PHY 712 Electrodynamics
11-11:50 AM MWF Olin 103

Class notes for Lecture 3:

Reading: Chapter 1 (especially 1.11) in JDJ;

1. **Continued discussion/derivation of Ewald summation methods**
2. **Example for CsCl**

PHY 712 Electrodynamics

MWF 11-11:50 AM	**Olin 103**	Webpage: **http://www.wfu.edu/~natalie/s22phy712/**

Instructor: Natalie Holzwarth	**Office:**300 OPL	**e-mail:**natalie@wfu.edu

Course schedule for Spring 2022

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	JDJ Reading	Topic	HW	Due date
1	Mon: 01/10/2022	Chap. 1 & Appen.	Introduction, units and Poisson equation	#1	01/14/2022
2	Wed: 01/12/2022	Chap. 1	Electrostatic energy calculations	#2	01/19/2022
3	Fri: 01/14/2022	Chap. 1	Electrostatic energy calculations	#3	01/21/2022
	Mon: 01/17/2022		MLK Holiday -- no class		
4	Wed: 01/19/2022	Chap. 1 & 2	Electrostatic potentials and fields		

PHY 712 -- Assignment #3

January 14, 2022

Continue reading Chap. 1 in **Jackson**.

1. Using the Ewald summation methods developed in class, find the electrostatic interaction energy of a NaCl lattice having a cubic lattice constant a. Check that your result does not depend of the Ewald parameter η. You are welcome to copy (and modify) the maple file used in class. A FORTRAN code is also available upon request.

The details are presented in the pdf file – Extranotes2.pdf

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Lecture Notes

- Lecture 1 -- Introduction and electrostatics PP slides PDF Extra PP slides Extra PDF
- Lecture 2 -- Electrostatic energy PP slides PDF Extra PP slides Extra PDF Detailed PDF
- Lecture 3 -- Ewald summation methods PP slides PDF CsCl Maple CsCl PDF

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Last modfied: Thursday, 13-Jan-2022 23:28:06 EST

Last time, we argued that we need to carry out the following summation of all pairs of ions using Ewald's very clever trick with the erf and erfc functions:

$$W = \frac{1}{8\pi\varepsilon_0}\sum_{i\neq j}\frac{q_i q_j}{|\mathbf{r_i}-\mathbf{r_j}|} = \frac{1}{8\pi\varepsilon_0}\left(\sum_{i\neq j}\frac{q_i q_j \mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\mathbf{r_i}-\mathbf{r_j}|)}{|\mathbf{r_i}-\mathbf{r_j}|} + \sum_{i\neq j}\frac{q_i q_j \mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\mathbf{r_i}-\mathbf{r_j}|)}{|\mathbf{r_i}-\mathbf{r_j}|}\right)$$

Must be evaluated in "reciprocal" space

Can be converged as is (in real space)

In order to make progress, we need to systematically enumerate all of the ion positions in the system

