PHY 712 Electrodynamics
10-10:50 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**

Course schedule for Spring 2025

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	JDJ Reading	Topic	HW	Due date
1	Mon: 01/13/2025	Chap. 1 & Appen.	Introduction, units and Poisson equation	#1	01/15/2025
2	Wed: 01/15/2025	Chap. 1	Electrostatic energy calculations	#2	01/17/2025
3	Fri: 01/17/2025	Chap. 1	Electrostatic energy calculations	#3	01/22/2025
	Mon: 01/20/2025	No Class	Martin Luther King Jr. Holiday		

PHY 712 – Problem Set #3

Assigned: 01/17/2025   Due: 01/22/2025

Continue reading Chapters I in **Jackson**. Complete **one** of the following problems. (Extra credit for completing both.)

1. Calculate and numerically evaluate the electrostatic energy of the following 5 ion molecule, scaling your result by the factor

$$\frac{1}{4\pi\varepsilon_0}\frac{q^2}{a}.$$

   Comment on the significance of the sign of your result. Note that $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ denote unit vectors in the three Cartesian directions.

   - Charge $= -4q$ Position $= 0$
   - Charge $= q$ Position $= (a/2)(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$
   - Charge $= q$ Position $= (a/2)(-\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})$
   - Charge $= q$ Position $= (a/2)(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}})$
   - Charge $= q$ Position $= (a/2)(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$

2. 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.

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:

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

Must be evaluated in "reciprocal" space

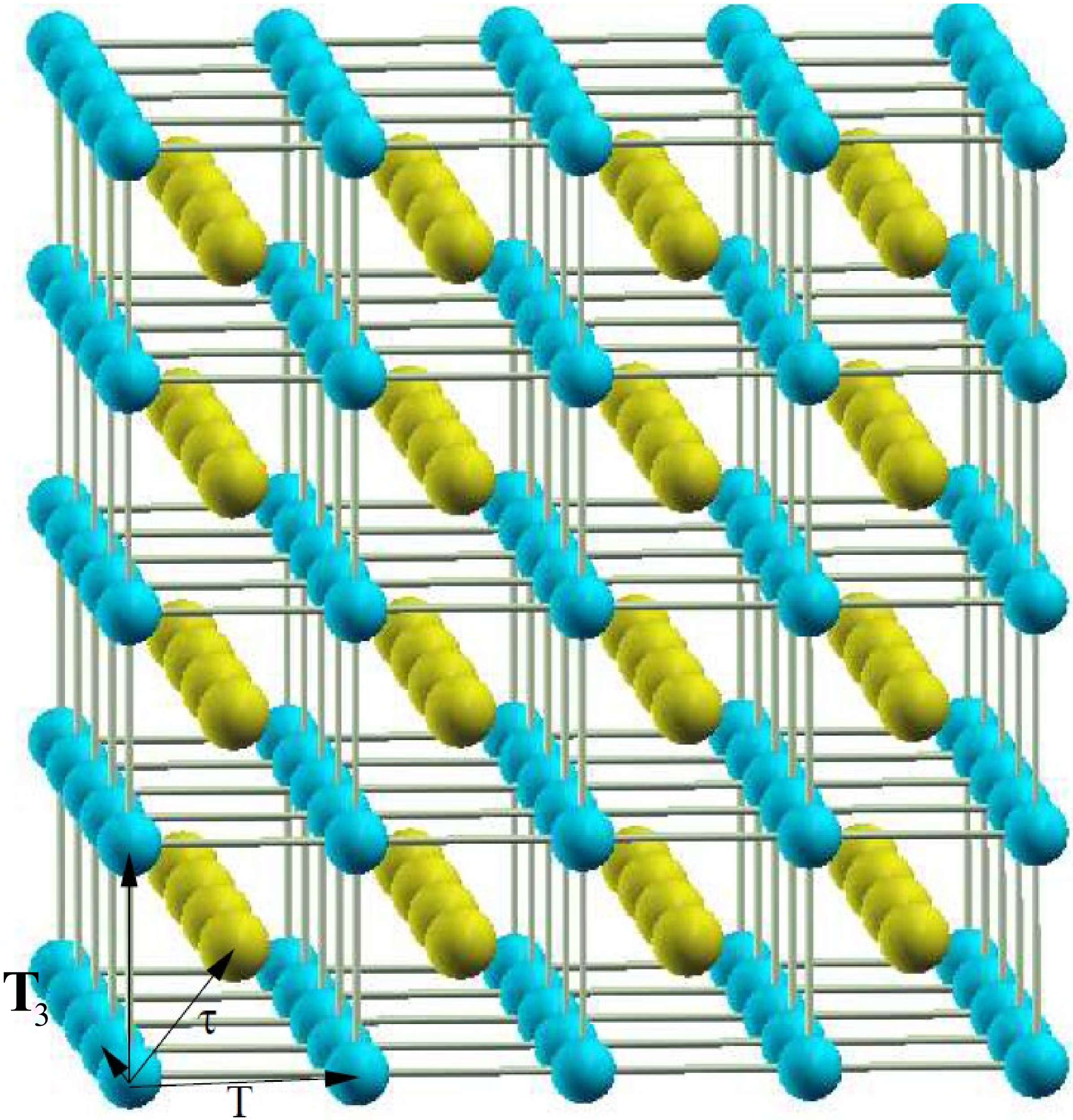
Can be converged as is (in real space)

