Solving elliptic equations, in particular, the Poisson equation

$$\nabla^2 \phi(\vec{r}) = -4\pi\rho(\vec{r}) \quad \text{(CGS)}$$

Instead of doing finite differences, we can use what mathematically is Green's function method and physically, Coulomb's law.

If $G(\vec{r}, \vec{r}\,')$ is defined as $\nabla^2 G(\vec{r}, \vec{r}\,') = -\delta(\vec{r} - \vec{r}\,')$, then the solution of

$$\nabla^2 u(\vec{r}) = -f(\vec{r})$$

in infinite space is $u = \int f(\vec{r}\,') G(\vec{r}, \vec{r}\,') dV'$.

In 3D *G* is the potential of a point charge 1/4π:

$$G(\vec{r}, \vec{r}\,') = \frac{1}{4\pi|\vec{r} - \vec{r}\,'|}$$

$$\text{For } f = 4\pi\rho, \qquad \phi = \int 4\pi\rho(\vec{r}\,') G(\vec{r}, \vec{r}\,') dV = \int \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} dV'$$

Coulomb law + superposition principle.

2 The 2D Poisson equation is obtained in 3D when the problem is translationally invariant in the third dimension so $\frac{\partial^2 \phi}{\partial z^2} = 0$:

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2}$$

So to create a physical situation in 3D corresponding to the 2D Poisson eq., it is not enough to just if we take a planar system of charges, but we need to extend them infinitely in z direction, so each point charge is replaced by an infinitely thin rod || z with the same linear charge density. So G in 2D is the potential of a rod with charge density $1/4\pi$:

$$G(\vec{r}, \vec{r}\,') = -\frac{1}{2\pi} \ln|\vec{r} - \vec{r}\,'|.$$

This can be useful for the undergraduate version of Problem 2 from the assignment.

Of course, in both 2D and 3D, $G(\vec{r}, \vec{r}\,') = G(|\vec{r} - \vec{r}\,'|)$.

Back to 3D

Considered the potential of a charged surface with surface charge density $\sigma(\vec{r})$

$$\phi = \int \frac{\sigma(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} dS' = \int 4\pi\sigma(\vec{r}\,') G(|\vec{r} - \vec{r}\,'|) dS'$$

Suppose $\sigma(\vec{r})$ is not known, but it is known that $\phi = \phi_0 = \text{const}$.

By discretizing, get a system of linear equations:

$$\phi_i = \sum_{j \neq i} 4\pi\sigma_j G(|\vec{r}_i - \vec{r}_j|) \Delta S_j = \phi_0$$

Put $j \neq i$ to avoid singularity. N equations for N unknowns σ_i. Solve for σ_i. Can then get ϕ everywhere as

$$\phi(\vec{r}) = \sum_i 4\pi\sigma_i G(|\vec{r} - \vec{r}_i|) \Delta S_j$$

This is the simplest variant of the boundary element method. Can be useful for Problem 2 in the assignment.

Let's get back to the problem of solving the Poisson equation in a finite domain with Dirichlet or Neumann boundary conditions.

$$\nabla^2 \phi(\vec{r}) = -4\pi\rho(\vec{r}) \qquad \phi(\vec{r})\big|_\Gamma = g(\vec{r}) \quad \text{or} \quad \left.\frac{\partial \phi(\vec{r})}{\partial n}\right|_\Gamma = g(\vec{r})$$

Can we represent the solution of this problem as the potential of some system of charges in free space? If so, what should this system be?

Obviously, inside the domain the charge distribution should correspond to the right-hand side of our equation.

This will satisfy the equation, but may not satisfy the boundary conditions.

Need to add charges on the boundary and/or outside the domain.

