

1. Introduction

1.1 Electrostatics

- Electrostatic potential
- differential equation
- Coulomb sum
- Bjerrum length

We assume N charges $q_i e$ at positions r_i . This corresponds to a charge density

$$\rho e = \sum_{i=1}^N q_i e \delta(r - r_i). \quad (1.1)$$

If the charges move slowly, then we can ignore magnetic forces, and the force on each particle is

$$F_i = q_i e E(r_i) \quad (1.2)$$

and the total electrostatic energy

$$U_E = \int \rho(r) e E(r) dr, \quad (1.3)$$

where E is the electrostatic field with the properties

$$\nabla \cdot E = \rho e / \epsilon \quad (1.4)$$

$$\nabla \times E = 0. \quad (1.5)$$

The latter implies that E is the gradient of an up to a constant unique scalar electrostatic potential Φ such that $E = -\nabla\Phi$. Inserting into (1.4) gives

$$-\nabla^2 \Phi = \rho e / \epsilon, \quad (1.6)$$

which is a defining differential equation for Φ . For a single charge, it has the solution:

$$-\nabla^2 \frac{q_i e}{4\pi\epsilon} \frac{1}{r - r_i} = q_i e \delta(r - r_i) / \epsilon \quad (1.7)$$

It is convenient to define the *Bjerrum length*

$$l_B = \frac{e^2}{4\pi\epsilon k_B T}, \quad (1.8)$$

which is the distance at which two unit charges feel an electrostatic interaction equal to $1k_B T$; this means for example that by spontaneous thermal fluctuations, two oppositely charged unit charges can be separated by a distance up to l_B . The Bjerrum length in water at room temperature is 0.7nm due to its large relative permittivity of $\epsilon/\epsilon_0 \approx 80$.

Then the electrostatic forces and potential are

$$F_i = k_B T l_B \sum_{j \neq i} \frac{q_i q_j}{|r_i - r_j|^3} (r_i - r_j) \quad \text{and} \quad U_E = \frac{1}{2} k_B T l_B \sum_{i=1}^N \sum_{j \neq i} \frac{q_i q_j}{|r_i - r_j|}, \quad (1.9)$$

where the (infinite) self interactions of point charges are omitted. The differential equation for Φ is

$$-\nabla^2 \Phi = 4\pi \frac{l_B k_B T}{e} \rho. \quad (1.10)$$

In the following, the Bjerrum length and $k_B T$ will be omitted.

1.2 Boundary conditions and conditional convergence

- periodic boundary conditions
- different summation orders
- convergence factors
- dipole term

To avoid finite size effects, computer simulations are typically performed with periodic boundary conditions. This means, we consider an infinite set of charges $q_i e$ at positions $r_i + n_{klm}$, where

$$n_{klm} = (kl_x, ll_y, ml_z) \quad \forall k, l, m \in \mathbb{Z}, \quad (1.11)$$

where l_x, l_y, l_z are the periodic cell sizes in the three spatial dimensions. We assume *charge neutrality*, that is

$$\sum_{i=1}^N q_i = 0. \quad (1.12)$$

We consider the electrostatic energy of the N primary charges with all others, that is

$$U_E = \frac{1}{2} \sum_{i=1}^N \sum_{k,l,m} \sum_{j=1}^N{}' \frac{q_i q_j}{r_i - r_j - n_{k,l,m}}, \quad (1.13)$$

where $'$ denotes that for $n_{k,l,m} = 0$, the $j = i$ -term is omitted. While being the obvious extension of Eqn. (1.9) to a periodic system, this is in fact not a well defined equation. The reason is that the sum is not absolutely convergent; the value of U_E depends on the order of summation over k, l, m . Since we assume that our N particles are representative for the bulk of a large, macroscopic sample that is approximated by the periodic sum, a reasonable choice is a summation in radially ascending shells:

$$U_E = \frac{1}{2} \sum_{i=1}^N \sum_{S=0}^{\infty} \sum_{n_{k,l,m}^2=S} \sum_{j=1}^N{}' \frac{q_i q_j}{r_i - r_j - n_{k,l,m}}. \quad (1.14)$$