Using CsCl as our example system

Cs

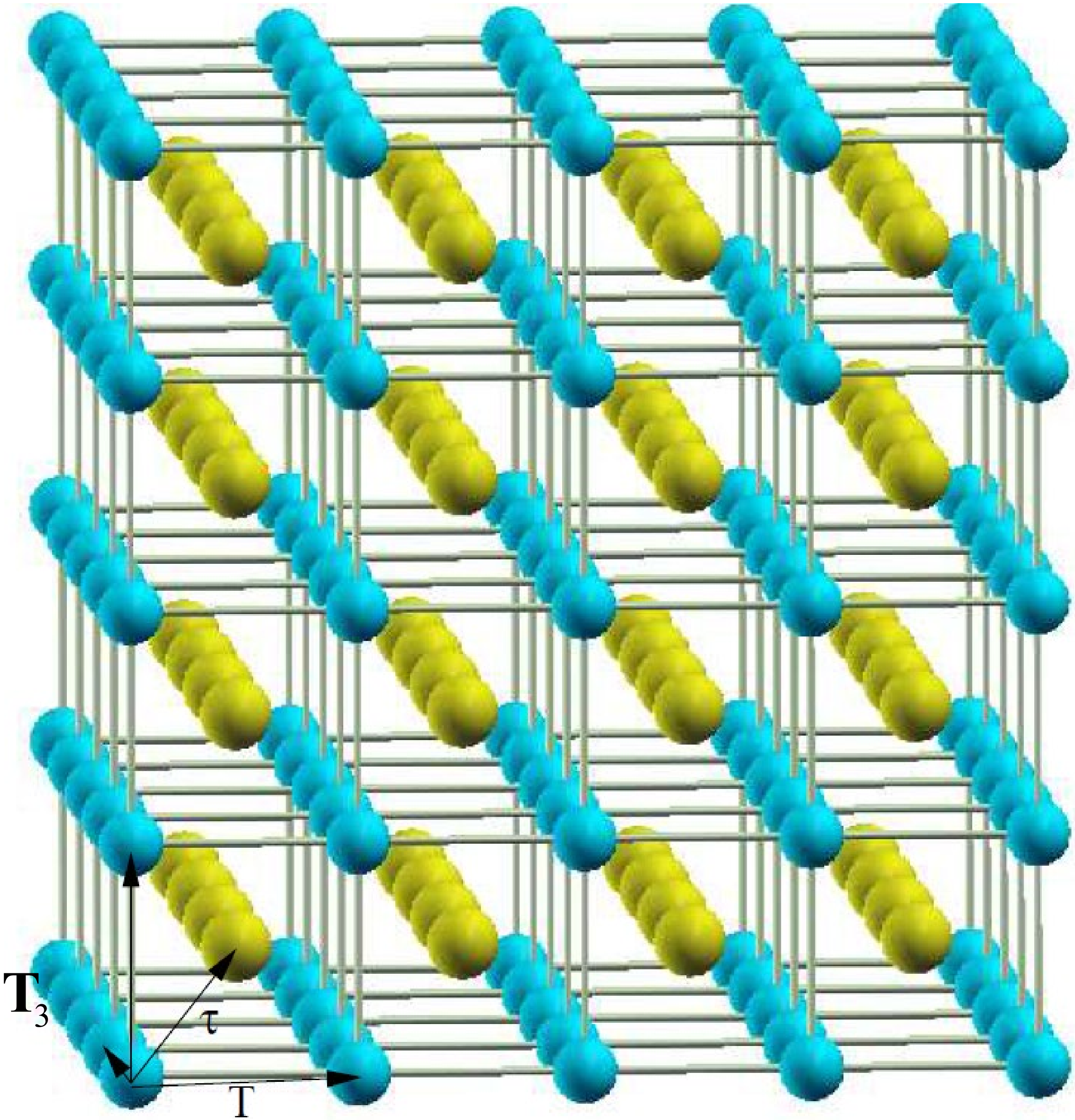
Cl

Notice that a unit cell contains one Cl and one Cs

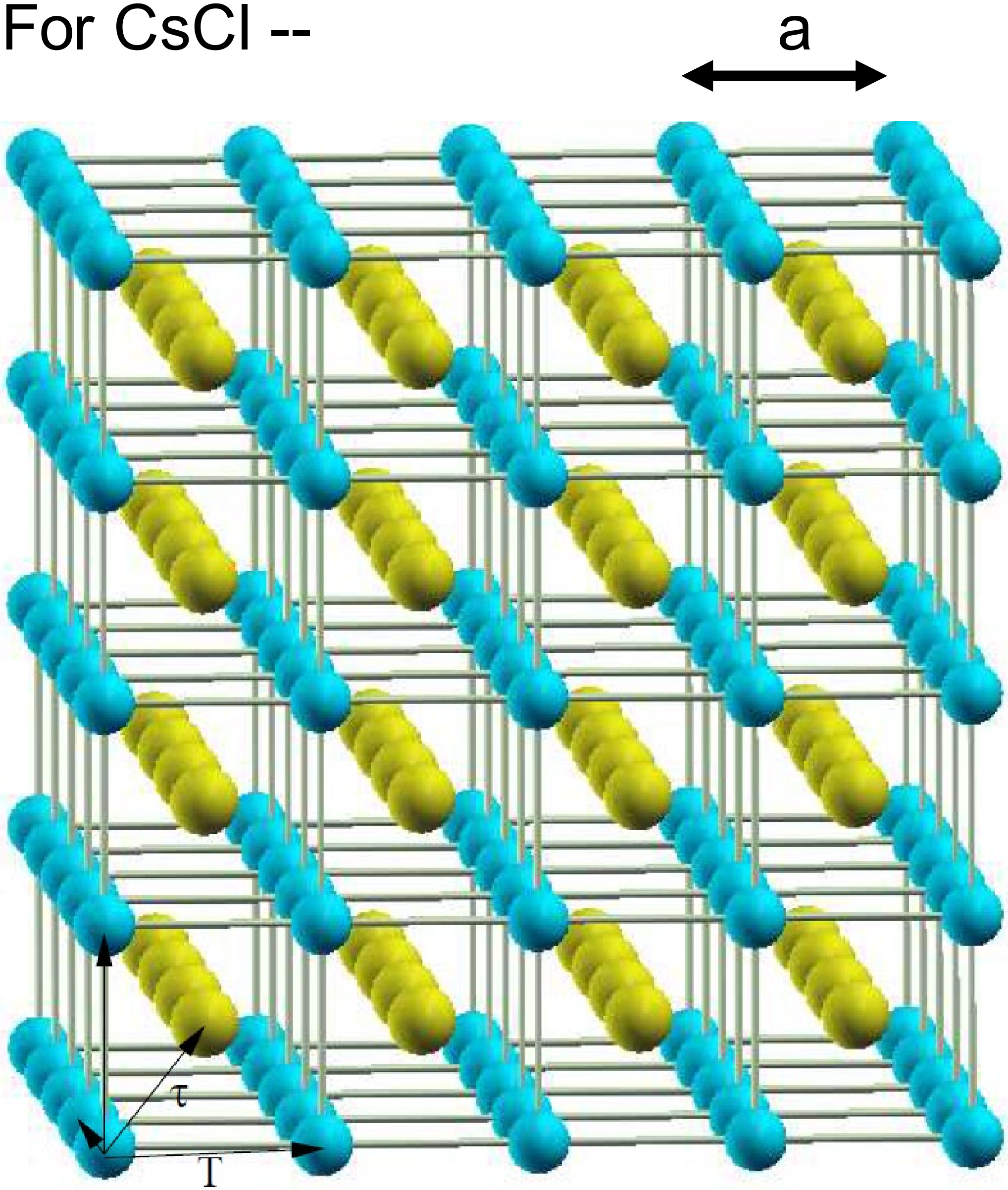
$$\mathbf{r}_i = \boldsymbol{\tau}_\alpha + \mathbf{T}$$

for $\alpha = \mathrm{Cl}$ or Cs

and $\mathbf{T} = n_1\mathbf{T}_1 + n_2\mathbf{T}_2 + n_3\mathbf{T}_3$



For CsCl --



$$\tau_{\mathrm{Cs}} = 0 \text{ and } \tau_{\mathrm{Cl}} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}).$$

$$\mathbf{T}_1 = \mathrm{a}\hat{\mathbf{x}} \quad \mathbf{T}_2 = \mathrm{a}\hat{\mathbf{y}} \quad \mathbf{T}_3 = \mathrm{a}\hat{\mathbf{z}}.$$

Note that in general --

$$\sum_{ij} = N \sum_{\alpha\beta\mathbf{T}}$$

Note that, using $\mathbf{r}_i = \boldsymbol{\tau}_\alpha + \mathbf{T}$

$$W = \frac{1}{8\pi\epsilon_0}\sum_{i\neq j}\frac{q_i q_j}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} = \frac{N}{8\pi\epsilon_0}\sum_{\alpha,\beta,\mathbf{T}}\frac{q_\alpha q_\beta}{\left|\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}\right|}$$

omit term $\alpha = \beta$

when $\mathbf{T}=0$

$$\boldsymbol{\tau}_{\alpha\beta} \equiv \boldsymbol{\tau}_\alpha - \boldsymbol{\tau}_\beta$$

$$\frac{W}{N} = \frac{1}{8\pi\epsilon_0}\sum_{\alpha,\beta,\mathbf{T}}\frac{q_\alpha q_\beta}{\left|\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}\right|}$$