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



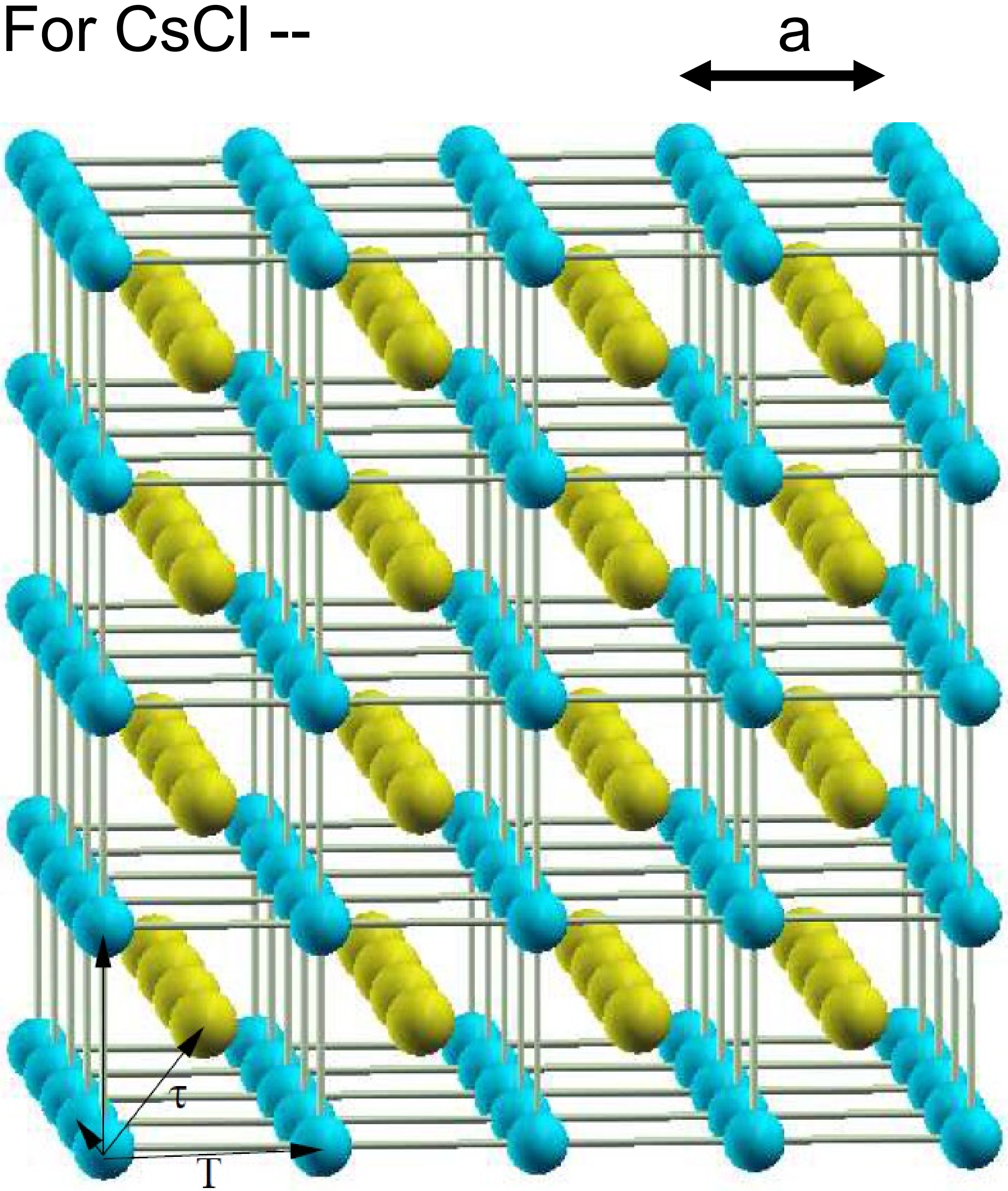
Notice that a unit cell contains one Cl and one Cs

