Dealing with Long-Range Electrostatic Interactions
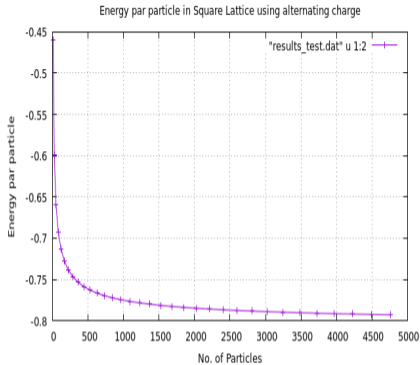## Ewald Summation

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- We consider N classical point particles in a two-dimensional box.
- Particles interact via $\frac{1}{r}$ Coulomb potential.
- Coulomb interaction does not decay within half the lattice distance, unlike short-range interactions.
- Long-range nature prohibits the use of a cutoff distance for accuracy.
- Large number of particles required, demanding significant computational power.

The interaction energy arising from the Coulomb interaction between the particles is expressed as:
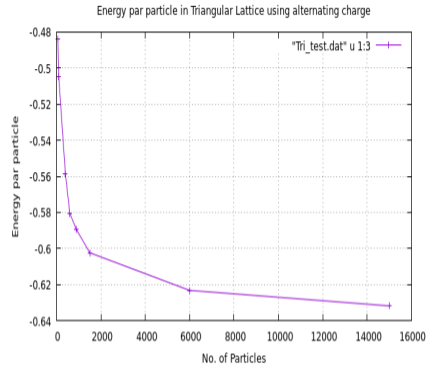
$$E = \frac{1}{4\pi\epsilon_0} \sum_{i,j}^{N}{}' \frac{q_i q_j}{|r_i - r_j|} \tag{1}$$

where the prime on the sum indicates that $i \neq j$.

- We must use alternating charge convention or a charge-neutralizing uniform background to maintain charge neutrality in the system. In the thermodynamic limit, this prevents the system energy from diverging.
- Consequently, the sum in Eq. 1 is identified as a conditionally convergent sum.
- To understand the convergence problem, we calculated pair-wise distances between all particles to simulate square and triangular lattices (Fig. 1) under fixed density condition ($\rho = 1$).
- The energy per particle in these systems should ideally converge to a fixed energy value known as the **Madelung** Energy value of the lattice.

Figura 1: Energy per particle in (a) square lattice and (b) triangular lattice

The sum converges very slowly to the Madelung constant values of the lattice. For example, the Madelung constant value for the triangular lattice is $M_C \sim -1.9605$.

Convergence of Ewald Summation

Convergence

Ewald summation method aims to compute electrostatic potentials and forces in periodic systems. The real-space and Fourier-space parts of the Ewald sum converge absolutely.

Conditional Convergence

The direct Coulomb sum of the alternating charges is conditionally convergent.

Example

Consider the series:

$$\sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n}$$

This is the alternating harmonic series, which is conditionally convergent.

Eliminating Boundary Effects

- To eliminate boundary effects, we must consider the bulk thermodynamic limit.
- Conventionally, this is achieved by replicating the unit cell configuration into image cells and surrounding the main unit cell with these image cells.
- This technique preserves both the translational and rotational symmetries.

$$E = \frac{1}{4\pi\epsilon_0} \sum_{\mathbf{n}} \sum_{i,j}^{N}{}' \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n} \cdot \mathbf{L}|} \tag{2}$$
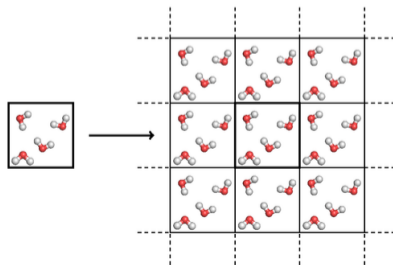
- The unit cell is denoted as layer zero, with other layers representing image cells around the unit cell. Layer L contains a total of $2L(L+1)$ image cells.
- Despite using this method to eliminate boundary effects, the convergence of the energy value per particle to the Madelung constant is slow.
- Additionally, the computational cost is very high due to the large number of image cells required.
- To achieve the required accuracy of error order $\mathcal{O}(10^{-4})$, a very large number of particles is necessary.

