Calculation of the Coulomb energy in quasi-two-dimensional systems

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In this paper we obtain expressions for the Coulomb energy in infinite quasi-two-dimensional systems in the form of fast converging Ewald sums in the three-dimensional coordinate and two-dimensional inverse space needed for accurate formulation of periodic boundary conditions in computer simulations. Numerical tests evidence that the acceptable accuracy in the total energy is achieved by taking into account rather small number of terms in the sum for the inverse space responsible for the long-range part of interaction.

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In computer simulations of the Coulomb systems, one of the most difficult problems is to combine the periodic boundary conditions with the long-range Coulomb interactions between particles. A fundamental approach to solve this problem for three-dimensional (3D) case was given by Ewald in 1921 [1]. The idea was to convert the infinite series of Coulomb sums over periodically repeating configurational cells, which converges very slowly, to two rapidly converging series in the direct (coordinate) and the inverse space by splitting the interaction in two parts and using the Fourier transformation for the long-range part of the interaction. Since then, the computation of the Coulomb energy by means of Ewald sums became an important part of simulation technique and is widely used, specifically, in Monte Carlo (MC) studies of 3D Coulomb systems [2–4].

In recent years, a growing interest has been observed in the so-called quasi-two-dimensional (quasi-2D) Coulomb systems, i.e., the systems confined in one and infinite in the two other directions. Physical examples of such systems are strongly coupled charged colloidal suspensions geometrically confined in a thin layer between two plates, dusty plasmas trapped in one-dimensional potential profiles, electronical bilayers in semiconductors, etc. The interest in studying these systems was inspired by experimental and computational observations of various spatial structures, in particular, hexatic phase in 2D melting transition [5–10].

Apparently, in computer simulations of quasi-2D systems, the problem of accurate evaluation of the Coulomb energy persists. In this case the periodic boundary conditions have to be imposed only in two dimensions, which makes the conventional 3D Ewald sums inapplicable. However, in spite of great interest and a large number of works on quasi-2D Coulomb systems, this point seems to have been poorly mentioned in the literature. The goal of the present work is to consider this problem, i.e., to obtain relevant expressions for a quasi-2D case and to illustrate their accuracy by numerical examples.

Let us examine a one-dimensionally (along Z axis) confined Coulomb system. Following the treatment conventional for computer (say, MC) simulations, we consider a finite rectangular cell (of a size $L_x=L_y=L$, $L_z=H$) with a finite number N of particles such that the total charge in the cell is equal to zero. In quasi-2D case the cell is assumed to periodically repeat itself in XY directions to infinity. The problem is to evaluate the Coulomb energy for a given configuration $\{\mathbf{r}_i\}$ of particles

$$V_{Coul}=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{m}}^{\infty}{}' \frac{Q_iQ_j}{|\mathbf{r}_i-\mathbf{r}_j+L\mathbf{m}|} \tag{1}$$

taking account of the interactions with the infinite array of repeating cells. Here the two-dimensional vector $\mathbf{m}$ with the integer components $m_x=0,\pm1,\ldots,\pm\infty$; $m_y=0,\pm1,\ldots,\pm\infty$ enumerates the cells in the array; Q_i and $\mathbf{r}_i=(x_i,y_i,z_i)$ are the charge and the radius vector of the ith particle, and the prime sign at the sum means that the term with $i=j$ and $m_x=m_y=0$ should be omitted.

Following the ideas conventional for derivation of 3D Ewald sums, we consider each particle being surrounded by two oppositely charged clouds with Gaussian density distributions, so that they compensate one another. The relevant charge density in the basic cell can be written in the form $\rho(\mathbf{r})=\rho_1(\mathbf{r})+\rho_2(\mathbf{r})$, where

$$\rho_1(\mathbf{r})=\sum_{i=1}^{N} Q_i\delta(\mathbf{r}-\mathbf{r}_i)-\frac{\alpha^3}{\pi^{3/2}}\sum_{i=1}^{N} Q_i\exp[-\alpha^2(\mathbf{r}-\mathbf{r}_i)^2], \tag{2}$$

$$\rho_2(\mathbf{r})=\frac{\alpha^3}{\pi^{3/2}}\sum_{i=1}^{N} Q_i\exp[-\alpha^2(\mathbf{r}-\mathbf{r}_i)^2]. \tag{3}$$

