## Appendix 4: A brief summary of statistical physics

- **Particle distinguishability**:
  - Particles are distinguishable if they are not **identical**. e.g. electron and proton in an atom are distinguishable .
  - Identical particles are distinguishable if they are clearly separated.
  - Identical particles are indistinguishable if their separations are comparable with their deBroglie wavelengths, with significant overlapping wavefunctions, e.g. electrons in an atom.
- **(A) Classical statistics: Maxwell-Boltzmann distribution** (for a system of distinguishable particles, e.g. ideal gas of molecules) (follows from the second law of thermodynamics): probability that a molecule is in a state of energy $E$ is

$$f_{MB}(E) \sim e^{-E/k_BT}$$

**(B) Quantum statistics:**

- **Fermi-Dirac distribution** for a system of indistinguishable fermions (particles with half-integer spin, e.g., electrons in solids, neutrons in neutron stars, etc.):

For fermions only one particle is allowed in each state.

The probability that a fermion is in a state of energy $E$ is

$$f_{FD}(E) = \frac{1}{e^{(E-E_F)/k_BT}+1}$$

where $E_F$ is the Fermi energy.
$E_F$ is related to particle density.

- **Bose-Einstein distribution** for a system of indistinguishable bosons (particles with integer spin, e.g. photons in black-body radiation, Cooper pairs in superconductors):

For bosons, any number of particles are allowed in each state. (**Bose-Einstein condensation)**

The probability that a boson is in a state of energy $E$ is

$$f_{BE}(E) = \frac{1}{e^{(E-\mu)/k_BT}-1}$$

where $\mu$ is the chemical potential.
For photons, $\mu = 0$.
Under certain conditions, fermions can pair up to form bosons and then condense.

- **Particles at high enough energy** (i.e., small deBroglie wavelengths) are distinguishable and thus all distributions are identical $\sim e^{-E/k_BT}$ .

## Appendix 5: Madelung constants of NaCl-type crystals

**1D chain**:

$$\alpha_{1D} = \lim_{N\to\infty}\left[-\sum_{\substack{n=-N\\ n\neq 0}}^{N}\frac{(-1)^n}{n}\right] = \lim_{N\to\infty}\left[-2\sum_{n=1}^{N}\frac{(-1)^n}{n}\right] = 2\ell n 2$$

**2D square**:

$$\alpha_{2D} = \lim_{N\to\infty}\left[-\sum_{\substack{n_1=-N\\(n_1,n_2)\neq(0,0)}}^{N}\sum_{n_2=-N}^{N}\frac{(-1)^{n_1+n_2}}{\sqrt{n_1^2+n_2^2}}\right] = \lim_{N\to\infty}\left[-4\sum_{n_1=0}^{N}\sum_{n_2=1}^{N}\frac{(-1)^{n_1+n_2}}{\sqrt{n_1^2+n_2^2}}\right]$$

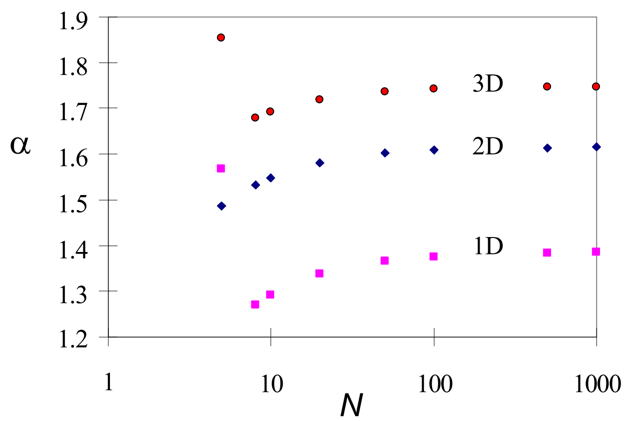
$$= 1.615$$

**3D NaCl**:

$$\alpha_{3D} = \lim_{N\to\infty}\left[-\sum_{n_1=-N}^{N}\sum_{\substack{n_2=-N\\(n_1,n_2,n_3)\neq(0,0,0)}}^{N}\sum_{n_3=-N}^{N}\frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2+n_2^2+n_3^2}}\right]$$

$$= \lim_{N\to\infty}\left[-2\sum_{n_1=-N}^{N}\sum_{n_2=-N}^{N}\sum_{n_3=1}^{N}\frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2+n_2^2+n_3^2}}\right] + \alpha_{2D} = 1.747$$

Numerical calculation using MathCad:
It indicates a slow convergence.