Convergence Acceleration Methods:

- Ewald summation
- Multipole method
- NEFT-based algorithm (Newly Developed)

Ewald summation, developed by Paul Peter Ewald, is a convergence acceleration technique where we divide the sum into two parts introducing a foreign function as the coefficient. This technique also ensures the sum to be absolutely convergent.

$$\sum \frac{1}{|\mathbf{r}|} = \sum \frac{f(\mathbf{r})}{|\mathbf{r}|} + \sum \frac{1 - f(\mathbf{r})}{|\mathbf{r}|} \tag{3}$$

Now, we suitably choose a rapidly decreasing function as $f(\mathbf{r})$ which decreases faster than the increment of the $\frac{1}{|\mathbf{r}|}$ function with respect to $\mathbf{r}$. The most used function for this case is the complementary error function denoted by $\mathrm{erf}_c(r) = 1 - \mathrm{erf}(r)$ with the expression for the error function as

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt.$$

Then we evaluate one part in real space and another part in Fourier space.

The Coulomb potential for a single unit positive charge is:

$$\phi(r) = \frac{1}{r} \tag{4}$$

This function has two important properties:

- For very small $r \to 0$, the potential goes to extreme high values, indeed becomes positive infinity at $r = 0$.
- On the other hand, it diminishes at a slow rate for large r, prohibiting the implementation of any cutoff radius due to a large amount of truncation error.

To handle this, we break up the potential into two parts, each following one property exclusively:

$$\phi(r) = \phi^{\text{short}}(r) + \phi^{\text{long}}(r) \tag{5}$$

For a given window function $W(r)$ which is unity for small r but falls rapidly to zero for large r, the two functions $\phi^{\text{short}}(r)$ and $\phi^{\text{long}}(r)$ can be expressed as:

$$\phi^{\text{short}}(r) = W(r)\phi(r)$$
$$\phi^{\text{long}}(r) = [1 - W(r)]\phi(r)$$

Hence, the potential energy contribution:

$$\Phi^{\text{short}}(r) = \sum_n \phi^{\text{short}}(|\vec{r} - \vec{r}_n|) \tag{6}$$

$$\Phi^{\text{long}}(r) = \sum_n \phi^{\text{long}}(|\vec{r} - \vec{r}_n|) \tag{7}$$

where $n = (n_x, n_y, n_z)$ is a three-dimensional lattice vector.

Short-ranged and Long-ranged potentials

Short Ranged Potential Term ($\Phi^{\text{short}}(r)$)

- Decays rapidly with minimal contribution from large r.
- Evaluate sum in **real space** with high accuracy.

Long Ranged Potential Term ($\Phi^{\text{long}}(r)$)

- Does not converge in real space.
- Evaluate sum in **Fourier space**:

$$\tilde{\Phi}^{\text{long}}(\nu) = \sum_{\nu} \tilde{\phi}^{\text{long}}(\nu)$$

Here, ν is the Fourier variable conjugate to n.

Simultaneous use of real and Fourier spaces allows greater accuracy with fewer summation steps.

Error and Complementary Error Function

Gaussian Integral

The area under a Gaussian is represented as:

$$\int_{-\infty}^{\infty} e^{-t^2} dt = \sqrt{\pi}$$

We express the standard integral as:

$$\frac{2}{\sqrt{\pi}} \int_{0}^{\infty} e^{-t^2} dt = 1$$

By truncating the upper limit to a finite value x, we get the error function:

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} dt$$

The complementary error function is denoted as:

$$erfc(x) = 1 - erf(x)$$
$$= \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt$$