Here α is the so-called splitting parameter that determines the relative contributions to the energy in the coordinate and inverse spaces. Let us consider the potential produced by a given configuration of particles. The contribution stemming from the density $\rho_1(\mathbf{r})$ in the basic cell remains the same as in 3D case

$$\phi_1(\mathbf{r})=\sum_{i=1}^{N}\frac{Q_i\,\mathrm{erfc}(\alpha|\mathbf{r}-\mathbf{r}_i|)}{|\mathbf{r}-\mathbf{r}_i|}. \tag{4}$$

Since the splitting parameter is usually chosen so that $\alpha L\simeq 3$–5, the potential decreases with the distance rapidly enough and the associated potential energy in the coordinate space with regard to repeating cell images can be calculated by restricting the relevant sum by the adjacent cells only

$$V_{dir}=\frac{1}{2}\sum_{i}^{N}\sum_{j}^{N}\sum_{|m_x|,|m_y|\leqslant 1}{}' \frac{Q_iQ_j\,\mathrm{erfc}(\alpha|\mathbf{r}_i-\mathbf{r}_j+L\mathbf{m}|)}{|\mathbf{r}_i-\mathbf{r}_j+L\mathbf{m}|}. \tag{5}$$

Here the sums are taken only over those particles in adjacent cells, for which the difference in any of three coordinates does not exceed certain maximal cutoff length L_{max}. In most of the cases, a nearest image (NI) approximation with $L_{max}=L/2$ is used. Up to this point, our considerations were quite similar to those exploited by the derivation of conventional 3D Ewald sums. The difference emerges, as we consider the contributions stemming from the charge density $\rho_2(\mathbf{r})$ responsible for the long-range part of interactions. In quasi-2D case, to allow for the periodicity in XY directions, we have to use 2D Fourier transformations

$$\rho_2(\mathbf{r})=\sum_{\mathbf{q}}\tilde{\rho}_2(\mathbf{q},z)e^{-i\mathbf{q}\cdot\mathbf{u}}, \tag{6}$$

$$\phi_2(\mathbf{r})=\sum_{\mathbf{q}}\tilde{\phi}_2(\mathbf{q},z)e^{-i\mathbf{q}\cdot\mathbf{u}}, \tag{7}$$

where the Fourier transform $\tilde{\rho}_2(\mathbf{q},z)$ can be found directly, by

$$\tilde{\rho}_2(\mathbf{q},z)=\frac{1}{L^2}\int\rho_2(\mathbf{r})d^2\mathbf{u}=\frac{\alpha}{\pi^{1/2}L^2}e^{-q^2/4\alpha^2}\times\sum_i\exp[-\alpha^2(z-z_k)^2]e^{i\mathbf{q}\cdot\mathbf{u}_k}. \tag{8}$$

Here we introduced a two-dimensional radius vector $\mathbf{u}=(x,y)$. The integration is taken over the cell section at a given coordinate z with allowance for periodically repeating charge densities. The summations in Eqs. (6) and (7) are taken over the discrete set of two-dimensional wave vectors $\mathbf{q}=2\pi\mathbf{n}/L$ (with $\mathbf{n}$ being a 2D integer wave number), which automatically provides the allowance for the periodicity.

The unknown potential amplitudes $\tilde{\phi}_2(\mathbf{q},z)$ have to be found from the equation

$$\frac{d^2\tilde{\phi}_2(\mathbf{q},z)}{dz^2}-\mathbf{q}^2\tilde{\phi}_2(\mathbf{q},z)=-4\pi\tilde{\rho}_2(\mathbf{q},z), \tag{9}$$

which is the consequence of the Poisson equation for the potential $\phi_2(\mathbf{r})$ in the coordinate space. Now our goal will be to solve the boundary problem (9) with the boundary conditions $\tilde{\phi}_2(\mathbf{q},\pm\infty)\leqslant$const. To this end, we use the Green function technique. The relevant Green function for the problem (9) in the case that $\mathbf{q}\neq\mathbf{0}$ reads (see, for instance, [11]) $\mathcal{G}(z,z')=-e^{-q|z-z'|}/2q$ and, therefore, the solution is

