derivation of Ewald Summation

by hjm

$$z = (x, y, z) = (r, \theta, \varphi)$$

z点受到的所有电荷产生的电势：

$$\emptyset(z) = \frac{1}{4\pi\varepsilon_0}\sum_n \sum_{j=1}^{N} \frac{q_j}{|z - z_j + nL|}$$

z点受到的除i之外的电荷产生的电势：

$$\emptyset_{[i]}(z) = \frac{1}{4\pi\varepsilon_0}\sum_n \sum_{j=1(\neq i)}^{N} \frac{q_j}{|z - z_j + nL|}$$

$$\emptyset_{[i]}(z) = \frac{1}{4\pi\varepsilon_0}\sum_n \sum_{j=1(\neq i)}^{N} \int \frac{\rho_j(z')}{|z - z' + nL|} d^3z'$$

电荷j产生的电荷密度：

$$\begin{aligned} \rho_j(z) &= q_j\delta(z - z_j) \\ &= q_j\left(\delta(z - z_j) - G(z - z_j) + G(z - z_j)\right) \\ &= \underbrace{q_j\left(\delta(z - z_j) - G(z - z_j)\right)}_{\rho_j^s(z)} + \underbrace{q_i G(z - z_j)}_{\rho_j^l(z)} \end{aligned}$$

高斯分布：

$$G(z) = \frac{\alpha^3}{\pi^{\frac{3}{2}}} e^{-\alpha^2 r^2}$$

z点受到的电荷密度 ρ 产生的电势方程（泊松方程）：

$$\nabla^2\emptyset(z) = -\frac{\rho(z)}{\varepsilon_0}$$

$$\nabla^2\emptyset_j^l(z) = -\frac{\rho_j^l(z)}{\varepsilon_0}$$

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\emptyset) = -q_j\frac{\alpha^3}{\varepsilon_0\pi^{\frac{3}{2}}} e^{-\alpha^2 r^2}$$

$$\frac{\partial^2}{\partial r^2}(r\emptyset) = -q_j\frac{\alpha^3}{\varepsilon_0\pi^{\frac{3}{2}}} r e^{-\alpha^2 r^2}$$

$$\frac{\partial}{\partial r}(r\emptyset) = q_j\frac{\alpha}{2\varepsilon_0\pi^{\frac{3}{2}}} e^{-\alpha^2 r^2} + C_1$$

$$r\emptyset = q_j\frac{\alpha}{2\varepsilon_0\pi^{\frac{3}{2}}}\int_0^r e^{-\alpha^2 r^2} dr + C_1 r + C_2$$

$$\begin{aligned} \emptyset &= q_j\frac{\alpha}{2\varepsilon_0\pi^{\frac{3}{2}} r}\int_0^r e^{-\alpha^2 r^2} dr + C_1 + C_2\frac{1}{r} \\ &= q_j\frac{\alpha}{2\varepsilon_0\pi^{\frac{3}{2}} r}\frac{1}{\alpha}\int_0^r e^{-\alpha^2 r^2} d(\alpha r) + C_1 + C_2\frac{1}{r} \\ &= q_j\frac{1}{4\pi\varepsilon_0 r}\mathrm{erf}(\alpha r) + C_1 + C_2\frac{1}{r} \end{aligned}$$

$$\lim_{r\to\infty}\mathrm{erf}(r) = 1$$

$$\lim_{r\to\infty}\emptyset(z) = q_j\frac{1}{4\pi\varepsilon_0 r}(Coulomb's\ law)$$

$$\Rightarrow C_1 = C_2 = 0$$

电荷j产生的电势：

$$\therefore \emptyset_j^l(z) = q_j\frac{1}{4\pi\varepsilon_0 r}\mathrm{erf}(\alpha r)$$

$$\emptyset_j^s(z) = q_j\frac{1}{4\pi\varepsilon_0 r}\mathrm{erfc}(\alpha r)$$

z点受到的除i之外的电荷产生的电势：

$$\begin{aligned} \emptyset_{[i]}(z) &= \emptyset_{[i]}^s(z) + \emptyset_{[i]}^l(z) \\ &= \sum_n \sum_{j=1(\neq i)}^{N} \emptyset_j^s(z) + \sum_n \sum_{j=1(\neq i)}^{N} \emptyset_j^l(z) \\ &= \sum_n \sum_{j=1(\neq i)}^{N} q_j\frac{\mathrm{erfc}(\alpha|z - z_j + nL|)}{4\pi\varepsilon_0|z - z_j + nL|} \\ &+ \sum_n \sum_{j=1(\neq i)}^{N} q_j\frac{\mathrm{erf}(\alpha|z - z_j + nL|)}{4\pi\varepsilon_0|z - z_j + nL|} \end{aligned}$$

