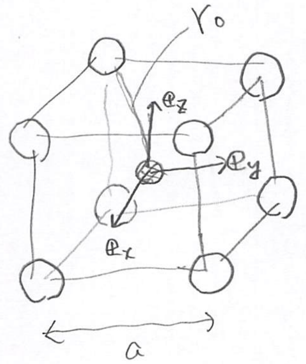
CsCl のマーデルング定数を求める.



$$|\mathbf{e}_x| = |\mathbf{e}_y| = |\mathbf{e}_z| = \frac{r_0}{\sqrt{3}} = \frac{a}{2}.$$

1. 座標変換

$$\begin{cases} \mathbf{e}_{x'} = -\mathbf{e}_x + \mathbf{e}_y + \mathbf{e}_z \\ \mathbf{e}_{y'} = +\mathbf{e}_x - \mathbf{e}_y + \mathbf{e}_z \\ \mathbf{e}_{z'} = +\mathbf{e}_x + \mathbf{e}_y - \mathbf{e}_z \end{cases}$$

$$|\mathbf{e}_{x'}|^2 = |\mathbf{e}_{y'}|^2 = |\mathbf{e}_{z'}|^2 = 3.$$

$$\mathbf{e}_{x'} \cdot \mathbf{e}_{y'} = \mathbf{e}_{y'} \cdot \mathbf{e}_{z'} = \mathbf{e}_{x'} \cdot \mathbf{e}_{z'} = -1.$$

$$\begin{cases} 2\mathbf{e}_x = \mathbf{e}_{y'} + \mathbf{e}_{z'} \\ 2\mathbf{e}_y = \mathbf{e}_{x'} + \mathbf{e}_{z'} \\ 2\mathbf{e}_z = \mathbf{e}_{x'} + \mathbf{e}_{y'} \end{cases}$$

$$\begin{aligned} |\mathbf{r}|^2 &= |x'\mathbf{e}_{x'} + y'\mathbf{e}_{y'} + z'\mathbf{e}_{z'}|^2 \\ &= 3(x'^2 + y'^2 + z'^2) - 2(x'y' + y'z' + x'z') \end{aligned}$$

2．各イオンはプライム系でどこにいるか．

• プライムなし系では．

x, y, z 座標がすべて奇数 → マイナス電荷（注目イオンと異符号）

x, y, z 座標がすべて偶数 → プラス電荷

• プライム系で

マイナス：

$$\mathbb{r} = (2l-1)\mathbb{e}_x + (2m-1)\mathbb{e}_y + (2n-1)\mathbb{e}_z$$

$$= (2l-1)\frac{1}{2}(\mathbb{e}_{y'} + \mathbb{e}_{z'}) + (2m-1)\frac{1}{2}(\mathbb{e}_{x'} + \mathbb{e}_{z'}) + (2n-1)\frac{1}{2}(\mathbb{e}_{x'} + \mathbb{e}_{y'})$$

$$= (m+n-1)\mathbb{e}_{x'} + (l+n-1)\mathbb{e}_{y'} + (l+m-1)\mathbb{e}_{z'}$$

$$\Rightarrow \begin{aligned} x' &= m+n-1 \\ y' &= l+n-1 \\ z' &= l+m-1 \end{aligned} \quad \Rightarrow \quad \begin{aligned} 2l &= -x+y+z+1 \\ 2m &= x-y+z+1 \\ 2n &= x+y-z+1 \end{aligned}$$

⇓

x', y', z' がすべて奇数 or 1コ奇数，2コ偶数

プラス

$$\mathbb{r} = 2l\mathbb{e}_x + 2m\mathbb{e}_y + 2n\mathbb{e}_z$$

$$= l(\mathbb{e}_{y'} + \mathbb{e}_{z'}) + m(\mathbb{e}_{x'} + \mathbb{e}_{z'}) + n(\mathbb{e}_{x'} + \mathbb{e}_{y'})$$

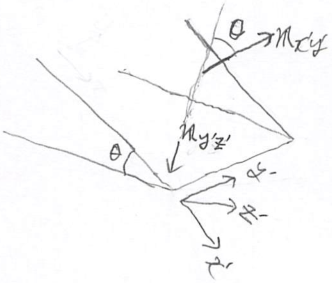
$$= (m+n)\mathbb{e}_{x'} + (l+n)\mathbb{e}_{y'} + (l+m)\mathbb{e}_{z'}$$

$$\Rightarrow \begin{aligned} x' &= m+n \\ y' &= l+n \\ z' &= l+m \end{aligned} \quad \Rightarrow \quad \begin{aligned} 2l &= -x+y+z \\ 2m &= x-y+z \\ 2n &= x+y-z \end{aligned}$$