$$\begin{aligned}\tilde{\phi}_2(\mathbf{q},z)&=-4\pi\int dz'\mathcal{G}(z,z')\tilde{\rho}_2(\mathbf{q},z')\\&=\frac{\pi}{L^2}\sum_k\frac{Q_i}{q}\left\{e^{q\Delta z_k}\,\mathrm{erfc}\left(\frac{q}{2\alpha}+\alpha\Delta z_k\right)\right.\\&\left.+e^{-q\Delta z_k}\,\mathrm{erfc}\left(\frac{q}{2\alpha}-\alpha\Delta z_k\right)\right\}e^{i\mathbf{q}\cdot\mathbf{u}_k},\end{aligned} \tag{10}$$

where $\Delta z_k=z-z_k$. The corresponding contribution to the potential $\phi_2(\mathbf{r})$ is given by Eq. (7), which leads to the following expression for the contribution to the configurational energy in the inverse space:

$$V_{inv}=\frac{\pi}{L^2}\sum_{i}^{N}\sum_{j}^{N}\sum_{|\mathbf{q}|\neq 0}\frac{Q_iQ_j}{q}e^{qz_{ij}}\,\mathrm{erfc}\left(\frac{q}{2\alpha}+\alpha z_{ij}\right)\times\cos(\mathbf{q}\cdot\mathbf{u}_{ij}). \tag{11}$$

Here we introduced the notation $z_{ij}=z_i-z_j$ and $\mathbf{u}_{ij}=\mathbf{u}_i-\mathbf{u}_j$, and took into account the invariance of the total sum with respect to transpositions $z_{ij}\rightarrow-z_{ij}$.

In contrast to the 3D case, we have to take into account the wave vector $\mathbf{q}=\mathbf{0}$. This is due to the fact that the total charge of a cell section at a given coordinate z is, in general, not equal to zero. It means that the total two-dimensional charge neutrality (at given z) does not hold and the contributions from the zeroth Fourier component have to be taken into account. This particular case should be treated separately, since the Green function for the problem (9) for $q=0$ is essentially different, $\mathcal{G}_0(z,z')=|z-z'|/2$. Note, that this Green function is just the solution to the Poisson equation for a charged plane placed at $z=z'$. The calculations quite similar to those carried out above yield

$$V_{0,inv}=-\frac{\sqrt{\pi}}{\alpha L^2}\sum_{i,j}Q_iQ_j[e^{-\alpha^2z_{ij}^2}+\alpha z_{ij}\sqrt{\pi}\,\mathrm{erf}(\alpha z_{ij})]. \tag{12}$$

Finally, we have to take into account one more term (self-energy) arising due to the spurious interaction between a particle and its Gaussian cloud. The associated energy contribution, $V_{self}=\alpha\Sigma_iQ_i^2/\sqrt{\pi}$ does not differ from the one entering usual 3D Ewald sums and has to be substracted from the expression for the total potential energy. Thus, the final expression for the Coulomb energy reads

$$V_{Coul}=V_{dir}+V_{inv}+V_{0,inv}-V_{self} \tag{13}$$

with the quantities entering this relation being determined by Eqs. (5), (11), and (12).

It is worth mentioning that in a strictly 2D case the expressions (11) and (12) essentially simplify: $V_{0,inv}=0$,

$$V_{inv}=\frac{\pi}{L^2}\sum_i\sum_j\sum_{|\mathbf{q}|\neq 0}\frac{Q_iQ_j}{q}\,\mathrm{erfc}\left(\frac{q}{2\alpha}\right)\cos(\mathbf{q}\cdot\mathbf{u}_{ij}), \tag{14}$$

and do not exceed in complexity the conventional 3D Ewald sums.

TABLE I. Direct calculation of the Coulomb energy by Eq. (1) for the given configuration with allowance for subsequently increasing number of image cells. The quantity N_{cell} determines the number of terms in the sum (1) as $-N_{cell} \leqslant m_\sigma \leqslant N_{cell}$, where $\sigma = x,y$. For comparison, the Coulomb energy calculated within the NI approximation in Eq. (1) is $V_{Coul} = -363.124\,087$.