real part(cutoff内直接计算):

$$\emptyset_{[i]}^s(z) = \sum_n \sum_{j=1(\neq i)}^{N} q_j\frac{\mathrm{erfc}(\alpha|z - z_j + nL|)}{4\pi\varepsilon_0|z - z_j + nL|}$$

wave part(倒易空间计算):

$$\emptyset_{[i]}^s(z) = \sum_n \sum_{j=1}^{N} q_j\frac{\mathrm{erf}(\alpha|z - z_j + nL|)}{4\pi\varepsilon_0|z - z_j + nL|}$$

self correction:

由于wave part的FT计算时无法单独忽略自身(注意wave part公式里没有“$\neq i$”)，
自己和自己的作用也会被包含进去，因此最后需要减掉这一项

$$\begin{aligned} \emptyset_i^{self} &= \lim_{z\to 0} q_j\frac{\mathrm{erf}(\alpha z)}{4\pi\varepsilon_0 z} \\ &= \frac{q_j}{4\pi\varepsilon_0}\lim_{z\to 0}\frac{\mathrm{erf}(\alpha z)}{z} \\ &= \frac{q_j}{4\pi\varepsilon_0}\lim_{y\to 0}\frac{2\alpha}{\sqrt{\pi}} e^{-y^2} \\ &= \frac{\alpha q_j}{2\pi^{\frac{3}{2}}\varepsilon_0} \end{aligned}$$

$$y = \alpha z$$

$$z = \frac{1}{\alpha} y$$

$$dz = \frac{1}{\alpha} dy$$

$$\frac{d}{dz}\mathrm{erf}(\alpha z) = \alpha\frac{d}{dy}\mathrm{erf}(y) = \frac{2\alpha}{\sqrt{\pi}} e^{-y^2}$$

$$\vec{z} = (x, y, z)$$

电荷j产生的施加给z点的电荷密度：

$$\rho_j^l(\vec{z}) = q_i G\left(z - z_j\right)$$

z点的所有电荷施加的长程电荷密度：

$$\rho^l(\vec{z}) = \sum_n \sum_{j=1}^{N} q_j G\left(\vec{z} - \vec{z}_j + nL\right)$$

高斯分布：

$$G(\vec{z}) = \frac{\alpha^3}{\pi^{\frac{3}{2}}} e^{-\alpha^2 |\vec{z}|^2}$$

泊松方程：

$$\nabla^2 \phi(z) = -\frac{\rho(z)}{\varepsilon_0} \longrightarrow |\vec{w}|^2 \tilde{\phi}^l(\vec{w}) = \frac{\tilde{\rho}^l(\vec{w})}{\varepsilon_0}$$

(证明见附录[1])

wave part

$$\tilde{\rho}^l(\vec{w}) = \int_V \rho^l(\vec{z}) e^{-i\vec{w}\vec{z}} d^3\vec{z}$$

$$= \int_V \sum_n \sum_{j=1}^{N} q_j G\left(\vec{z} - \vec{z}_j + nL\right) e^{-i\vec{w}\vec{z}} d^3\vec{z}$$

$$= \sum_{j=1}^{N} q_j \int_{R^3} G\left(\vec{z} - \vec{z}_j\right) e^{-i\vec{w}\vec{z}} d^3\vec{z}$$

$$= \frac{\alpha^3}{\pi^{\frac{3}{2}}} \sum_{j=1}^{N} q_j \int_{R^3} e^{-\alpha^2 |\vec{z} - \vec{z}_j|^2} e^{-i\vec{w}\vec{z}} d^3\vec{z}$$

$$= e^{-\frac{|\vec{w}|^2}{4\alpha^2}} \sum_{j=1}^{N} q_j e^{-i\vec{w}\vec{z}_j}$$