Note – this works for CsCl and more generally

$$\frac{W}{N} = \frac{1}{8\pi\epsilon_0} \sum_{\alpha,\beta,\mathbf{T}}' \frac{q_\alpha q_\beta}{|\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}|} = w_1 + w_2$$

$$w_2 \equiv \frac{1}{8\pi\epsilon_0} \sum_{\alpha,\beta,\mathbf{T}}' \frac{q_\alpha q_\beta \ \mathrm{erfc}\left(\frac{1}{2}\sqrt{\eta}\,|\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}|\right)}{|\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}|} \equiv \frac{e^2}{8\pi\epsilon_0}\mathcal{I}_2$$

For CsCl:

$$\tau_{\mathrm{Cs}} = 0 \text{ and } \tau_{\mathrm{Cl}} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}).$$

q_{Cs}=e

q_{Cl}=-e

$$\mathbf{T}_1 = \mathrm{a}\hat{\mathbf{x}} \quad \mathbf{T}_2 = \mathrm{a}\hat{\mathbf{y}} \quad \mathbf{T}_3 = \mathrm{a}\hat{\mathbf{z}}.$$

$$\mathcal{T}_2 \equiv \sum_{\mathbf{T}\neq\mathbf{0}} 2\frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\mathbf{T}|)}{|\mathbf{T}|} - \sum_{\mathbf{T}} 2\frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\tau_{\mathrm{Cl}} + \mathbf{T}|)}{|\tau_{\mathrm{Cl}} + \mathbf{T}|}.$$

For evaluating the summation in reciprocal space, additional considerations are needed --

It can be shown that --

$$\sum_{\mathbf{T}} \delta^3(\mathbf{r}-\mathbf{T}) = \frac{1}{\Omega}\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}},$$

Volume of unit cell in real space

In this discussion, will assume we have a 3-dimensional periodic system. It can be easily generalized to 1- or 2- dimensional systems. In general, a translation vector can be described a linear combination of the three primitive translation vectors $\mathbf{T_1}$, $\mathbf{T_2}$, and $\mathbf{T_3}$:

$$\mathbf{T} = n_1\mathbf{T_1} + n_2\mathbf{T_2} + n_3\mathbf{T_3}, \tag{12}$$

where $\{n_1, n_2, n_3\}$ are integers. Note that the unit cell volume Ω can be expressed in terms of the primitive translation vectors according to:

$$\Omega = |\mathbf{T_1}\cdot(\mathbf{T_2}\times\mathbf{T_3})|. \tag{13}$$

The reciprocal lattice vectors $\mathbf{G}$ can generally be written as a linear combination of the three primitive reciprocal lattice vectors $\mathbf{G_1}$, $\mathbf{G_2}$, and $\mathbf{G_3}$:

$$\mathbf{G} = m_1\mathbf{G_1} + m_2\mathbf{G_2} + m_3\mathbf{G_3}, \tag{14}$$

where $\{m_1, m_2, m_3\}$ are integers. The primitive reciprocal lattice vectors are determined from the primitive translation vectors according to the identities:

$$\mathbf{G_i} \cdot \mathbf{T_j} = 2\pi\delta_{\mathbf{ij}}. \tag{15}$$

Note that the "volume" of the primitive reciprocal lattice is given by

$$|\mathbf{G_1} \cdot (\mathbf{G_2} \times \mathbf{G_3})| = \frac{(2\pi)^3}{\Omega}. \tag{16}$$

Example --

CsCl structure

There are two kinds of sites – $\tau_{\mathrm{Cs}} = 0$ and $\tau_{\mathrm{Cl}} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$.

$$\mathbf{T_1} = \mathbf{a}\hat{\mathbf{x}} \quad \mathbf{T_2} = \mathbf{a}\hat{\mathbf{y}} \quad \mathbf{T_3} = \mathbf{a}\hat{\mathbf{z}}.$$

$$\mathbf{G_1} = \frac{2\pi}{\mathbf{a}}\hat{\mathbf{x}} \quad \mathbf{G_2} = \frac{2\pi}{\mathbf{a}}\hat{\mathbf{y}} \quad \mathbf{G_3} = \frac{2\pi}{\mathbf{a}}\hat{\mathbf{z}}.$$