N_{cell}	1	10	50	100	500	1000
V_{Coul}	−274.708939	−268.609542	−268.518336	−268.508698	−268.501015	−268.500056

For practical applications, it is important to have an idea of how fast the series obtained above converge and what accuracy can be achieved with reasonable computational efforts. For this purpose, we performed a number of numerical tests of relations (5), (11), and (13). The tests were performed for a number of configurations generated at random for various numbers of particles, charge asymmetry and the ratio H/L. For illustration, we present below the results for one random configuration with the following parameters: $H = L = 1$, with the number and charge of particles being $N_{[1]} = 10$, $Q_{[1]} = +5$; and $N_{[2]} = 50$, $Q_{[2]} = -1$ (the subscripts denote here the species of particles).

In Table I we give the results of direct calculations of the Coulomb energy by Eq. (1) with subsequently increasing dimension of the array of image cells up to 1000. The results of tests of the relations (5), (11), and (13) for the range of splitting parameter $\alpha = 3$–6 are displayed in Table II.

As can be seen from the results, the sums in inverse space converge rather fast due to the presence of the functions $\mathrm{erfc}(q/2\alpha)$. In particular, to provide the accuracy 10^{-4} in calculations of the Coulomb energy, it is sufficient to use a rather small number of wave vectors ($n_{max} = 5, \alpha = 5$), along with the NI approximation in the coordinate space. This behavior was observed for all the configurations that were

TABLE II. Contributions (5), (11), and the Coulomb energy of the given configuration calculated by Eq. (13) as a function of the splitting parameter α and the maximal wave number n_{max}, which determines the number of terms in the sum (11) as $-2\pi n_{max}/L \leqslant q_\sigma \leqslant 2\pi n_{max}/L$, where $\sigma = x,y$. The quantities marked "NI" relate to the NI approximation in the coordinate space, and those marked * are calculated with the cutoff length $L_{max} = L$ in Eq. (5).

α	V_{dir}^{NI}	V_{dir}^{*}	n_{max}	V_{inv}	V_{Coul}^{NI}	V_{Coul}^{*}
3.0	−31.1768146	−31.6876391	1	269.949426	−268.998013	−269.508838
			2	270.943437	−268.004002	−268.514826
			3	270.946481	−268.000958	−268.511782
			4	270.946482	−268.000957	−268.511781
			5	270.946482	−268.000957	−268.511781
4.0	5.64433550	5.56611942	1	389.904282	−281.478882	−281.557098
			2	402.521717	−268.861447	−268.939663
			3	402.958839	−268.424324	−268.502540
			4	402.962275	−268.420889	−268.499105
			5	402.962281	−268.420883	−268.499099
			6	402.962281	−268.420883	−268.499099
5.0	29.2064988	29.2005568	1	497.983188	−319.094688	−319.100630
			2	543.501801	−273.576074	−273.582016
			3	548.411359	−268.666517	−268.672459
			4	548.582217	−268.495658	−268.501600
			5	548.584705	−268.493171	−268.499113
			6	548.584728	−268.493148	−268.499090
			7	548.584728	−268.493148	−268.499090
6.0	41.9930802	41.9928351	1	587.314242	−386.233927	−386.234173
			2	683.892901	−289.655268	−289.655513
			3	703.395722	−270.152447	−270.152692
			4	704.975162	−268.573007	−268.573253
			5	705.046733	−268.501436	−268.501682
			6	705.049248	−268.498922	−268.499167
			7	705.049324	−268.498845	−268.499090
			8	705.049325	−268.498844	−268.499090

tested. It should be pointed out that a much higher accuracy 10^{-7} with smaller number of terms in the inverse space ($n_{max}=4$, $\alpha=4$) can be obtained by taking the cutoff parameter in coordinate space $L_{max}=L$ in Eq. (5), rather than NI approximation.

To conclude, we have obtained explicit expressions for the Coulomb energy in infinite quasi-2D systems in the form of fast converging Ewald sums in 3D coordinate and 2D inverse space needed for accurate formulation of periodic boundary conditions in computer simulations. Numerical tests evidence that the acceptable accuracy in the total energy is achieved by taking into account rather small number of terms in the sum for the inverse space responsible for the long-range part of the interaction.

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