(这一步推导过程见附录[4])

$$\tilde{\phi}^l(\vec{w}) = \frac{e^{-\frac{|\vec{w}|^2}{4\alpha^2}}}{|\vec{w}|^2 \varepsilon_0} \sum_{j=1}^{N} q_j e^{-i\vec{w}\vec{z}_j}$$

$$\phi^l(\vec{z}) = \frac{1}{L^3} \sum_{\vec{w} \neq 0} \tilde{\phi}(\vec{w})\, e^{i\vec{w}\vec{z}}$$

exafmm/ewald.h

potential def:

$$\phi(z) = \sum_n \sum_{j=1}^{N} \frac{q_j}{|z - z_j + nL|}$$

real part:

$$\phi_{[i]}^s(z) = \sum_n \sum_{j=1(\neq i)}^{N} q_j \frac{\operatorname{erfc}\left(\alpha |z - z_j + nL|\right)}{|z - z_j + nL|}$$

$$F_{[i]}^s(z) = \nabla \phi_{[i]}^s$$

结果及证明在附录[2]
(实际上这个是负电场，力还需要乘-q)

dft:

$$\tilde{\rho}^l(\vec{w}) = \sum_{j=1}^{N} q_j e^{-i\vec{w}\vec{z}_j}$$

wave part:

$$\tilde{\phi}^l(\vec{w}) = \frac{4\pi}{L^3} \frac{e^{-\frac{|\vec{w}|^2}{4\alpha^2}}}{|\vec{w}|^2} \tilde{\rho}^l(\vec{w})$$

idft:

$$\phi^l(\vec{z}) = \sum_{\vec{w} \neq 0} \tilde{\phi}(\vec{w})\, e^{i\vec{w}\vec{z}}$$

$$F^l(\vec{z}) = \nabla \phi^l(\vec{z})$$

结果及证明在附录[3]
(实际上这个是负电场，力还需要乘-q)

self correction:

$$\phi_i^{self} = \frac{2\alpha q_j}{\sqrt{\pi}}$$

$$F_i^{self} = \nabla \phi_i^{self} = 0$$

附录[1]：reciprocal空间的泊松方程

$$f=e^{i\vec{w}\vec{z}}=e^{i(kx+my+pz)}$$

$$\frac{\partial f}{\partial x}=e^{i\vec{w}\vec{z}}ik$$

$$\frac{\partial^2 f}{\partial x^2}=e^{i\vec{w}\vec{z}}i^2k^2=-e^{i\vec{w}\vec{z}}k^2$$

$$\begin{aligned}\therefore \nabla^2 f&=\left(\frac{\partial^2 f}{\partial x^2}+\frac{\partial^2 f}{\partial y^2}+\frac{\partial^2 f}{\partial z^2}\right)\\&=-e^{i\vec{w}\vec{z}}k^2-e^{i\vec{w}\vec{z}}m^2-e^{i\vec{w}\vec{z}}p^2\\&=e^{i\vec{w}\vec{z}}(-k^2-m^2-p^2)\\&=-|\vec{w}|^2e^{i\vec{w}\vec{z}}\end{aligned}$$

↓

$$\nabla^2\emptyset(z)=-\frac{\rho(z)}{\varepsilon_0}$$

$$\nabla^2\int\tilde{\emptyset}(\vec{w})e^{i\vec{w}\vec{z}}d\vec{z}=-\frac{1}{\varepsilon_0}\int\tilde{\rho}(\vec{w})e^{i\vec{w}\vec{z}}d\vec{z}$$

$$\int\tilde{\emptyset}(\vec{w})\nabla^2\left(e^{i\vec{w}\vec{z}}\right)d\vec{z}=-\frac{1}{\varepsilon_0}\int\tilde{\rho}(\vec{w})e^{i\vec{w}\vec{z}}d\vec{z}$$

$$\int\tilde{\emptyset}(\vec{w})-|\vec{w}|^2e^{i\vec{w}\vec{z}}d\vec{z}=-\frac{1}{\varepsilon_0}\int\tilde{\rho}(\vec{w})e^{i\vec{w}\vec{z}}d\vec{z}$$

$$\boxed{|\vec{w}|^2\tilde{\emptyset}(\vec{w})=\frac{\tilde{\rho}(\vec{w})}{\varepsilon_0}}$$