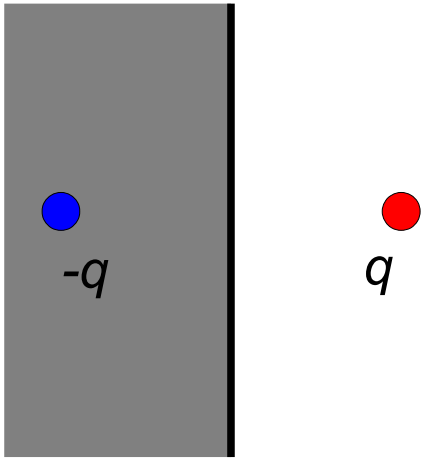


Image charges: an equal and opposite charge placed symmetrically behind the plane to ensure that the plane has $\phi = 0$.

But, of course, we also know that if we have a thin metal plate, this situation must be created by the charges on the plate itself

5 Can we always satisfy the boundary conditions by putting some charge distribution on the boundary, rather than beyond? Yes, sort of.

$$\nabla^2\phi=-4\pi\rho \qquad\qquad \nabla^2 G(\vec{r},\vec{r}\,')=-\delta(\vec{r}-\vec{r}\,')$$

$$\nabla\cdot[G(|\vec{r}-\vec{r}\,'|)\nabla(\phi(\vec{r}))-\phi(\vec{r})\nabla(G(|\vec{r}-\vec{r}\,'|))]=\nabla G(|\vec{r}-\vec{r}\,'|)\cdot\nabla(\phi(\vec{r}))$$

$$+G(|\vec{r}-\vec{r}\,'|)\nabla^2(\phi(\vec{r}))-\nabla(\phi(\vec{r}))\cdot\nabla G(|\vec{r}-\vec{r}\,'|)-\phi(\vec{r})\nabla^2(G(|\vec{r}-\vec{r}\,'|))$$

$$=-4\pi\rho(\vec{r})G(|\vec{r}-\vec{r}\,'|)+\phi(\vec{r})\delta(\vec{r}-\vec{r}\,')$$

Integrate over the whole domain, apply Gauss theorem

$$\int_V \nabla\cdot\vec{F}(\vec{r})\,dV=\int_{\partial V}\vec{F}(\vec{r})\cdot\vec{n}\,dS$$

$$\oint_\Gamma dS\left(G(|\vec{r}-\vec{r}\,'|)\frac{\partial}{\partial n}(\phi(\vec{r}))-\phi(\vec{r})\frac{\partial}{\partial n}(G(|\vec{r}-\vec{r}\,'|))\right)$$

$$=\int_V dV\left[-4\pi\rho(\vec{r})G(|\vec{r}-\vec{r}\,'|)+\phi(\vec{r})\delta(\vec{r}-\vec{r}\,')\right]$$

$$=\phi(\vec{r}\,')-\int_V dV\,4\pi\rho(\vec{r})G(|\vec{r}-\vec{r}\,'|).$$

$$\phi(\vec{r}\,') = \int_V dV\, 4\pi\rho(\vec{r})G(|\vec{r}-\vec{r}\,'|)$$
$$+\oint_\Gamma dS\left(G(|\vec{r}-\vec{r}\,'|)\frac{\partial}{\partial n}(\phi(\vec{r}))-\phi(\vec{r})\frac{\partial}{\partial n}(G(|\vec{r}-\vec{r}\,'|))\right)$$

The first term is the contribution of the bulk charge inside the domain. In 3D,

$$\int_V dV\, 4\pi\rho(\vec{r})G(|\vec{r}-\vec{r}\,'|) = \int dV'\frac{\rho(\vec{r})}{|\vec{r}-\vec{r}\,'|}.$$

The first surface term does look like the contribution of some charge density.

We had $\phi = \int \frac{\sigma(\vec{r})}{|\vec{r}-\vec{r}\,'|}dS = \int 4\pi\sigma(\vec{r})G(|\vec{r}-\vec{r}\,'|)dS$, so $\sigma(\vec{r}) = \frac{1}{4\pi}\frac{\partial\phi(\vec{r})}{\partial n}$

For ϕ = 0 the second surface term vanishes, so this is all we have. But what is this second term in general?