The error function rises rapidly to unity when x becomes large. On the other hand, the complementary error function steeply falls to zero for $x \to 0$. So the complementary error function $erfc(x)$ is a suitable choice for the window function $W(r)$.
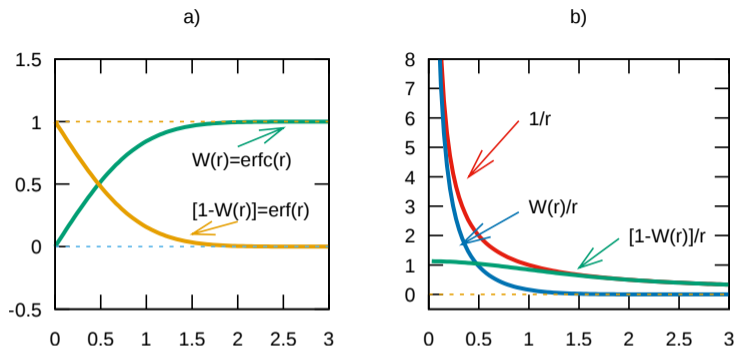
Figura 3: a) Yellow curve represents the error function and the green curve represents the complementary error function. b) Here the red curve denotes the slow falling of the Coulomb potential, the blue curve represents the short ranged potential term along with the green curve which represents the long ranged potential term.

We consider N point charges located at positions $r_1, r_2, \ldots, r_N$, each with charges $q_1, q_2, \ldots, q_N$ respectively.

The potential energy generated at position r by any ion at r_i due to its charge q_i is:

$$\phi_i(r) = \frac{q_i}{|r - r_i|},$$

while the total potential energy due to all ions is:

$$\phi(r) = \sum_{i=1}^{N} \frac{q_i}{|r - r_i|}.$$

Due to the long-range nature of Coulombic interaction, convergence of the total energy becomes problematic. To address this, we consider periodic image cells around the main unit cell for convergence acceleration. Under this situation, the potential field terms add up due to the contribution from the image charges and can be expressed as:

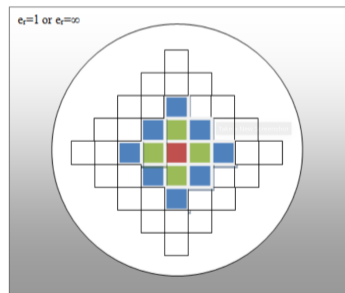$$\phi(r) = \sum_n \sum_{j=1}^{N} \frac{q_j}{|r - r_j + n \cdot L|}.$$

Figura 4: Construction of image cells in 2D

VIRGINIA TECH

In real situations, we do not consider the self-interaction term arising from the interaction of a point charge with itself.

We define the potential field generated by all charges excluding the self-contribution as:

$$\phi_{[i]}(r) \equiv \phi(r) - \phi_i(r) = \sum_n \sum_{j=1}^{N}{}' \frac{q_j}{|r - r_j + n \cdot L|}$$

where the $'$ symbol omits the term $j = i$ when $n = 0$.

The energy of the system is then given by:

$$E = \frac{1}{2} \sum_{i=1}^{N} q_i \phi_{[i]}(r_i)$$

We introduce a factor of $\frac{1}{2}$ to overcome the double counting contribution.

Charge Distribution and its Representation

We consider point charges situated at specific points in a three-dimensional lattice. These point charges can be represented by **delta functions** centered at the lattice points.

The charge density for a point charge q_i is given by:

$$\rho_i(r) = q_i \delta(r - r_i)$$

The Poisson equation relates the potential field generated by the charge density:

$$\nabla^2 \phi_i(r) = -\frac{\rho_i(r)}{\epsilon_0}$$

We can write the potential field in continuous notation as:

$$\phi_i(r) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho_i(r')}{|r - r'|} d^3 r'$$

Hence, the total potential field generated due to all charges, including image charges but excluding self-interaction, is written as:

$$\phi_{[i]} = \frac{1}{4\pi\epsilon_0} \sum_n \sum_{j=1}^{N} {}' \int \frac{\rho_j(r')}{|r - r' + n \cdot L|} d^3 r'$$

We can add and subtract a normal charge distribution at each point charge location without any loss of generality. So, we write the charge distribution as:

$$\rho_i(r) = q_i \left[\delta(r - r_i) - N(r - r_i, \sigma) \right] + q_i N(r - r_i, \sigma)$$
$$= \rho_i^S(r) + \rho_i^L(r)$$

Where $N(r - r_i, \sigma) = \frac{1}{(2\pi\sigma^3)^{\frac{3}{2}}} e^{-\frac{|(r-r_i)|^2}{2\sigma^2}}$ is the normal charge distribution with spread σ.