Different summation orders are possible, which result in different values for U_E . In addition, U_E can be defined via different routes. For example, one can solve the differential Eqn. (1.10) under periodic boundary conditions, then

$$U_E = \frac{1}{2} \sum_{i=1}^N q_i \Phi(r_i). \quad (1.15)$$

This definition of the electrostatic potential is called *intrinsic*. Finally, one can use *convergence factors* to define U_E :

$$U_E := \lim_{\beta \rightarrow 0} \frac{1}{2} \sum_{i=1}^N \sum_{S=0}^{\infty} f(S, \beta) \sum_{n_{k,l,m}^2=S} \sum_{j=1}^N{}' \frac{q_i q_j}{r_i - r_j - n_{k,l,m}}, \quad (1.16)$$

where the convergence factor $f(S, \beta)$ has the following properties:

1. $f(S, \beta)$ is a continuous function for $\beta \geq 0$
2. $f(S, 0) = 1$
3. $f(S + 1, \beta) \leq f(S, \beta)$ for all S, β
4. $0 \leq f(S, \beta) \leq 1$ for all S, β .

That is, *formally* we recover the original series for $\beta = 0$. However, if at fixed $\beta > 0$, $f(S, \beta)$ decays fast enough (for example exponentially), then

$$\sum_{S=0}^{\infty} f(S, \beta) \sum_{n_{k,l,m}^2=S} \sum_{j=1}^N \frac{q_i q_j}{r_i - r_j - n_{k,l,m}}, \quad (1.17)$$

is absolutely convergent and well defined, so that also the limit (1.16) is well defined.

The convergence factor approach is the most general one, since it allows to obtain the same results as the other approaches; we will use this approach to prove some of the methods for evaluating the Coulomb sum. For example, the convergence factor $e^{-\beta S^2}$ corresponds to summation in ascending spherical shells. The convergence factor $e^{-\beta|r+S|^2}$ leads to the intrinsic potential.

However, the difference between summation orders is not as big as expected. Smith has shown that for example

$$U_{\text{spherical}} = U_{\text{intrinsic}} + \frac{2\pi}{3V} M^2 \quad (1.18)$$

$$U_{\text{slabwise}} = U_{\text{intrinsic}} + \frac{2\pi}{V} M_z^2, \quad (1.19)$$

where $U_{\text{spherical}}$ denotes the summation result for summation in ascending shells, U_{slabwise} diskwise summation in two dimensions, and after that symmetric summation in the remaining dimension, and $U_{\text{intrinsic}}$ the intrinsic solution.

Note that the *dipole term* $\frac{2\pi}{3V} M^2$ has in fact a physical interpretation, if written as

$$\frac{2\pi}{(2\epsilon'_r + 1)V} M^2, \quad (1.20)$$

where ϵ'_r is the dielectric permittivity of a medium that is supposed to surround the crystal (remember that we interpret the crystal as growing in ascending shells). For vacuum, $\epsilon'_r = 1$, so that we recover the term as in Eqn. (1.18). Another important value are metallic boundary conditions, for which the term vanishes. In case the system contains free ions, this is the only reasonable boundary condition, since otherwise this term imposes a harmonic potential that drives the particles back to an imaginary central cell.

Note also that for this term the unfolded positions r_i matter. For calculating the energy (1.13), it seems that the position r_i only matter up to multiples of l_x , l_y and l_z . After all, we are investigating a large, periodic crystal, and shifting r_i for example by l_x in the x -direction, the internal structure of the crystal will not change. However, the dipole term will change; moreover, it will be discontinuous, even if particle coordinates are modified only by multiples of l_x . Therefore, it is important to use unfolded, that is continuous coordinates for its calculation.

Instead of three dimensional periodicity, one can also consider two- or onedimensionally periodic systems; this is used for studying inter-/surfaces or wires and nanotubes. One can also generalize the periodicity to non-orthorombic simulation boxes. Another problem arises when for example calculating solvation free energies. In this case, a single charge is added to the system, which consequently becomes non-neutral. As one can easily, the energy of a non-neutral system is necessarily infinite. However, one can assume a homogeneous neutralizing background, which being homogeneous does not generate forces on the particles. Therefore, the dynamics of the system is unbiased by the background. But to calculate the energy, this background is necessary, since otherwise the result depends on the applied method, and even on non-physical tuning parameters.

2 Ewald method

2.1 Neutralization

3 mesh-accelerated Ewald methods (P^3M , SPME)

- parallelization

4 Tree codes and fast multipole methods

5 MMM, MMM2D, MMM1D

6 Electrostatic Layer Correction (ELC)

7 Maggs' method (MEMD)