"Proof" of identity --

Consider the geometric series

$$\sum_{k=-M}^{+M} e^{ik(\mathbf{G_1}\cdot\mathbf{r})} = \frac{\sin\left((M+\frac{1}{2})\mathbf{G_1}\cdot\mathbf{r}\right)}{\sin(\mathbf{G_1}\cdot\mathbf{r/2})}. \qquad (17)$$

The behavior of the right hand side of Eq. (17) is that it is small in magnitude very except when the denominator vanishes. This occurs whenever $\mathbf{G_1}\cdot\mathbf{r/2} = \mathbf{n_1}\pi$, where n_1 represents any integer. If we take the limit $M \rightarrow \infty$, we find that the function represents the behavior of a sum of delta functions:

$$\lim_{M\rightarrow\infty} \frac{\sin\left((M+\frac{1}{2})\mathbf{G_1}\cdot\mathbf{r}\right)}{\sin(\mathbf{G_1}\cdot\mathbf{r}/2)} = 2\pi \sum_{n_1} \delta(\mathbf{G_1}\cdot(\mathbf{r}-\mathbf{n_1 T_1}). \qquad (18)$$

The summation over all lattice translations $n_1\mathbf{T_1}$ is due to the fact that $\sin(\mathbf{G_1}\cdot\mathbf{r}/2) = 0$ whenever $\mathbf{r} = \mathbf{n_1 T_1}$. Carrying out the geometric summations in the right hand side of Eq. 7 for all three reciprocal lattice vectors and taking the limit as in Eq. 18,

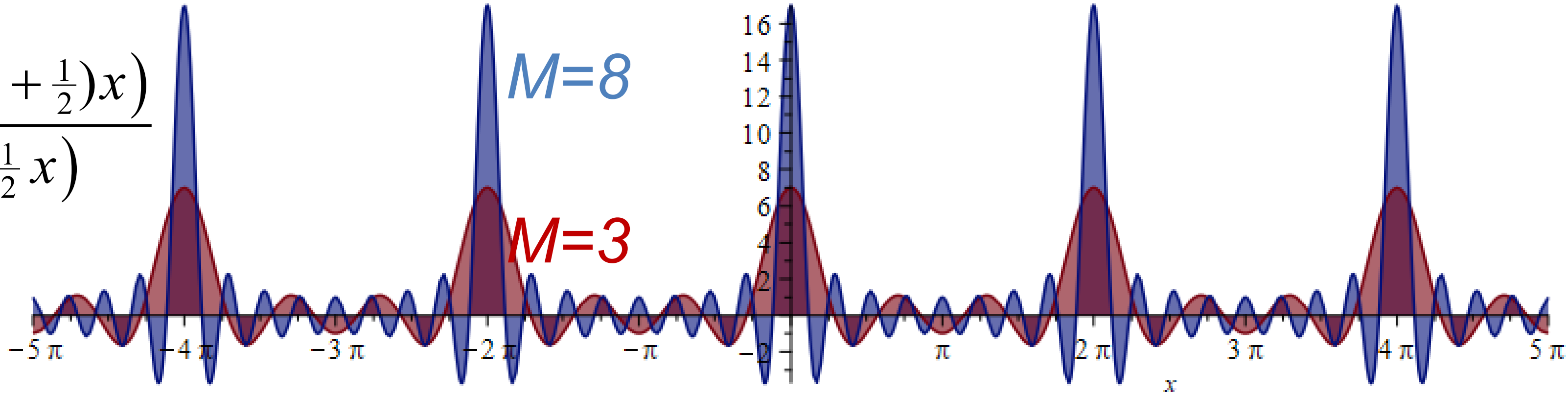
$$\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} = (2\pi)^3 \sum_{n_1,n_2,n_3} \delta(\mathbf{G_1}\cdot(\mathbf{r}-\mathbf{n_1T_1}))\delta(\mathbf{G_2}\cdot(\mathbf{r}-\mathbf{n_2T_2}))\delta(\mathbf{G_3}\cdot(\mathbf{r}-\mathbf{n_3T_3})). \qquad (19)$$