Note that $\lim_{\sigma \to 0} N(r, \sigma) = \delta(r)$.

We can split the potential fields as follows:

$$\phi_i(r) = \phi_i^S(r) + \phi_i^L(r)$$

$$\phi_i^S(r) = \frac{q_i}{4\pi\epsilon_0} \int \frac{\delta(r - r') - N(r - r', \sigma)}{|r - r'|} d^3 r'$$

$$\phi_i^L(r) = \frac{q_i}{4\pi\epsilon_0} \int \frac{N(r - r', \sigma)}{|r - r'|} d^3 r'$$

As we are interested in the potential field generated by ions excluding the self-interaction due to charge i, the potential field can be split as:

$$\phi_{[i]}(r) = \phi_{[i]}^S(r) + \phi_{[i]}^L(r)$$

This also leads to the splitting of the Coulomb interaction energy term, which is expressed in terms of potential field terms:

$$\begin{aligned}
E &= \frac{1}{2}\sum_{j=1}^{N} q_j \phi_{[i]}^S(r_i) + \frac{1}{2}\sum_{j=1}^{N} q_j \phi_{[i]}^L(r_i) \\
&= \frac{1}{2}\sum_{j=1}^{N} q_j \phi_{[i]}^S(r_i) + \frac{1}{2}\sum_{j=1}^{N} q_j \phi^L(r_i) - \frac{1}{2}\sum_{j=1}^{N} q_j \phi_i^L(r_i) \\
&= E^S + E^L + E^C
\end{aligned}$$

Gaussian Charge Distribution

The scalar field produced by the normal charge distribution satisfies the Poisson equation:

$$\nabla^2 \phi_N(r) = -\frac{N(r)}{\epsilon_0}$$

Assuming spherical symmetry, we write:

$$\frac{1}{r}\frac{\partial^2(r\phi_N(r))}{\partial r^2} = -\frac{1}{\epsilon_0(2\pi\sigma^3)^{\frac{3}{2}}}e^{-\frac{r^2}{2\sigma^2}}$$

$$\frac{\partial(r\phi_N(r))}{\partial r} = -\frac{1}{\epsilon_0(2\pi\sigma^3)^{\frac{3}{2}}}\int_r^{\infty}e^{-\frac{r^2}{2\sigma^2}}\,dr$$

$$= \frac{\sigma^2}{\epsilon_0(2\pi\sigma^3)^{\frac{3}{2}}}e^{-\frac{r^2}{2\sigma^2}}$$

$$r\phi_N(r) = \frac{\sigma^2}{\epsilon_0(2\pi\sigma^3)^{\frac{3}{2}}}\int_0^r e^{-\frac{r^2}{2\sigma^2}}\,dr$$

We have already noted that $erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$, which implies:

$$erf\left(\frac{r}{\sqrt{2}\sigma}\right) = \frac{2}{\sqrt{\pi}} \int_0^{\frac{r}{\sqrt{2}\sigma}} e^{-t^2} dt$$

Hence, we can write the potential generated due to Gaussian charges as:

$$\phi_N(r) = \sqrt{\frac{\pi}{2}} \frac{\sigma^2}{\epsilon_0 (2\pi\sigma^3)^{\frac{3}{2}} r} erf\left(\frac{r}{\sqrt{2}\sigma}\right)$$

$$\phi_N(|r - r_i|) = \frac{1}{4\pi\epsilon_0 |r - r_i|} erf\left(\frac{|r - r_i|}{\sqrt{2}\sigma}\right)$$

Short Ranged Interaction Term

We can write ϕ_i^S as:

$$\phi_i^S(r - r_i) = \frac{q_i}{4\pi\epsilon_0} \frac{1}{|r - r_i|} \left[1 - erf\left(\frac{|r - r_i|}{\sqrt{2}\sigma} \right) \right]$$

$$= \frac{q_i}{4\pi\epsilon_0} \frac{1}{|r - r_i|} erfc\left(\frac{|r - r_i|}{\sqrt{2}\sigma} \right)$$

$$= \frac{q_i}{4\pi\epsilon_0} \frac{1}{|r - r_i|} erfc\left(\alpha|r - r_i| \right)$$