Consider 2 surfaces, one displaced from the other along the normal by an infinitesimal amount δ. Suppose the charge densities are equal and opposite.

$$\phi(\vec{r}\,') = \int 4\pi\left[\sigma(\vec{r})G(|\vec{r}-\vec{r}\,'|)-\sigma(\vec{r})G(|\vec{r}+\vec{n}\delta-\vec{r}\,'|)\right]dS$$
$$= \int 4\pi\left[\sigma(\vec{r})G(|\vec{r}-\vec{r}\,'|)-\sigma(\vec{r})\left\{G(|\vec{r}-\vec{r}\,'|)+\frac{\partial G}{\partial n}\delta\right\}\right]dS = -\int 4\pi\delta\sigma(\vec{r})\frac{\partial G}{\partial n}dS.$$

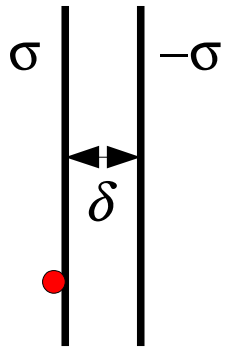
$$\phi(\vec{r}\,') = \int_V dV\, 4\pi\rho(\vec{r})G(|\vec{r}-\vec{r}\,'|)$$
$$+\oint_\Gamma dS\left(G(|\vec{r}-\vec{r}\,'|)\frac{\partial}{\partial n}(\phi(\vec{r}))-\phi(\vec{r})\frac{\partial}{\partial n}(G(|\vec{r}-\vec{r}\,'|))\right)$$

So the second surface term looks like the contribution of a "double layer" of positive and negative charges.

Depending on whether Dirichlet or Neumann conditions are given, only the first or the second surface term is known. Discretize the surface, replace the integral with a sum. If we do as before, we get

$$\phi(\vec{r}_i)=\phi_0(\vec{r}_i)+\sum_{j\neq i} G(|\vec{r}_j-\vec{r}_i|)\left.\frac{\partial\phi(\vec{r})}{\partial n}\right|_{\vec{r}_j}\Delta S-\sum_{j\neq i}\phi(\vec{r}_j)\left.\frac{\partial G(|\vec{r}-\vec{r}\,'|)}{\partial n}\right|_{\vec{r}=\vec{r}_j,\vec{r}\,'=\vec{r}_i}\Delta S$$

However, this is not quite correct, because the contribution of the last term with $i = j$ is not negligible.



$\sigma = \phi(\vec{r}_i)/4\pi\delta$ The potential at the red point is $\phi(\vec{r}_i)/2$.

This is added to the right-hand side of the equation.

Get a system of linear equations for $\phi(\vec{r}_i)$ or $\left.\frac{\partial\phi(\vec{r})}{\partial n}\right|_{\vec{r}_i}$

Of course, more sophisticated schemes can be used for integration over the surface. Will still get a linear system, though.

Boundary element method reduces the problem to a lower dimensionality problem. Smaller matrices, but normally dense! Makes sense when we need information about surfaces and only a few (if any) interior points. Also, much easier for the homogeneous problem ($\rho = 0$).

Note also that in the first version of the method, we have considered a charged surface in infinite space. If we had to do this problem by finite differences, we would have to introduce boundaries at a finite distance, which would be an additional approximation (besides discretization).

Of course, Poisson equation is not the only problem for which the Green's function and the boundary element formulation is possible. E.g., Stokes flow – the Green's function is called the Stokeslet.

Now consider a situation where we still have an infinite space, but the charges, rather than being localized, are distributed over a very large volume.

Example: molecular dynamics simulations where we consider many interacting particles filling the space (a model of a material) and solve the equations of motion.