⇓

x', y', z' がすべて偶数 or 1コ偶数，2コ奇数．

3. 末端の処理

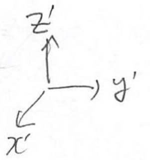


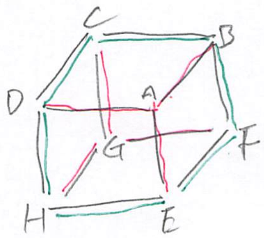
$x'y'$面と $y'z'$面の法ベクトル $n_{x'y'}$, $n_{y'z'}$ を求める

$$
\begin{aligned}
n_{x'y'} &= e_{x'} \times e_{y'} \\
&= (-e_x + e_y + e_z) \times (e_x - e_y + e_z) \\
&= \cancel{e_x \times e_y} - e_x \times e_z + \cancel{e_y \times e_x} + e_y \times e_z + e_z \times e_x - e_z \times e_y \\
&= -2\, e_x \times e_z + 2\, e_y \times e_z \\
&= 2(e_y - e_z)
\end{aligned}
$$

$$
\begin{aligned}
n_{y'z'} &= e_{y'} \times e_{z'} \\
&= (e_x - e_y + e_z) \times (e_x + e_y - e_z) \\
&= e_x \times e_y - e_x \times e_z - e_y \times e_x + \cancel{e_y \times e_z} + e_z \times e_x + \cancel{e_z \times e_y} \\
&= 2\, e_x \times e_y - 2\, e_x \times e_z \\
&= 2(e_y + e_z)
\end{aligned}
$$

$$
\begin{aligned}
n_{z'x'} &= e_{z'} \times e_{x'} \\
&= (e_x + e_y - e_z) \times (-e_x + e_y + e_z) \\
&= e_x \times e_y + \cancel{e_x \times e_z} - e_y \times e_x + e_y \times e_z + \cancel{e_z \times e_x} - e_z \times e_y \\
&= 2\, e_x \times e_y + 2\, e_y \times e_z \\
&= 2(e_x + e_z)
\end{aligned}
$$





$$\left\{\begin{aligned}
\cos\theta_{AB} &= -\frac{1}{8}\, n_{x'y'}\cdot n_{z'x'} = -\frac{1}{8}\cdot 4\,(e_y - e_z)\cdot(e_x + e_z) = +\frac{1}{2} \\
\cos\theta_{AE} &= -\frac{1}{8}\, n_{z'x'}\cdot n_{y'z'} = -\frac{1}{2} \\
\cos\theta_{AD} &= -\frac{1}{8}\, n_{x'y'}\cdot n_{y'z'} = 0 \\
\theta_{AB} &= \theta_{GH},\quad \theta_{AE} = \theta_{CG},\quad \theta_{AD} = \theta_{FG}
\end{aligned}\right.$$

$$\left\{\begin{aligned}
\cos\theta_{BC} &= -\frac{1}{8}\,(-n_{y'z'})\cdot n_{x'y'} = 0 \\
\cos\theta_{CD} &= -\frac{1}{8}\,(-n_{z'x'})\cdot n_{x'y'} = -\frac{1}{2} \quad \rightarrow 120^\circ \\
\cos\theta_{DH} &= -\frac{1}{8}\, n_{y'z'}\cdot(-n_{z'x'}) = \frac{1}{2} \quad \rightarrow 60^\circ \\
\theta_{BC} &= \theta_{EH},\quad \theta_{CD} = \theta_{EF},\quad \theta_{DH} = \theta_{BF}
\end{aligned}\right.$$

頂点の立体角.

$$\Omega_A = \Omega_G = \theta_{AB} + \theta_{AD} + \theta_{AE} - \pi = \frac{\pi}{3} + \frac{\pi}{2} + \frac{2}{3}\pi - \pi = \frac{\pi}{2}$$

$$\Omega_B = \Omega_H = \theta_{AB} + \theta_{BC} + \theta_{DF} - \pi = \frac{1}{3}\pi + \frac{\pi}{2} + \frac{1}{3}\pi - \pi = \frac{\pi}{6}$$

$$\Omega_D = \Omega_F = \theta_{AD} + \theta_{CD} + \theta_{DH} - \pi = \frac{\pi}{2} + \frac{2}{3}\pi + \frac{1}{3}\pi - \pi = \frac{\pi}{2}$$

$$\Omega_E = \Omega_C = \theta_{AE} + \theta_{EF} + \theta_{EH} = \frac{2}{3}\pi + \frac{2}{3}\pi + \frac{\pi}{2} - \pi = \frac{4+4+3-6}{6}\pi = \frac{5}{6}\pi$$

4 結果

3×3×3	1.608600
5×5×5	1.822236
7×7×7	1.801646
9×9×9	1.803670
11×11×11	1.803144
13×13×13	1.803381
15×15×15	1.803253
17×17×17	1.803329
19×19×19	1.803281
21×21×21	1.803313
201	1.803300
801	1.803300