Where $\boxed{\alpha = \frac{1}{\sqrt{2}\sigma}}$.

$$\phi_i^L(r - r_i) = \frac{q_i}{4\pi\epsilon_0} \frac{1}{|r - r_i|} erf\left(\alpha|r - r_i| \right)$$

The short-ranged potential term converges fast when image cells are considered together. Now, we can also write the contribution of all charges, including the image cells, as:

$$\phi_{[i]}^{S}(r - r_i) = \frac{1}{4\pi\epsilon_0} \sum_n \sum_{j=1}^{N} \frac{q_j}{|r - r_i + n.L|} erfc\left(\alpha|r - r_i + n.L|\right)$$

The energy contribution for this term is:

$$E^S = \frac{1}{2} \sum_{i=1}^{N} q_i \phi_{[i]}(r_i)$$

$$E^S = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_n \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{|r_i - r_j + n.L|} erfc\left(\alpha|r_i - r_j + n.L|\right)$$

- **When Needed:**
  - In simulations involving point charges to prevent divergence in energy calculations.
  - When particles are treated as point charges and no other computational techniques are used to implicitly account for self-interaction effects.

- **When Not Needed or Omitted:**
  - When particles are modeled with a finite size or other computational techniques address self-interaction effects.
  - In systems where the self-interaction energy is negligible compared to other contributions.

Self Interaction Term

$$E^C(r) = \frac{1}{2} \sum_{i=1}^{N} q_i \phi_i^L(r_i)$$

$$= \frac{1}{2} \frac{1}{4\pi\epsilon_0} \lim_{R \to 0} \sum_{i=1}^{N} q_i \left[\frac{q_i}{R} erf(\alpha R) \right]$$

$$= \frac{1}{2} \frac{\alpha}{4\pi\epsilon_0} \sum_{i=1}^{N} q_i^2 \lim_{x \to 0} \left[\frac{erf(x)}{x} \right], \quad x = \alpha R$$

$$= \frac{\alpha}{\sqrt{\pi} 4\pi\epsilon_0} \sum_{i=1}^{N} q_i^2$$

ϕ_i^L, the long-range potential term, decays slowly in real space. To ensure faster convergence, it's crucial to evaluate its contribution in **reciprocal space**.
The total charge density is:

$$\rho^L(r) = \sum_n \sum_{i=1}^{N} \rho_i^L(r + n.L)$$

Since the potential field and charge density are periodic functions of the lattice vector, we can obtain their Fourier-transformed components:

$$\tilde{\phi}(k) = \int_V d^3r \, \phi(r) e^{-ik.r}$$

$$\tilde{\rho}(k) = \int_V d^3r \, \rho(r) e^{-ik.r}$$

$$\phi(r) = \frac{1}{V} \sum_k \tilde{\phi}(k) e^{ik.r} \tag{8}$$

$$\rho(r) = \frac{1}{V} \sum_k \tilde{\rho}(k) e^{ik.r} \tag{9}$$

Here, the summation is over reciprocal lattice vectors k_x, k_y, k_z.
The Poisson equation relating potential field and charge density is:

$$\nabla^2 \phi^L(r) = -\frac{\rho^L(r)}{\epsilon_0} \tag{10}$$

$$\nabla^2 \phi^L(r) = -k^2 \phi^L(r) = -\frac{\rho^L(r)}{\epsilon_0} \tag{11}$$

In reciprocal space, it gives:

$$k^2 \tilde{\phi}^L(k) = \frac{\tilde{\rho}^L(k)}{\epsilon_0} \tag{12}$$

Please keep this equation in mind: $\boxed{\tilde{\phi}^L(k) = \dfrac{\tilde{\rho}^L(k)}{k^2 \epsilon_0}}$