Often, to have a good approximation of an infinite system while still keeping the problem tractable computationally, periodic boundary conditions (PBC) are used. Then, in principle, each particle interacts with all its images and images of other particles, i.e., there is an infinite number of iterations. When the interactions are short-range (e.g., Lennard-Jones potential decaying as $1/r^6$), the minimal image convention can be imposed and a cutoff introduced. But in many systems we have charged particles (ions) interacting via the Coulomb potential. In this case having even a large cutoff distance is too crude.

10 Suppose we have a rectangular cell of sizes *Lx*, *Ly*, *Lz* and *N* particles in the cell. The potential energy is

$$U = \frac{1}{2} \sum_{n_x, n_y, n_z = -\infty}^{\infty} {}' \sum_{i,j=1}^{N} \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j + \vec{n} * \vec{L}|}$$

The prime means that the terms with $i = j$ and $n_x = n_y = n_z = 0$ are not included. $\vec{n} * \vec{L} \equiv n_x \vec{L}_x + n_y \vec{L}_y + n_z \vec{L}_z$

Assume that the cell as a whole is neutral (if not, the energy will obviously diverge). But the dipole moment of the cell will in general not be zero. Suppose the magnitude of the dipole moment is *p*. Considering the cell with $n_x = n_y = n_z = 0$, the potential at that cell created by the cell with $|\vec{n}| = n$ is by absolute value ~p/(nL)^2. The number of cells in a given "layer" (or interval of *n*) is ~ (width of the layer)n^2. Therefore, the sum of the absolute values of the contributions will be $\sum_{n=0}^{\infty} \frac{p}{n^2 L^2} n^2$, which diverges.

The sum taken with the correct signs may still converge, but this means that it is conditionally convergent.

Conditional convergence means that the sum depends on the order of summation and in fact, any value can be obtained depending on the order!

This is because in this case even for a very large system its finite size and specific shape cannot be ignored. Indeed, the system will have nonzero polarization $\vec{P}=\vec{p}/(L_x L_y L_z)$. This is equivalent to having a surface charge density $\sigma=\vec{P}\cdot\vec{n}$. The field created by it will depend on the shape and this dependence does not vanish even in the infinite size limit.

On the other hand, we can consider a boundary-value problem for a single cell with periodic boundary conditions

$$\phi(0,y,z)=\phi(L_x,y,z) \qquad \left.\frac{\partial\phi(x,y,z)}{\partial x}\right|_{x=0}=\left.\frac{\partial\phi(x,y,z)}{\partial x}\right|_{x=L_x}$$

$$\int_0^{L_x}\int_0^{L_y}\int_0^{L_z}\phi(x,y,z)\,dxdydz=0$$

Then the problem is well-defined. It can be solved and then the shape-dependent contribution can be added.

Ewald method

Idea: add to and subtract from each point charge a Gaussian cloud of the same total charge but opposite sign.

$$\rho_i(\vec{r}) = q_i \delta(\vec{r} - \vec{r}_i) - q_i \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2 |\vec{r} - \vec{r}_i|^2}$$

A single (point charge+cloud) combination has 0 charge, is spherically symmetric and the charge density decays rapidly, therefore the field and the potential decay rapidly as well and interaction with other such combinations is very short-ranged and easy to compute.

The contributions of the clouds then need to be subtracted. But the corresponding charge distribution is a smooth infinitely differentiable function, so its Fourier transform converges rapidly.

$$\rho_i(\vec{r}) = q_i\,\delta(\vec{r}-\vec{r}_i) - q_i\frac{\beta^3}{\pi^{3/2}}e^{-\beta^2|\vec{r}-\vec{r}_i|^2}$$