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

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 --



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

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

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

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

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

For CsCl:

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

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

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

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

For evaluating w_1 which needs to be evaluated 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:

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

Preview – what happens if $\sum_{\mathbf{T}} \delta^3(\mathbf{r}-\mathbf{T}) = \frac{1}{\Omega}\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}},$ is true?

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

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

$$= \frac{1}{8\pi\epsilon_0}\left(\sum_{\alpha,\beta,\mathbf{T}} \frac{q_\alpha q_\beta \ \mathrm{erf}\left(\frac{1}{2}\sqrt{\eta}\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|\right)}{\left|\boldsymbol{\tau}_{\alpha\beta}+\mathbf{T}\right|} - \sqrt{\frac{\eta}{\pi}}\sum_{\alpha} q_\alpha^2\right)$$

Subtract out self-energy contribution

Continued --

Preview – what happens if
is true?

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

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

This becomes,

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

where the last term, which is infinite, comes from the $\mathbf{G}=\mathbf{0}$ contribution.

Back to "proof" --

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

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

CsCl structure

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

Example --

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

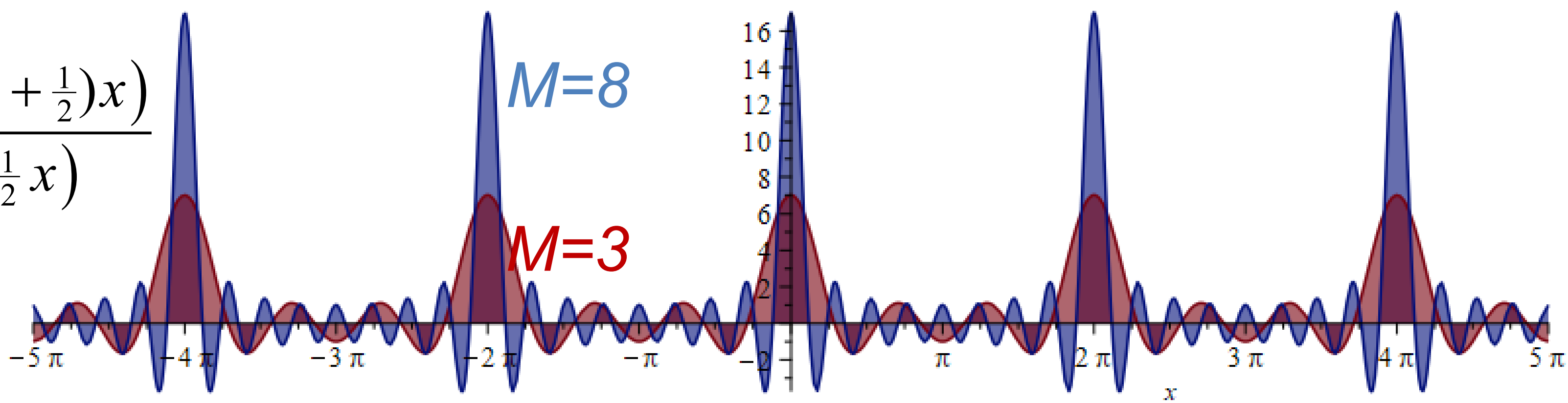
$$\mathbf{G_1} = \frac{\mathbf{2}\pi}{\mathbf{a}}\hat{\mathbf{x}} \quad \mathbf{G_2} = \frac{\mathbf{2}\pi}{\mathbf{a}}\hat{\mathbf{y}} \quad \mathbf{G_3} = \frac{\mathbf{2}\pi}{\mathbf{a}}\hat{\mathbf{z}}.$$