Note, that the charge density in reciprocal space is

$$\rho^L(r) = \sum_n \sum_{i=1}^{N} q_i N(|r - r_i + n.L|, \sigma) \tag{13}$$

In Fourier space, the charge density becomes

$$
\begin{aligned}
\tilde{\rho}^L(k) &= \int_V \rho^L(r) e^{-ik.r} d^3r \\
&= \int_V d^3r \sum_{i=1}^N q_i N\left(|r - r_i + n.L|, \sigma\right) e^{-ik.r} \qquad (14) \\
&= \sum_{i=1}^N q_i \int \frac{1}{(2\pi\sigma^2)^{\frac{3}{2}}} e^{\frac{|r-r_i|^2}{2\sigma^2}} e^{-ik.|r-r_i|} e^{-ik.r_i} d^3r \\
&= \sum_{i=1}^N q_i e^{-ik.r_i} \int \frac{1}{(2\pi\sigma^2)^{\frac{3}{2}}} e^{-\frac{-y^2}{2\sigma^2} - ik.y} d^3y \\
&= q_i \sum_{i=1}^N e^{-ik.r_i} e^{-\frac{\sigma^2 k^2}{2}} \qquad (15)
\end{aligned}
$$

Using Eq. 10 and inverse Fourier transformation,

$$\tilde{\phi}^L(k) = \frac{1}{\epsilon_0} \sum_{i=1}^{N} \frac{q_i}{k^2} e^{-ik\cdot r_i} e^{-\frac{\sigma^2 k^2}{2}} \tag{16}$$

Therefore, in real space, the long-rage interaction term is

$$\phi^L(r) = \frac{1}{V} \sum_{k\neq 0} \tilde{\phi}^L(k) e^{ik\cdot r}$$

$$= \frac{1}{V\epsilon_0} \sum_{k\neq 0} \sum_{i=1}^{N} \frac{q_i}{k^2} e^{-ik\cdot(r-r_i)} e^{-\frac{\sigma^2 k^2}{2}} \tag{17}$$

The energy contribution from the long-range potential:

$$E^L = \frac{1}{2} \sum_{j=1}^{N} q_j \phi^L(r_j)$$

$$= \frac{1}{2V\epsilon_0} \sum_{k \neq 0} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{k^2} e^{ik.(r_i - r_j)} e^{-\frac{\sigma^2 k^2}{2}} \tag{18}$$

Combining all three energy terms, the total Coulomb interaction energy becomes

$$E = E^S + E^L - E^C$$

$$= \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{n} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{q_i q_j}{|r_i - r_j + n.L|} erfc\left(\alpha|r_i - r_j + n.L|\right)$$

$$+ \frac{1}{2V\epsilon_0} \sum_{k \neq 0} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{k^2} e^{ik.(r_i - r_j)} e^{-\frac{\sigma^2 k^2}{2}} - \frac{\alpha}{\sqrt{\pi} 4\pi\epsilon_0} \sum_{i=1}^{N} q_i^2 \tag{19}$$
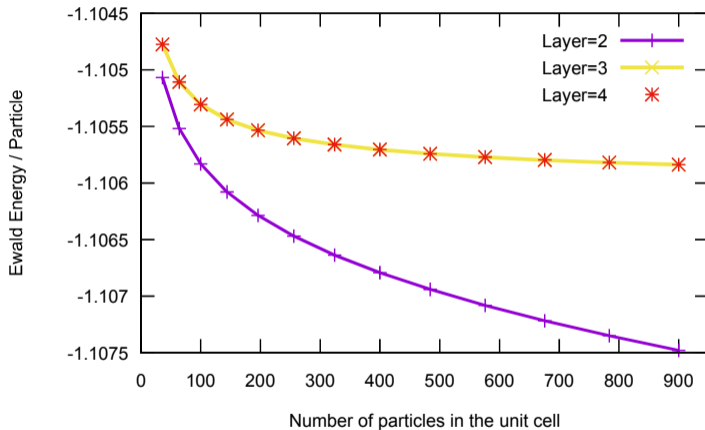
Figura 5: Achieving the bulk limit condition (2D square lattice Medelung constant = -1.10609)