Some details --

$$\sum_{k=-M}^{+M} e^{ik(\mathbf{G_1}\cdot\mathbf{r})} = \frac{\sin\left((M+\frac{1}{2})\mathbf{G_1}\cdot\mathbf{r}\right)}{\sin(\mathbf{G_1}\cdot\mathbf{r}/2)}.$$

Behavior of function for various values of *M*:

$$\frac{\sin\left((M+\frac{1}{2})x\right)}{\sin\left(\frac{1}{2}x\right)}$$



Final result --

$$\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} = \frac{(2\pi)^3}{|\mathbf{G_1}\cdot(\mathbf{G_2}\times\mathbf{G_3})|}\sum_{\mathbf{T}} \delta^3(\mathbf{r}-\mathbf{T}) = \Omega\sum_{\mathbf{T}} \delta^3(\mathbf{r}-\mathbf{T})$$

$$\sum_{\mathbf{T}} \delta^3(\mathbf{r}-\mathbf{T}) = \frac{1}{\Omega}\sum_{\mathbf{G}} \mathrm{e}^{i\mathbf{G}\cdot\mathbf{r}},$$

$$\frac{W}{N}=\frac{1}{8\pi\epsilon_0}\sum_{\alpha,\beta,\mathbf{T}}{}' \frac{q_\alpha q_\beta}{\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|}=w_1+w_2$$

$$w_1\equiv\frac{1}{8\pi\epsilon_0}\sum_{\alpha,\beta,\mathbf{T}}{}' \frac{q_\alpha q_\beta\ \mathrm{erf}\left(\frac{1}{2}\sqrt{\eta}\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|\right)}{\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|}\equiv\frac{e^2}{8\pi\epsilon_0}\mathcal{T}_1$$

$$\sum_{\alpha,\beta,\mathbf{T}}{}' \frac{q_\alpha q_\beta\ \mathrm{erf}\left(\frac{1}{2}\sqrt{\eta}\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|\right)}{\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|}$$

$$=\sum_{\alpha,\beta}\left(\sum_{\mathbf{T}}\frac{q_\alpha q_\beta\ \mathrm{erf}\left(\frac{1}{2}\sqrt{\eta}\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|\right)}{\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|}-\delta_{\alpha\beta}q_\alpha^2\lim_{x\to 0}\left(\frac{\mathrm{erf}\left(\frac{1}{2}\sqrt{\eta}x\right)}{x}\right)\right)$$

$$\lim_{x\to 0}\left(\frac{\mathrm{erf}\left(\frac{1}{2}\sqrt{\eta}x\right)}{x}\right)=\sqrt{\frac{\eta}{\pi}}$$

$$\sum_{\mathbf{T}} \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\tau_{\alpha\beta}+\mathbf{T}|)}{|\tau_{\alpha\beta}+\mathbf{T}|} = \int d^3r \sum_{\mathbf{T}} \delta^3(\mathbf{r}-\mathbf{T}) \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\tau_{\alpha\beta}+\mathbf{r}|)}{|\tau_{\alpha\beta}+\mathbf{r}|}$$

$$\frac{1}{\Omega}\sum_{\mathbf{G}} \int d^3r e^{i\mathbf{G}\cdot\mathbf{r}} \frac{\mathrm{erf}(\frac{1}{2}\sqrt{\eta}|\tau_{\alpha\beta}+\mathbf{r}|)}{|\tau_{\alpha\beta}+\mathbf{r}|} =$$

$$\frac{4\pi}{\Omega}\left(\sum_{\mathbf{G}\neq 0} \frac{e^{-i\mathbf{G}\cdot\tau_{\alpha\beta}}\ e^{-G^2/\eta^2}}{G^2} + \frac{1}{2}\int_0^{\frac{1}{2}\sqrt{\eta}} \frac{du}{u^3}\right)$$

divergent results

Derivation includes :