附录[2]：短程力推导

令：

$$\vec{z}=[x,y,z]$$

$$f=\frac{\operatorname{erfc}\left(\alpha|\vec{z}-\vec{z}_j+nL|\right)}{|\vec{z}-\vec{z}_j+nL|}=\frac{\operatorname{erfc}(\alpha r)}{r}$$

$$r=|\vec{z}-\vec{z}_j+nL|=\sqrt{\left(x-x_j+nL\right)^2+\left(y-y_j+nL\right)^2+\left(z-z_j+nL\right)^2}$$

则：

$$\begin{aligned}\frac{\partial r}{\partial x}&=\frac{x-x_j+nL}{\sqrt{\left(x-x_j+nL\right)^2+\left(y-y_j+nL\right)^2+\left(z-z_j+nL\right)^2}}\\&=\frac{x-x_j+nL}{r}\end{aligned}$$

$$\begin{aligned}\frac{\partial f}{\partial x}&=\frac{\partial}{\partial r}\frac{\partial r}{\partial x}\left(\frac{1}{r}\right)\operatorname{erfc}(\alpha r)+\frac{1}{r}\frac{\partial}{\partial r}\frac{\partial r}{\partial x}(\operatorname{erfc}(\alpha r))\\&=\frac{\partial r}{\partial x}\left(\frac{\partial}{\partial r}\left(\frac{1}{r}\right)\operatorname{erfc}(\alpha r)+\frac{1}{r}\frac{\partial}{\partial r}(\operatorname{erfc}(\alpha r))\right)\\&=\frac{x-x_j+nL}{r}\left(-\frac{1}{r^2}\operatorname{erfc}(\alpha r)-\frac{1}{r}\frac{2\alpha}{\sqrt{\pi}}e^{-\alpha^2r^2}\right)\\&=-\frac{x-x_j+nL}{r^3}\left(\operatorname{erfc}(\alpha r)+\frac{2\alpha r}{\sqrt{\pi}}e^{-\alpha^2r^2}\right)\end{aligned}$$

$$\begin{aligned}\nabla f&=\left(\frac{\partial f}{\partial x},\frac{\partial f}{\partial x},\frac{\partial f}{\partial x}\right)\\&=-\left(\frac{x-x_j+nL}{r^3},\frac{y-y_j+nL}{r^3},\frac{z-z_j+nL}{r^3}\right)\left(\operatorname{erfc}(\alpha r)+\frac{2\alpha r}{\sqrt{\pi}}e^{-\alpha^2r^2}\right)\\&=-\frac{\vec{z}-\vec{z}_j+nL}{r^3}\left(\operatorname{erfc}(\alpha r)+\frac{2\alpha r}{\sqrt{\pi}}e^{-\alpha^2r^2}\right)\end{aligned}$$

$$\therefore \nabla\emptyset_{[i]}^{s}=\sum_n\sum_{j=1(\neq i)}^{N}\nabla f q_j=-\sum_n\sum_{j=1(\neq i)}^{N}q_j\frac{\vec{z}-\vec{z}_j+nL}{r^3}\left(\operatorname{erfc}(\alpha r)+\frac{2\alpha r}{\sqrt{\pi}}e^{-\alpha^2r^2}\right)$$

附录[3]：长程力推导

$$\vec{w} = [k, m, p], \vec{r} = [x, y, z]$$

$$\emptyset(r) = \Re\left(\sum_{\vec{w}\neq 0} \Phi(k) e^{i\vec{w}\vec{r}}\right)$$

$$\begin{aligned}
\nabla_r \emptyset(r) &= \nabla_r \Re\left(\sum_{\vec{w}\neq 0} \Phi(k) e^{i\vec{w}\vec{r}}\right) \\
&= \Re\left(\nabla_r \sum_{\vec{w}\neq 0} \Phi(k) e^{i\vec{w}\vec{r}}\right) \\
&= \Re\left(\nabla_{x,y,z} \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right) \\
&= \left[\Re\left(\nabla_x \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right), \Re\left(\nabla_y \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right), \Re\left(\nabla_z \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right)\right] \\
&= \left[\Re\left(ik \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right), \Re\left(im \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right), \Re\left(ip \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right)\right] \\
&= \left[\Re\left(i \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right) k, \Re\left(i \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right) m, \Re\left(i \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right) p\right] \\
&= \Re\left(i \sum_{\vec{w}\neq 0} \Phi(k) e^{i(kx+my+pz)}\right) [k, m, p] \\
&= \Re\left(i \sum_{\vec{w}\neq 0} \Phi(k) e^{e^{i\vec{w}\vec{r}}}\right) \vec{w}
\end{aligned}$$

