Ewald sum for electronic bilayer systems

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The potential energy of a bilayer two-dimensional system of charges, subject to periodic boundary conditions, is derived. The technique of the Ewald sum has been employed so that the formulas can be applied directly in Monte Carlo and molecular-dynamics computer simulations. Numerical evaluation of the potential energy is carried out to confirm the parameter independence.

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I. INTRODUCTION

A bilayer system consisting of two two-dimensional layers of charges separated by a distance d comparable to the interparticle separation a (the Wigner-Seitz radius) within the layers has been a subject of recent experimental research [1]. There have been some theoretical investigations of such systems [2,3], but we are not aware of any exact study using molecular-dynamics (MD) or Monte Carlo (MC) computer simulations. For example, there are no exact results for the interlayer pair distribution function $g_{12}(r)$ or the intralayer pair distribution function $g_{11}(r)$, and these play an important role in any theoretical analysis of such a system.

Periodic boundary conditions are an essential feature of MD or MC computer simulation studies. They remove surface effects and enable a small number of particles to simulate a portion of an infinitely large system. However, Coulomb forces between charged particles, which fall off slowly as $1/r$, create a serious problem in computer simulations, since their range is greater than half of the box length for a typical simulation of a few hundred particles. The problem of long-range forces is usually tackled using the Ewald sum [4], a technique for efficiently summing the interaction of an ion with all its periodic images. It expresses the potential energy in terms of two convergent summations, one in real space and one in reciprocal-lattice space. The results of such an approach are in the existing literature and are widely used for three-dimensional [5] and single-layer two-dimensional [6,7] one-component plasmas. In this paper, we present the calculation and analysis of the Ewald sum for a bilayer system. Our formulas yield the appropriate potential and forces, under periodic boundary conditions and minimum imaging convention, and thus can be used in a MD or MC computer simulation study of such a system.

II. METHOD

The system consists of electrons obeying classical statistics, and charge neutrality is ensured by a uniform positive background. The electrons are distributed in two planes, separated by a constant distance, but each electron is constrained to move only in the plane of its original distribution. Let the planes be at $z=0$ and $z=d$. Consider square cells with side length L in each plane with basic cells centered at $(0,0,0)$ and $(0,0,d)$. Let there be N electrons in each cell with an identical distribution in every cell of a given plane; however, the distribution in the two planes may be different. Let the positions of the electrons in the planes $z=d$ and $z=0$ be $\vec{\rho}_i=(\tilde{x}_i,\tilde{y}_i,0)$ and $\vec{r}_i=(x_i,y_i,0)$, respectively, for i from 1 to N and let $\vec{d}=(0,0,d)$.

Let U denote the total potential energy of the two basic cells due to interactions of these electrons with all others; U takes into account the periodic boundary conditions and minimum imaging convention. It is, therefore, appropriate for computer simulations and can be written as $U=U_1+U_2+U_{12}$, where

$$U_1=\tfrac{1}{2}{\sum_{\vec{p}}}' \sum_{i=1}^{N}\sum_{j=1}^{N} \varphi(|\vec{r}_i-\vec{r}_j+\vec{p}|),$$

$$U_2=\tfrac{1}{2}{\sum_{\vec{p}}}' \sum_{i=1}^{N}\sum_{j=1}^{N} \varphi(|\vec{\rho}_i-\vec{\rho}_j+\vec{p}|), \tag{1}$$

$$U_{12}=\sum_{\vec{p}} \sum_{i=1}^{N}\sum_{j=1}^{N} \varphi(|\vec{\rho}_i-\vec{r}_j+\vec{p}+\vec{d}|).$$

The sum over $\vec{p}$ is a sum over integers μ_1,μ_2 with $\vec{p}=L(\mu_1,\mu_2)$; the prime on this sum indicates that if $i=j$, the $\vec{p}=\vec{0}$ term is to be omitted, and $\varphi(r)=e^2/r$ is the Coulomb potential with r subjected to the minimum imaging convention.