Consider $\rho(r) = \rho_0 e^{-\beta^2 r^2}$, $\rho_0 = q_i\frac{\beta^3}{\pi^{3/2}}$. Gauss theorem:

$$E(r)\cdot 4\pi r^2 = 4\pi\int_0^r \rho(r')\,4\pi r'^2\,dr' = 16\pi^2\frac{q_i}{\pi^{3/2}}\int_0^r(\beta r)^2 e^{-(\beta r)^2}\,d(\beta r)$$

$$= 16\pi^{1/2}q_i\int_0^{\beta r}x^2e^{-x^2}\,dx = -8\pi^{1/2}q_i\int_0^{\beta r}x\,de^{-x^2} = -8\pi^{1/2}q_i\left(\beta r\,e^{-(\beta r)^2} - \int_0^{\beta r}e^{-x^2}\,dx\right)$$

$$= 4\pi q_i\,\mathrm{erf}(\beta r) - 8\pi^{1/2}q_i\beta r\,e^{-(\beta r)^2}.$$

$$E(r) = \frac{q_i}{r^2}\mathrm{erf}(\beta r) - \frac{2}{\sqrt{\pi}}\frac{\beta}{r}q_i e^{-(\beta r)^2} \qquad \mathrm{erf}\,x = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-y^2)\,dy$$

$$\phi(r) = \int_r^\infty E(r')\,dr' = q_i\left(-\int_r^\infty \mathrm{erf}(\beta r')\,d(1/r') - \frac{2}{\sqrt{\pi}}\beta\int_r^\infty\frac{e^{-(\beta r')^2}}{r'}\,dr'\right)$$

$$= q_i\left(\frac{1}{r}\mathrm{erf}(\beta r) + \frac{2\beta}{\sqrt{\pi}}\int_r^\infty\frac{e^{-(\beta r')^2}}{r'}\,dr' - \frac{2\beta}{\sqrt{\pi}}\int_r^\infty\frac{e^{-(\beta r')^2}}{r'}\,dr'\right) = \frac{q_i}{r}\mathrm{erf}(\beta r).$$

For the combination of a point charge with the negative cloud,

$\phi(r) = \frac{q_i}{r}(1-\mathrm{erf}(\beta r)) = \frac{q_i}{r}\mathrm{erfc}(\beta r)$. Decays rapidly. $\phi(0) = \frac{q_i}{r}2\beta r/\sqrt{\pi} = \frac{2\beta q_i}{\sqrt{\pi}}$

The Fourier transforms of clouds

$$\rho^{(i)}(x)=\rho_{0x}^{(i)}\exp\left(-\beta^2(x-x_i)^2\right) \qquad \rho_{0x}^{(i)}=q_i^{1/3}\frac{\beta}{\sqrt{\pi}}$$

$$\tilde{\rho}^{(i)}(k_x)=\rho_{0x}^{(i)}\int_{-\infty}^{\infty}\exp\left(-\beta^2(x-x_i)^2\right)\exp(-ik_x x)\,dx$$

$$=\rho_{0x}^{(i)}\frac{\sqrt{\pi}}{\beta}\exp\left(-\frac{k_x^2}{4\beta^2}\right)\exp(-ik_x x_i)=q_i^{1/3}\exp\left(-\frac{k_x^2}{4\beta^2}\right)\exp(-ik_x x_i)$$

Introduce "periodized" charge density (i.e., one charge per period)

$$\rho_{\mathrm{PER}}^{(i)}(\vec{r})=\sum_{n_x,n_y,n_z}\rho^{(i)}(\vec{r}-\vec{n}*\vec{L}) \qquad \tilde{\rho}_{\mathrm{clouds}}=\frac{1}{V}\Sigma_{i=1}^{N}q_i \qquad V=L_xL_yL_z$$

Fourier transform turns into a Fourier series.