附录[4]

$$\int_{-\infty}^{\infty} e^{-\alpha^2 x^2} e^{-ikx} dx$$

$$= \int_{-\infty}^{\infty} e^{-\alpha^2 x^2 - ikx + \frac{k^2}{4\alpha^2} - \frac{k^2}{4\alpha^2}} dx$$

$$= e^{-\frac{k^2}{4\alpha^2}} \int_{-\infty}^{\infty} e^{-\alpha^2 x^2 - ikx + \frac{k^2}{4\alpha^2}} dx$$

$$= e^{-\frac{k^2}{4\alpha^2}} \int_{-\infty}^{\infty} e^{-\left(\alpha x + \frac{ik}{2\alpha}\right)^2} dx$$

$$= \frac{1}{\alpha} e^{-\frac{k^2}{4\alpha^2}} \int_{-\infty}^{\infty} e^{-\left(\alpha x + \frac{ik}{2\alpha}\right)^2} d\left(\alpha x + \frac{ik}{2\alpha}\right)$$

$$= \frac{1}{\alpha} e^{-\frac{k^2}{4\alpha^2}} \int_{-\infty}^{\infty} e^{-y^2} dy$$

$$= \frac{\sqrt{\pi}}{\alpha} e^{-\frac{k^2}{4\alpha^2}}$$

$$\int_{R^3} e^{-\alpha^2 |\vec{z} - \vec{z}_j|^2} e^{-i\vec{w}\vec{z}} d^3\vec{z}$$

$$= e^{-i\vec{w}\vec{z}_j} \int_{R^3} e^{-\alpha^2 |\vec{z} - \vec{z}_j|^2} e^{-i\vec{w}(\vec{z} - \vec{z}_j)} d^3(\vec{z} - \vec{z}_j)$$

$$= e^{-i\vec{w}\vec{z}_j} \int_{R^3} e^{-\alpha^2 |\vec{h}|^2} e^{-i\vec{w}\vec{h}} d^3\vec{h}$$

$$= e^{-i\vec{w}\vec{z}_j} \iiint_{-\infty}^{\infty} e^{-\alpha^2 (x^2 + y^2 + z^2)} e^{-i(kx + my + pz)} dxdydz$$

$$= e^{-i\vec{w}\vec{z}_j} \iiint_{-\infty}^{\infty} e^{-\alpha^2 x^2} e^{-\alpha^2 z^2} e^{-ikx} e^{-imy} e^{-ipz} dxdydz$$

$$= e^{-i\vec{w}\vec{z}_j} \int_{-\infty}^{\infty} e^{-\alpha^2 x^2} e^{-ikx} dx \int_{-\infty}^{\infty} e^{-\alpha^2 y^2} e^{-imy} dy \int_{-\infty}^{\infty} e^{-\alpha^2 z^2} e^{-ipz} dz$$

$$= e^{-i\vec{w}\vec{z}_j} \frac{\pi^{\frac{3}{2}}}{\alpha^3} e^{-\frac{k^2 + m^2 + p^2}{4\alpha^2}}$$

$$= e^{-i\vec{w}\vec{z}_j} \frac{\pi^{\frac{3}{2}}}{\alpha^3} e^{-\frac{|\vec{w}|^2}{4\alpha^2}}$$

$$\therefore \frac{\alpha^3}{\pi^{\frac{3}{2}}} \sum_{j=1}^{N} q_j \int_{R^3} e^{-\alpha^2 |\vec{z} - \vec{z}_j|^2} e^{-i\vec{w}\vec{z}} d^3\vec{z} = \frac{\alpha^3}{\pi^{\frac{3}{2}}} \sum_{j=1}^{N} q_j\, e^{-i\vec{w}\vec{z}_j} \frac{\pi^{\frac{3}{2}}}{\alpha^3} e^{-\frac{|\vec{w}|^2}{4\alpha^2}} = e^{-\frac{|\vec{w}|^2}{4\alpha^2}} \sum_{j=1}^{N} q_j\, e^{-i\vec{w}\vec{z}_j}$$

references

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3. https://zhuanlan.zhihu.com/p/406664860
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