A. Review of single-layer system

The potential U_1 which involves electrons in one plane has been treated by the Ewald method. We will review the pertinent details here for completeness, and as a precursor to our solution of the bilayer problem. We use dimensionless quantities: distances in units of the Wigner-Seitz radius a and energies in units of e^2/a.

The potential energy due to interaction between two particles and their images in the same layer is

$$v(r_{ij})=\sum_{\vec{p}}\frac{1}{|\vec{r}_i-\vec{r}_j+\vec{p}|}\{\mathrm{erfc}(\alpha|\vec{r}_i-\vec{r}_j+\vec{p}|)+\mathrm{erf}(\alpha|\vec{r}_i-\vec{r}_j+\vec{p}|)\} \tag{2}$$

for any $\alpha>0$. The second term has two-dimensional period L and a Fourier series of the form $\Sigma_{\vec{g}}B(g;\alpha)e^{i\vec{g}\cdot(\vec{r}_i-\vec{r}_j)}$ with $\vec{g}=2\pi(\lambda_1,\lambda_2)/L$ and $g=|\vec{g}|$, where λ_1,λ_2 are integers, and

$$\begin{aligned}B(g;\alpha)&=\frac{1}{L^2}\int\int d\vec{r}\frac{\mathrm{erf}(\alpha r)}{r}e^{-i\vec{g}\cdot\vec{r}}\\&=\frac{1}{L^2}\int_0^\infty dr\,\mathrm{erf}(\alpha r)2\pi J_0(gr)\\&=\frac{2\pi}{L^2}\frac{\mathrm{erfc}(g/2\alpha)}{g}\quad\text{if } g\neq 0,\end{aligned} \tag{3}$$

$$B(0;\alpha)=\frac{2\pi}{L^2}\lim_{g\to 0}\frac{\mathrm{erfc}(g/2\alpha)-1}{g}=-\frac{2\sqrt{\pi}}{L^2\alpha}. \tag{4}$$

The potential energy per cell is then

$$U_1=\frac{1}{2}{\sum_{\vec{p}}}'\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\mathrm{erfc}(\alpha|\vec{r}_i-\vec{r}_j+\vec{p}|)}{|\vec{r}_i-\vec{r}_j+\vec{p}|}-N(N-1)\frac{\sqrt{\pi}}{L^2\alpha}+\frac{\pi}{L^2}\sum_{\vec{g}\neq\vec{0}}\frac{\mathrm{erfc}(g/2\alpha)}{g}\left(\sum_{i=1}^{N}\sum_{j=1}^{N}\cos[\vec{g}\cdot(\vec{r}_i-\vec{r}_j)]-N\right), \tag{5}$$

with the Madelung energy term omitted. The parameter α is to be chosen so that both series in Eq. (5) converge rapidly; it is essential that the value of U_1 be independent of the choice of α. We made a careful numerical study of this requirement as described in Sec. III. Note that the second term will not contribute to the force.

If α is large enough, the only term that contributes to the sum in the real space is that with $\vec{p}=\vec{0}$, so it reduces to the normal minimum image convention. However, a large value of α would imply a large number of terms in the reciprocal space sum. In a simulation, the aim is to choose a value of α and a sufficient number of g vectors, so that the real-space sum can be truncated after $\vec{p}=\vec{0}$ and the g series converges rapidly. It should be kept in mind that the larger the number of g vectors, the larger is the time required to compute the forces on each of the electrons. Thus a compromise between the time required for a simulation and the accuracy may be necessary.