$$\rho_{\mathrm{PER}}^{(i)}(\vec{r})=\Sigma_{\vec{k}}\tilde{\rho}_{\mathrm{PER}}^{(i)}(\vec{k})\exp(i\vec{k}\cdot\vec{r}) \qquad \vec{k}=\left(\frac{2\pi m_x}{L_x},\frac{2\pi m_y}{L_y},\frac{2\pi m_z}{L_z}\right)$$

$$\tilde{\rho}_{\mathrm{PER}}^{(i)}(\vec{k})=\frac{1}{V}\tilde{\rho}^{(i)}(\vec{k})=\frac{q_i}{V}\exp\left(-\frac{k^2}{4\beta^2}\right)\exp(-i\vec{k}\cdot\vec{r}_i)$$

For all clouds in all cells $\tilde{\rho}_{\mathrm{clouds}}(\vec{k})=\frac{1}{V}\Sigma_{i=1}^{N}q_i\exp\left(-\frac{k^2}{4\beta^2}\right)\exp(-i\vec{k}\cdot\vec{r}_i)$

$$\tilde{\rho}_{\text{clouds}}(\vec{k}) = \frac{1}{V}\sum_{i=1}^{N} q_i \exp\left(-\frac{k^2}{4\beta^2}\right)\exp(-i\vec{k}\cdot\vec{r}_i)$$

$$\nabla^2\phi(\vec{r}) = -4\pi\rho(\vec{r})$$

In Fourier space, $k^2\tilde{\phi}_{\text{clouds}}(\vec{k}) = 4\pi\tilde{\rho}_{\text{clouds}}(\vec{k})$

$$\tilde{\phi}_{\text{clouds}}(\vec{k}) = \frac{4\pi}{k^2}\tilde{\rho}_{\text{clouds}}(\vec{k}) = \frac{4\pi}{V}\sum_{i=1}^{N} q_i \exp(-i\vec{k}\cdot\vec{r}_i)\frac{1}{k^2}\exp\left(-\frac{k^2}{4\beta^2}\right)$$

$\tilde{\phi}_{\text{clouds}}(\vec{0}) = 0$ to satisfy the mean *u* condition

Calculate the energy per cell

$$U=\frac{1}{2}\Sigma_{i=1}^{N} q_i \phi'(\vec{r}_i)$$

Prime eliminates the potential of charge i itself.

$$U=\frac{1}{2}\Sigma_{i=1}^{N} q_i \phi'_{\text{q+cl}}(\vec{r}_i)-\frac{1}{2}\Sigma_{i=1}^{N} q_i \phi'_{\text{cl}}(\vec{r}_i)$$

$$=\frac{1}{2}\sum_{i=1}^{N} q_i \phi'_{\text{q+cl}}(\vec{r}_i)-\frac{1}{2}\sum_{i=1}^{N} q_i \phi_{\text{cl}}(\vec{r}_i)+\frac{1}{2}\sum_{i=1}^{N} q_i \phi_{\text{cl}.i}(\vec{r}_i)=U_{\text{dir}}-U_{\text{rec}}+U_{\text{self}}$$

U_{dir} is calculated in direct space: $\phi_{\text{q+cl}.i}(r)=\frac{q_i}{r}\operatorname{erfc}(\beta r)$.

$$U_{\text{dir}}=\frac{1}{2}\Sigma_{n_x,n_y,n_z}\Sigma'^{N}_{i,j=1}\frac{q_i q_j \operatorname{erfc}(\beta|\vec{r}_i-\vec{r}_j+\vec{n}*\vec{L}|)}{|\vec{r}_i-\vec{r}_j+\vec{n}*\vec{L}|}$$

For each *i*, only a few *j* within the cutoff distance need to be included.