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

Summary --

$$\sum_{\alpha,\beta,\mathbf{T}}{}' \frac{q_\alpha q_\beta \ \mathrm{erf}\left(\frac{1}{2}\sqrt{\eta}\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|\right)}{\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|}$$

$$=\sum_{\alpha,\beta}\left(\sum_{\mathrm{T}} \frac{q_\alpha q_\beta \ \mathrm{erf}\left(\frac{1}{2}\sqrt{\eta}\left|\tau_{\alpha\beta}+\mathrm{T}\right|\right)}{\left|\tau_{\alpha\beta}+\mathrm{T}\right|} - \delta_{\alpha\beta} q_\alpha^2 \sqrt{\frac{\eta}{\pi}}\right)$$

$$=\sum_{\alpha,\beta} q_\alpha q_\beta \left(\frac{4\pi}{\Omega}\sum_{\mathbf{G}\neq 0}\frac{e^{-i\mathbf{G}\cdot\tau_{\alpha\beta}} \ e^{-G^2/\eta}}{G^2} + \frac{4\pi}{\Omega}\int_0^{\frac{1}{2}\sqrt{\eta}}\frac{du}{u^3} - \delta_{\alpha\beta} q_\alpha^2 \sqrt{\frac{\eta}{\pi}}\right)$$

Divergent term

Note that for a neutral system

$\sum_{\alpha,\beta} q_\alpha q_\beta = 0$ and divergent term vanishes

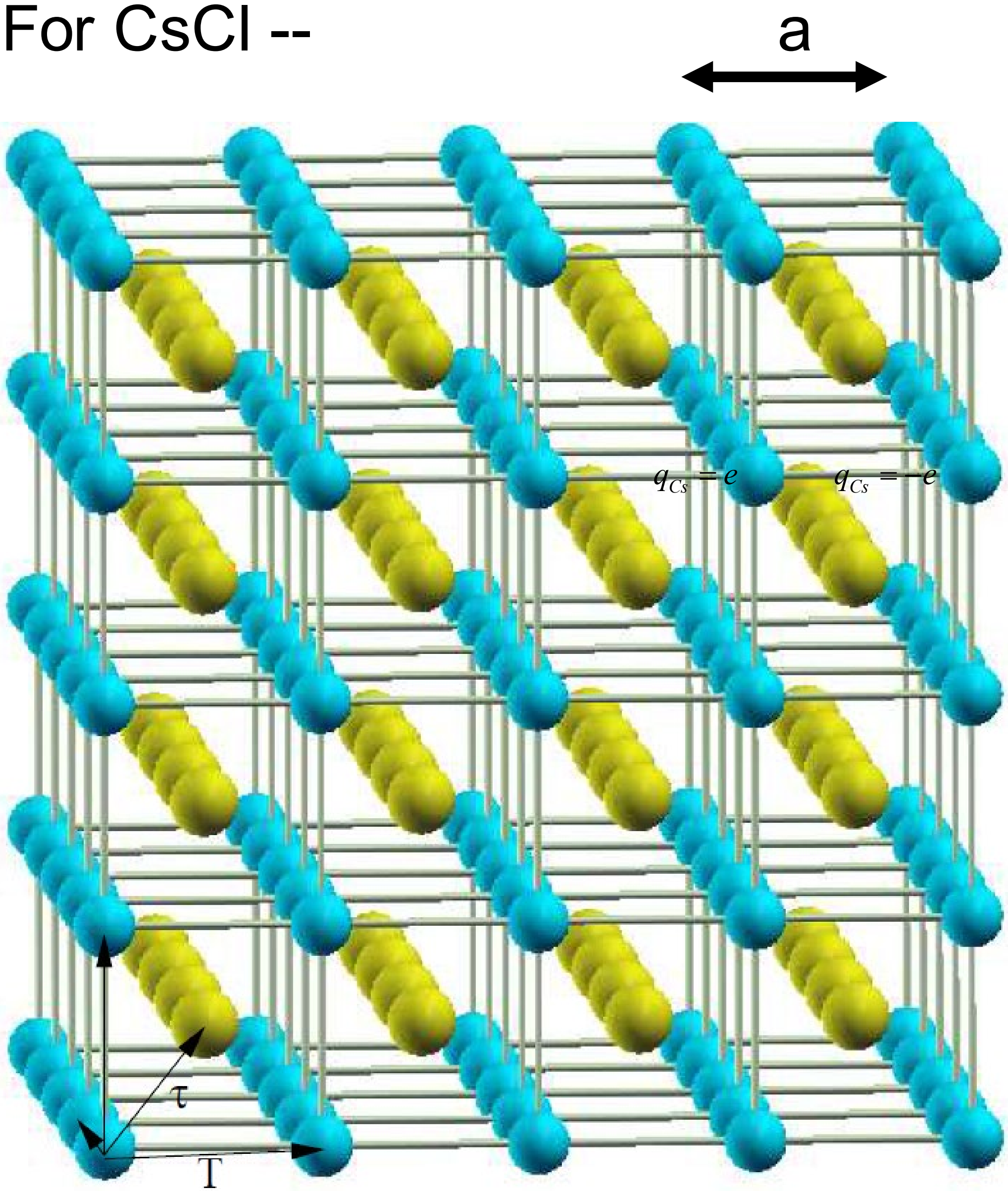
Problem – Electrostatic energy of a periodic non-neutral system is not defined!