Consider the summation;

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

Behavior of function for various values of *M*:

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



$x = \mathbf{G}_1 \cdot \mathbf{r}$

$\sum_{k=-M}^{M} e^{ikx}$ has large peaks at $x =$ multiples of 2π

“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 $M \to \infty$, we find that the function represents the behavior of a sum of delta functions:

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

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 $\mathbf{r} = \mathbf{n_1}\mathbf{T}_1$. 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,

$$\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} = (2\pi)^3 \sum_{n_1,n_2,n_3} \delta(\mathbf{G_1}\cdot(\mathbf{r}-\mathbf{n_1}\mathbf{T_1}))\delta(\mathbf{G_2}\cdot(\mathbf{r}-\mathbf{n_2}\mathbf{T_2}))\delta(\mathbf{G_3}\cdot(\mathbf{r}-\mathbf{n_3}\mathbf{T_3})). \qquad (19)$$

Final result --

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

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

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

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

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

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

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

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

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

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

divergent results

Derivation includes :

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

+ appropriate changes of variables and order of integration

Summary --

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

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

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

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.

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

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

Some details

$$\frac{W'}{N} = \frac{1}{8\pi\epsilon_0}\left(\sum_{\alpha,\beta,\mathbf{T}} \frac{q_\alpha q_\beta}{\left|\boldsymbol{\tau}_{\alpha\beta} + \mathbf{T}\right|} - \sum_\alpha q_\alpha \frac{Q}{\Omega} 4\pi \int_0^\infty \frac{r^2}{r} dr \right)$$

$$-\sum_\alpha q_\alpha \frac{Q}{\Omega} 4\pi \int_0^\infty \frac{r^2}{r} dr = -\frac{4\pi Q^2}{\Omega} \int_0^\infty r dr = -\frac{4\pi Q^2}{\Omega} \int_0^\infty \frac{du}{u^3}$$

$$= -\frac{4\pi Q^2}{\Omega}\left(\int_0^{\sqrt{\eta}/2} \frac{du}{u^3} + \int_{\sqrt{\eta}/2}^\infty \frac{du}{u^3} \right)$$