B. Two-layer system

The potential energy per unit cell due to the interactions between charges in different planes is given by

$$U_{12}=\sum_{\vec{p}}\sum_{i=1}^{N}\sum_{j=1}^{N}\times\frac{\mathrm{erfc}(\kappa|\vec{\rho}_i-\vec{r}_j+\vec{d}+\vec{p}|)+\mathrm{erf}(\kappa|\vec{\rho}_i-\vec{r}_j+\vec{d}+\vec{p}|)}{|\vec{\rho}_i-\vec{r}_j+\vec{d}+\vec{p}|} \tag{6}$$

for any $\kappa>0$. The second term is periodic with two-dimensional period L, and it has a Fourier series of the form

$$\sum_{\vec{g}}C(g;\kappa,d)\sum_{i=1}^{N}\sum_{j=1}^{N}e^{i\vec{g}\cdot(\vec{\rho}_i-\vec{r}_j)}.$$

The coefficients for $g\neq 0$ are

$$\begin{aligned}C(g;\kappa,d)&=\frac{1}{L^2}\int_0^\infty dr\,r\frac{\mathrm{erf}(\kappa\sqrt{r^2+d^2})}{\sqrt{r^2+d^2}}\int_0^{2\pi}d\theta\,e^{-igr\cos\theta}\\&=\frac{2\pi}{L^2}\int_0^\infty dr\frac{r}{\sqrt{r^2+d^2}}\mathrm{erf}(\kappa\sqrt{r^2+d^2})J_0(gr)\\&\equiv\frac{2\pi}{L^2}\psi(g;\kappa,d).\end{aligned} \tag{7}$$

The $g=0$ term is important and must be treated carefully; it requires evaluation of $\lim_{g\to 0}[g\psi(g;\kappa,d)-1]/g$. This is done by reversing the order in a double integral and expanding to first order in g:

$$\begin{aligned}g\psi(g;\kappa,d)&=\int_0^\infty dt\frac{t}{\sqrt{t^2+d^2g^2}}J_0(t)\frac{2}{\sqrt{\pi}}\int_0^{(\kappa/g)\sqrt{t^2+d^2g^2}}du\,e^{-u^2}\\&=\frac{2}{\sqrt{\pi}}\int_0^{\kappa d}du\,e^{-u^2}\int_0^\infty dt\frac{tJ_0(t)}{\sqrt{t^2+d^2g^2}}\\&\quad+\frac{2}{\sqrt{\pi}}\int_{\kappa d}^\infty du\,e^{-u^2}\int_{(g/\kappa)\sqrt{u^2-\kappa^2d^2}}^\infty dt\frac{tJ_0(t)}{\sqrt{t+d^2g^2}}\\&=e^{-dg}-\frac{2}{\sqrt{\pi}}\int_{\kappa d}^\infty du\,e^{-u^2}\int_0^{(g/\kappa)\sqrt{u^2-\kappa^2d^2}}dt\frac{tJ_0(t)}{\sqrt{t^2+d^2g^2}}\\&=1-dg-\frac{2}{\pi}\int_{\kappa d}^\infty du\\&\quad\times e^{-u^2}\left(\sqrt{\frac{g^2}{\kappa^2}(u^2-\kappa^2d^2)-d^2g^2}-dg\right)J_0(0)+\cdots\\&=1-dg-\frac{2}{\sqrt{\pi}}\int_{\kappa d}^\infty du\,e^{-u^2}\left(\frac{u}{\kappa}-d\right)g+\cdots\\&=1-dg-\left(\frac{1}{\sqrt{\pi}\kappa}e^{-\kappa^2d^2}-d\,\mathrm{erfc}(\kappa d)\right)g+\cdots.\end{aligned} \tag{8}$$

Thus,

$$\lim_{g\to 0}\frac{g\psi(g;\kappa,d)-1}{g}=-d\,\mathrm{erf}(\kappa d)-\frac{1}{\sqrt{\pi}\kappa}e^{-\kappa^2 d^2}. \quad (9)$$