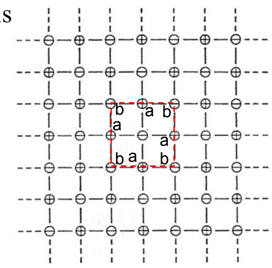



**Ewald-Evjen method**: (1932) for getting result quickly.

e.g. **2D square crystal.**

Consider **1st square in red:**

The ion **a** on the edge of the square is counted as **50%** inside and 50% outside the square.
So its contribution to Madelung constant is also 50%.
The ion **b** at the corner of the square is counted as **25%** inside and 75% outside.
∴ If we consider only the ions on & inside the square,



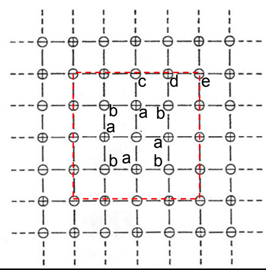

$$\alpha \approx -\left[-4(\frac{1}{2})(\frac{1}{1}) + 4(\frac{1}{4})(\frac{1}{\sqrt{2}})\right] = 1.29$$

Now consider a larger square & use the same method.
**2nd square**:
Ions **a** and **b** are now inside the square. So they are counted as 100%.
Ions **c**, **d** & **e** are counted as 50%, 50% & 25% respectively.

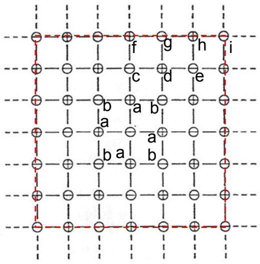
$$\therefore \quad \alpha \approx -\left[-4(1)(\frac{1}{1}) + 4(1)(\frac{1}{\sqrt{2}}) + 4(\frac{1}{2})(\frac{1}{2}) - 8(\frac{1}{2})(\frac{1}{\sqrt{5}}) + 4(\frac{1}{4})(\frac{1}{\sqrt{8}})\right]$$

$$= 1.606$$

Note: The total charge for the square is also zero if we use this counting method.



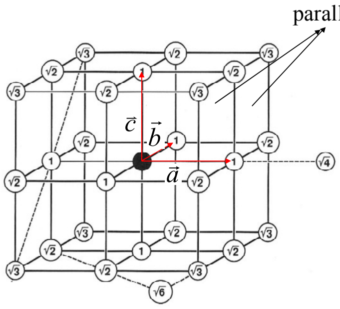
**3rd square**:
Ions **a**, **b**, **c**, **d** and **e** are now inside the square. So they are counted as 100%.
Ions **f**, **g**, **h** & **i** are counted as 50%, 50%, 50%, & 25% respectively.



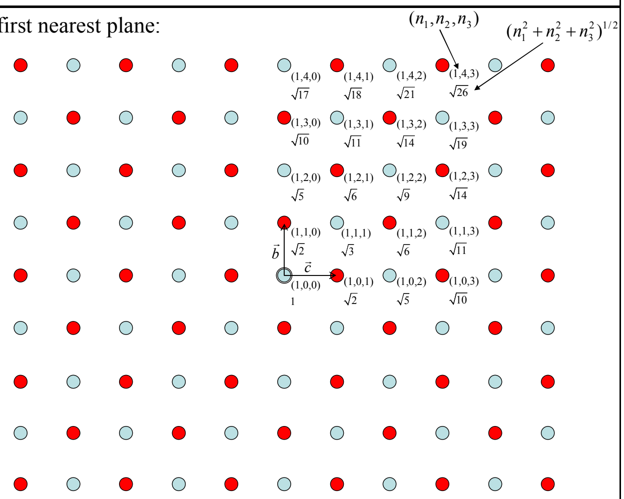

$$\therefore \quad \alpha \approx -[-4(1)(\frac{1}{1}) + 4(1)(\frac{1}{\sqrt{2}}) + 4(1)(\frac{1}{2}) - 8(1)(\frac{1}{\sqrt{5}}) + 4(1)(\frac{1}{\sqrt{8}}) - 4(\frac{1}{2})(\frac{1}{3}) + 8(\frac{1}{2})(\frac{1}{\sqrt{10}}) - 8(\frac{1}{2})(\frac{1}{\sqrt{13}}) + 4(\frac{1}{4})(\frac{1}{\sqrt{18}})]$$
$$= 1.610$$