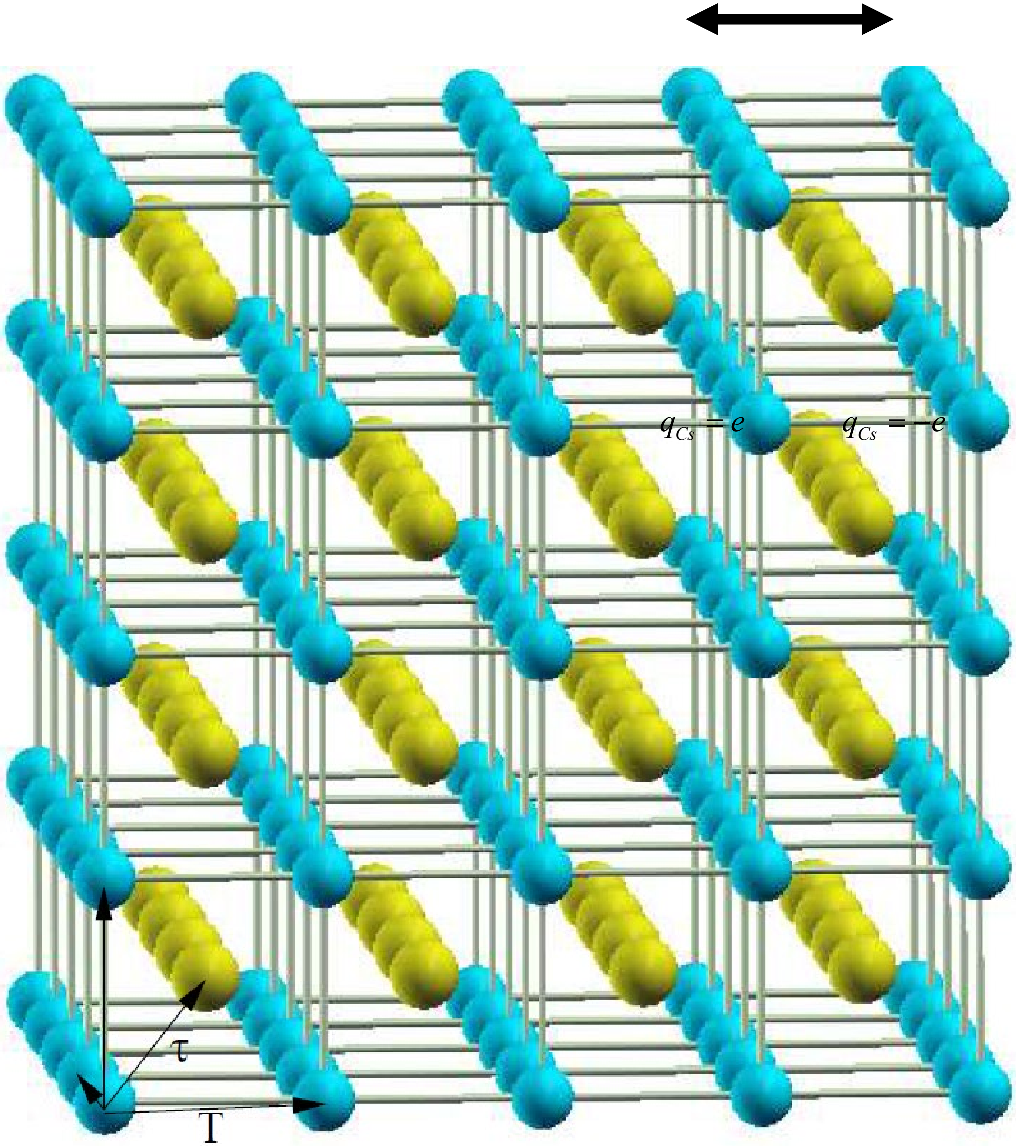
$$= -\frac{4\pi Q^2}{\Omega}\left(\int_0^{\sqrt{\eta}/2} \frac{du}{u^3} + \frac{2}{\eta} \right)$$

Cancels divergence

Extra contribution

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

For CsCl --



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

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

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

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

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

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

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

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

Using Maple example, we find that for a CsCl lattice constant a :

$$\frac{W}{N} = \frac{e^2}{8\pi\epsilon_0 a}\left(-4.0707\right)$$

This result is consistent with the Madelung constant.

The Madelung constant is referenced in many textbooks as:

$$\frac{W}{N} = -\frac{q^2}{4\pi\varepsilon_0}\left(\frac{\alpha}{R}\right) \qquad \text{where } R \equiv \text{ nearest neighbor separation}$$

From Kittel's textbook:

For NaCl α= 1.747565
CsCl α= 1.762675
ZnS α= 1.6381