Using Eqs. (7) and (9), the final result for the potential energy due to interactions between the layers is obtained:

$$U_{12}=\sum_{\vec{p}}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\mathrm{erfc}(\kappa|\vec{\rho}_i-\vec{r}_j+\vec{d}+\vec{p}|)}{|\vec{\rho}_i-\vec{r}_j+\vec{d}+\vec{p}|}-N^2\frac{2\pi}{L^2}\left(d\,\mathrm{erf}(\kappa d)+\frac{e^{-\kappa^2 d^2}}{\sqrt{\pi}\kappa}\right)+\frac{2\pi}{L^2}\sum_{\vec{g}\neq\vec{0}}\psi(g;\kappa,d)\sum_{i=1}^{N}\sum_{j=1}^{N}\cos[\vec{g}\cdot(\vec{\rho}_i-\vec{r}_j)]. \quad (10)$$

The corresponding single-layer formula (5) can be recovered from this by setting $d=0$, removing $i=j$ terms in the sums and counting only N particles. Comparing with the single-layer result, it should be noted that while the real-space terms look alike, the reciprocal-space terms are quite different and not a simple or obvious extension of the single-layer formula. The second term in Eq. (10) does not contribute to the force. Equation (10) and the corresponding force equation [given in Eq. (11)] are new results and provide an algorithm for a computer simulation of a bilayer system of charged particles.

III. NUMERICAL RESULTS

The single-layer expression (5) for U_1 was evaluated numerically in the following way.

(i) Choose the side length of the basic cell (we took $L=20.2$), some initial configuration of N particles in it (we used 128), and a value of α. The value of L corresponds to an areal density $n^{\star}\equiv na^2=1/\pi$.

(ii) Evaluate the three terms of Eq. (5) and their sum.

(iii) Repeat for other values of α, and then for other configurations. Excellent agreement confirming the α independence of the results was obtained. Figure 1 shows the terms of U_1 as a function of α for $\alpha L\in[5,16]$ for a certain configuration. Only the $\vec{p}=\vec{0}$ terms were included in the r-space term together with the minimum image convention. In the g-space term, we took the largest length of $\vec{\lambda}$, where $\vec{g}=2\pi\vec{\lambda}/L$, to be $\sqrt{45}$. The agreement of the sum is excellent: in fact all αL in [6,16] give $U_1=-127.235\mp 0.002$. This analysis was done for various configurations and for other equilibrium configurations corresponding to a fixed temperature.

The importance of the self-term is evident. Since the r-space terms contain α, the accuracy of these results justifies neglect of the $\vec{p}\neq\vec{0}$ terms there. The graphs suggest that a choice of αL between 8 and 12 would be practical for molecular-dynamics calculations: a smaller α is preferred, since it requires fewer terms in the g-space sum.

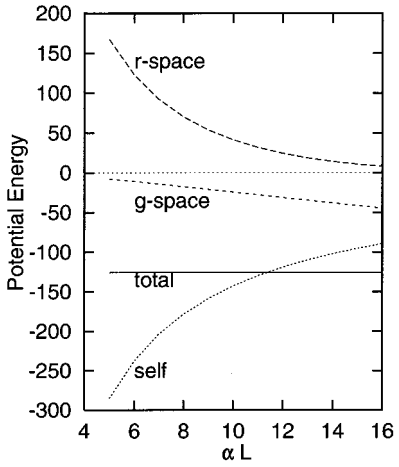

FIG. 1. Dependence of the potential-energy terms for a single-layer system on αL; both quantities are dimensionless.

The same type of study was performed to confirm the correctness of expression (10) for the potential due to interactions between two layers. We considered two separation distances: $d=1$ (equal to the Wigner-Seitz radius) and $d=0.5$. We used $L=20.2$ with 128 particles in each basic cell; different configurations were selected in the two planes. Calculations of the terms in U_{12} were performed for four values of the parameter κ; again we used $\vec{p}=\vec{0}$ with minimum image in the r-space term. For the g-space term, the integrals denoted by $\psi(g;\kappa,d)$ in Eq. (7) were evaluated as required for $|\vec{\lambda}|\leqslant\sqrt{45}$. Results for a typical bilayer configuration are given in Table I. The agreement for the total potential using four values of κ is excellent here, as it is for other configurations. Again, the importance of the self-term is evident and neglect of $\vec{p}\neq\vec{0}$ terms is justified. Admittedly, the g-space terms are small for the chosen configurations; however, the magnitudes of the forces arising from these terms are significant, and the κ independence of the total force has also been checked. We also checked the κ independence for other equilibrium configurations.