U_{rec} is calculated in reciprocal space:

$$U_{\text{rec}}=\frac{1}{2}\sum_{\vec{k}}\sum_{i=1}^{N} q_i \exp(i\vec{k}\cdot\vec{r}_i)\tilde{\phi}_{\text{clouds}}(\vec{k})$$

$$=\frac{2\pi}{V}\sum_{\vec{k}\neq\vec{0}}\sum_{i=1}^{N}\sum_{j=1}^{N} q_i q_j \exp(i\vec{k}\cdot\vec{r}_i)\exp(-i\vec{k}\cdot\vec{r}_j)\frac{1}{k^2}\exp\left(-\frac{k^2}{4\beta^2}\right)$$

$$=\frac{2\pi}{V}\sum_{\vec{k}\neq\vec{0}}|\tilde{q}(\vec{k})|^2\frac{1}{k^2}\exp\left(-\frac{k^2}{4\beta^2}\right).$$

$$U_{\text{self}}=-\frac{\beta}{\sqrt{\pi}}\Sigma_{i=1}^{N} q_i^2.$$

Parameter β determines the trade-off between the convergence rates of the two series. Larger β – more narrow Gaussians – cutoff for direct summation can be smaller, but the Fourier transform has stronger higher-frequency components and the associated series converges more slowly.

Best choice of β (adjusted depending on the system size) gives $O(N^{3/2})$ cost.

Note that the reciprocal term involves the calculation of structure factors

$$\tilde{q}(\vec{k}) = \Sigma_{i=1}^{N} q_i \exp(i\vec{k}\cdot\vec{r}_i)$$

This looks like a Fourier transform, so it would be nice to do FFT. But in the usual discrete Fourier transform the sum is over grid points, here the sum is over the points where the particles are located. Need to map the particles to grid points.

The general approach in which particles are allowed to move in continuous space, but then some properties based on them are calculated at fixed grid points is called particle-in-cell in the plasma simulation community.

Different variants of the particle-mesh approach. Differ by the method used to interpolate the exponentials to grid points (Lagrange interpolation, splines).

Particle-particle-particle-mesh (P^3M) approach. Interactions between close particles are calculated directly. Probably the most popular approach at present for molecular simulations.

Reduce the number of operations to O(N ln N).

Fast Multipole Method

Divide the cell into subcells, calculate the multipole moments of subcells, use these to compute interactions with particles far away. Division is hierarchical. Much more difficult to implement. In theory, O(N), but in practice is worse for simulations and so not very popular. But found applications in other areas.

Finite volume method

Divide the space into small volumes and look at the fluxes between the volumes. Specifically, consider division into small cubic volumes V_{ijk}.

In electrostatics, we have Gauss theorem:

$$\oint_{\partial V} \nabla \phi(\vec{r}) \cdot \vec{n}\, dS = -4\pi Q_{ijk}$$

$$\oint_{\partial V} \nabla \phi \cdot \vec{n}\, dS \approx -h^2 \left(\frac{\partial \phi}{\partial x}(x_{i+1/2}, y_j, z_k) - \frac{\partial \phi}{\partial x}(x_{i-1/2}, y_j, z_k) + \frac{\partial \phi}{\partial y}(x_i, y_{j+1/2}, z_k) \right.$$
$$\left. - \frac{\partial \phi}{\partial y}(x_i, y_{j-1/2}, z_k) + \frac{\partial \phi}{\partial z}(x_i, y_j, z_{k+1/2}) - \frac{\partial \phi}{\partial z}(x_i, y_j, z_{k-1/2}) \right)$$

Approximate by centred differences:

$$\oint_{\partial V} \nabla \phi \cdot \vec{n}\, dS \approx -h \big[\phi(x_{i+1}, y_j, z_k) - \phi(x_i, y_j, z_k) - \phi(x_i, y_j, z_k)$$
$$+ \phi(x_{i-1}, y_j, z_k) + \phi(x_i, y_{j+1}, z_k) - \phi(x_i, y_j, z_k)$$
$$- \phi(x_i, y_j, z_k) + \phi(x_i, y_{j-1}, z_k) + \phi(x_i, y_j, z_{k+1})$$
$$- \phi(x_i, y_j, z_k) - \phi(x_i, y_j, z_k) + \phi(x_i, y_j, z_{k-1}) \big] \approx -4\pi Q_{ijk}$$