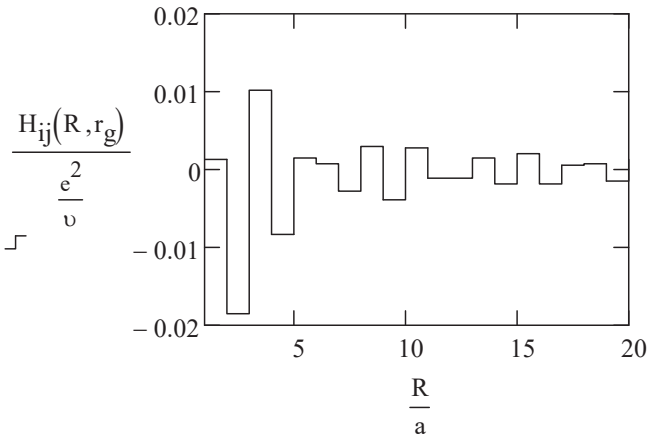

Figure 1. Variations of the jellium-lattice component (Eq. 4.2) per one charge, for Coulomb potential in primitive cubic lattice vs. sphere radius *R*, expressed in numbers of the minimal distance between nodes a and $r_g=0.3\,a$.

This new approach allows calculations of lattice energy in different finite systems with various interaction potentials and lattice structures, which does not suffer from convergence problems commonly seen in traditional lattice sums methods.

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