TABLE I. Dependence of potential-energy terms for a bilayer system on the parameter κ; all quantities in dimensionless units as defined.

d	κL	U_{12} (r space)	U_{12} (g space)	U_{12} (self)	U_{12}
0.5	6	360.1994	0.1035	−489.7370	−129.4341
0.5	8	243.8308	0.1464	−373.4060	−129.4289
0.5	10	175.3547	0.1810	−304.9620	−129.4263
0.5	15	87.8669	0.2474	−217.5158	−129.4016
1.0	6	268.0724	0.1002	−520.8738	−252.7012
1.0	8	161.5103	0.1395	−414.3475	−252.6976
1.0	10	102.3801	0.1679	−355.2451	−252.6970
1.0	15	35.7422	0.2167	−288.6396	−252.6808

IV. CONCLUSION

The correctness of Eq. (10) having been confirmed, one can now use Eqs. (1), (5), and (10) to obtain the total force on a particle due to particles in the same plane and in the other plane. For example, the result for particle 1 in plane $z=0$ is

$$\begin{aligned}\vec{F}(\vec{r}_i) &= -\nabla_{\vec{r}_1}(U_1+U_{12}) \\ &= \frac{2\pi}{L^2}\sum_{\vec{g}\neq\vec{0}}\vec{g}\left\{\frac{1}{g}\mathrm{erfc}\left(\frac{g}{2\alpha}\right)\sum_{j=2}^{N}\sin\vec{g}\cdot(\vec{r}_1-\vec{r}_j)\right. \\ &\quad \left.+\psi(g;\kappa,d)\sum_{j=1}^{N}\sin\vec{g}\cdot(\vec{r}_1-\vec{\rho}_j)\right\}+\sum_{\vec{p}}{}' \\ &\quad \sum_{j=1}^{N}\frac{\vec{s}_{ij}}{|\vec{s}_{1j}|^3}\left\{\mathrm{erfc}(\alpha|\vec{s}_{1j}|)+\alpha|\vec{s}_{ij}|\frac{2}{\sqrt{\pi}}e^{-\alpha^2|\vec{s}_{ij}|^2}\right\} \\ &\quad +\sum_{\vec{p}}\sum_{j=1}^{N}\frac{\vec{d}_{1j}}{|\vec{d}_{1j}|^3} \\ &\quad \times\left\{\mathrm{erfc}(\kappa|\vec{d}_{1j}|)+\kappa|\vec{d}_{1j}|\frac{2}{\sqrt{\pi}}e^{-\kappa^2|\vec{d}_{1j}|^2}\right\}, \qquad (11)\end{aligned}$$

where $\vec{s}_{1j}=\vec{r}_1-\vec{r}_j+\vec{p}$ and $\vec{d}_{1j}=\vec{r}_1-\vec{\rho}_j+\vec{d}+\vec{p}$.

These results suggest that a good choice of the parameters α and κ is $8/L$. Further work has shown that for this choice, acceptable accuracy can be obtained using $\sqrt{20}$ for the largest $|\vec{\lambda}|$; this corresponds to taking 38 terms in the g-space sums in the expressions for potential energy and the forces on the particles. At each instant considered in a dynamics calculation, the force acting on each of $2N$ particles must be computed: its g-space component contains $2N-1$ terms for every vector $\vec{g}$ included. Obviously, it is important to keep the maximum g as small as possible.

This paper was prompted by a need for molecular-dynamics calculations for an interacting bilayer plasma at different separations. We now have the appropriate expressions for the potential energy and forces required for such a study. Multilayer systems can also be studied using generalizations of these formulas.

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