**How to count the number of ions for each shell for the table in the notes?**

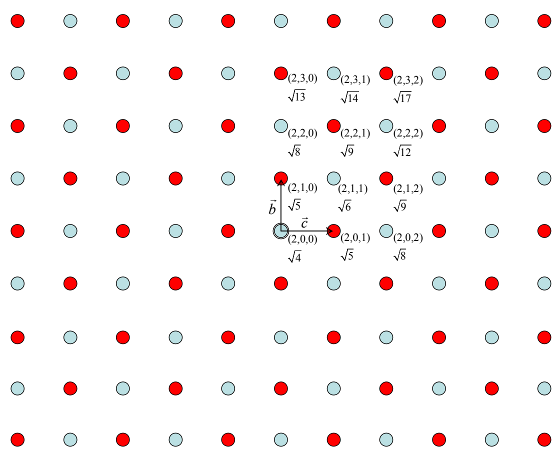
The first nearest plane parallel to $\vec{b}$ & $\vec{c}$




The first nearest plane:




The 2nd nearest plane:




The 1st shell: distance = $\sqrt{1}$
There are 3 types of ions:
$(n_1, n_2, n_3)$ = (1,0,0), (0,1,0), (0,0,1)
Consider (1,0,0) type as an example.
It has 2 combinations with (±1,0,0): (1,0,0), (-1,0,0),
Then in total, there are $(3)\times 2 = 6$ ions with distance = $\sqrt{1}$ .

The 2nd shell: distance = $\sqrt{2}$
There are 3 types of ions:
$(n_1, n_2, n_3)$ = (1,1,0), (1,0,1), (1,1,0)
Consider (1,1,0) type as an example.
It has 4 combinations with (±1,±1,0): (1,1,0), (1,-1,0), (-1,1,0), (-1,-1,0)
Then in total, there are $(3)\times 4 = 12$ ions with distance = $\sqrt{2}$.

The 8th shell: distance = $\sqrt{9}$
There are 6 types of ions:
$(n_1, n_2, n_3)$ = (2,2,1), (2,1,2), (1,2,2), (3,0,0), (0,3,0), (0,0,3)
Consider (2,2,1) type as an example.
It has 8 combinations with (±2, ±2, ±1): (2,2,1), (2,2,-1), (2,-2,1), (2,-2,-1), (-2,2,1), (-2,2,-1), (-2,-2,1), (-2,-2,-1).
For (3,0,0) type, there are only 2 combinations.
Then in total, there are $(2\times 2\times 2)\times 3 + 3\times 2 = 30$ ions with distance = $\sqrt{9}$ .

The 9th shell: distance = $\sqrt{10}$
There are 6 types of ions:
$(n_1, n_2, n_3)$ = (3,1,0), (3,0,1), (0,1,3), (0,3,1), (1,3,0), (1,0,3)
For each case there are 4 combinations.
Then in total, there are $(2\times 2)\times 6 = 24$ ions with distance = $\sqrt{10}$ .

We list the first 10 shells in the following table:

| $i$ | typical $n_1 n_2 n_3$ | number of ions ($N_i$) | $(n_1^2+n_2^2+n_3^2)^{1/2}$ | $\frac{(-1)^{n_1+n_2+n_3} N_i}{(n_1^2+n_2^2+n_3^2)^{1/2}}$ |
|---|---|---|---|---|
| 1 | 100 | 6 | $\sqrt{1}$ | −6.000 |
| 2 | 110 | 12 | $\sqrt{2}$ | +8.485 |
| 3 | 111 | 8 | $\sqrt{3}$ | −4.619 |
| 4 | 200 | 6 | $\sqrt{4}$ | +3.000 |
| 5 | 210 | 24 | $\sqrt{5}$ | −10.733 |
| 6 | 211 | 24 | $\sqrt{6}$ | +9.798 |
| 7 | 220 | 12 | $\sqrt{8}$ | +4.243 |
| 8 | 221, 300 | 30 | $\sqrt{9}$ | −10.000 |
| 9 | 310 | 24 | $\sqrt{10}$ | +7.589 |
| 10 | 311 | 24 | $\sqrt{11}$ | −7.236 |