Solution -- Add uniform compensating charge and find the electrostatic energy of periodic neutral system, carefully analyzing diverging terms to determine a convergent expression.

$$\frac{W}{N} = \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{8\pi\varepsilon_0} \left(\frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{e^{-i\mathbf{G}\cdot\tau_{\alpha\beta}}\ e^{-G^2/\eta}}{G^2} - \sqrt{\frac{\eta}{\pi}}\delta_{\alpha\beta} + \sum_{\mathbf{T}}{}' \frac{\operatorname{erfc}(\frac{1}{2}\sqrt{\eta}|\tau_{\alpha\beta} + \mathbf{T}|)}{|\tau_{\alpha\beta} + \mathbf{T}|} \right) - \frac{4\pi Q^2}{8\pi\varepsilon_0 \Omega\eta}$$

Where $Q \equiv \sum_\alpha q_\alpha$

For CsCl --



$$\tau_{\mathrm{Cs}} = 0 \text{ and } \tau_{\mathrm{Cl}} = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}).$$

$$\mathbf{T_1} = \mathbf{a}\hat{\mathbf{x}} \quad \mathbf{T_2} = \mathbf{a}\hat{\mathbf{y}} \quad \mathbf{T_3} = \mathbf{a}\hat{\mathbf{z}}.$$

$$q_{Cs} = e \qquad\qquad q_{Cl} = -e$$

$$\frac{W}{N} = \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{8\pi\varepsilon_0} \left(\frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq 0} \frac{e^{-i\mathbf{G}\cdot\tau_{\alpha\beta}} \; e^{-G^2/\eta}}{G^2} - \sqrt{\frac{\eta}{\pi}}\delta_{\alpha\beta} + \sum_{\mathbf{T}}{}' \frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\tau_{\alpha\beta} + \mathbf{T}|)}{|\tau_{\alpha\beta} + \mathbf{T}|} \right) - \frac{4\pi Q^2}{8\pi\varepsilon_0 \Omega \eta}$$

$$\frac{W}{N} = \frac{e^2}{8\pi\epsilon_0}\left(\mathcal{T}_1 + \mathcal{T}_2\right)$$

$$\mathcal{T}_1 \equiv \frac{4\pi}{\Omega} \sum_{\mathbf{G}\neq 0} 2\frac{(1 - e^{i\mathbf{G}\cdot\tau_{\mathrm{Cl}}})e^{-|\mathbf{G}|^2/\eta}}{|\mathbf{G}|^2} - 2\sqrt{\frac{\eta}{\pi}}$$

$$\mathcal{T}_2 \equiv \sum_{\mathbf{T}\neq 0} 2\frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\mathbf{T}|)}{|\mathbf{T}|} - \sum_{\mathbf{T}} 2\frac{\mathrm{erfc}(\frac{1}{2}\sqrt{\eta}|\tau_{\mathrm{Cl}} + \mathbf{T}|)}{|\tau_{\mathrm{Cl}} + \mathbf{T}|}$$

➔Can be evaluated using Maple or Mathematica or other programming language