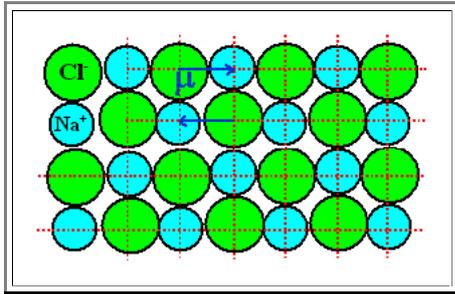


### 3.2.3 Ionic Polarization

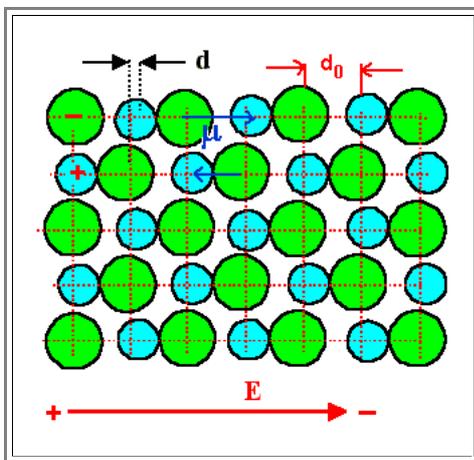
Consider a simple ionic crystal, e.g. **NaCl**.

- The lattice can be considered to consist of **Na<sup>+</sup> - Cl<sup>-</sup>** dipoles as shown below.



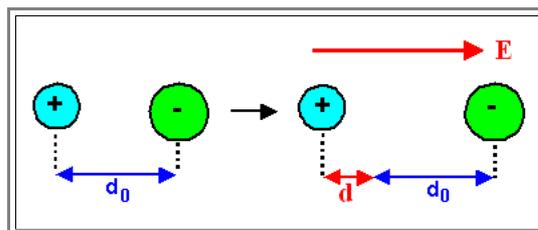
- Each **Na<sup>+</sup> - Cl<sup>-</sup>** pair is a *natural dipole*, no matter how you pair up two atoms.
- The polarization of a given volume, however, is *exactly zero* because for every dipole moment there is a neighboring one with exactly the same magnitude, but opposite sign.
- Note that the dipoles *can not rotate*; their direction is fixed.

In an electric field, the ions feel forces in opposite directions. For a field acting as shown, the lattice distorts a little bit (hugely exaggerated in the drawing)



- The **Na<sup>+</sup>** ions moved a bit to the right, the **Cl<sup>-</sup>** ions to the left.
- The dipole moments between adjacent **NaCl** - pairs in field direction are now different and there is a *net dipole moment* in a finite volume now.

From the picture it can be seen that it is sufficient to consider *one* dipole in field direction. We have the following situation:



- Shown is the situation where the distance between the ions *increases* by **d**; the symmetrical situation, where the distance *decreases* by **d**, is obvious.

How large is **d**? That is easy to calculate:

- The force **F<sub>1</sub>** increasing the distance is given by

$$F_1 = q \cdot E$$

- With **q** = net charge of the ion.

- The restoring force **F<sub>2</sub>** comes from the binding force, it is given as the derivative of the binding potential. Assuming a *linear relation* between binding force and deviation from the equilibrium distance **d<sub>0</sub>**, which is a good approximation for **d << d<sub>0</sub>**, we can write

$$F_2 = k_{\text{IP}} \cdot d$$

- With  $k_{\text{IP}}$  being the "*spring constant*" of the bond.  $k_{\text{IP}}$  can be calculated from the bond structure, it may also be expressed in terms of other constants that are directly related to the shape of the interatomic potential, e.g. the *modulus of elasticity* or *Youngs modulus*.
- If we do that we simply [find](#)

$$k_{\text{IP}} = Y \cdot d_0$$

- With  $Y$  = Youngs Modulus, and  $d_0$  = equilibrium distance between atoms.

From force equilibrium. i.e.  $F_1 - F_2 = 0$ , we immediately obtain the following relations:

- *Equilibrium distance*  $d$

$$d = \frac{q \cdot E}{Y \cdot d_0}$$

- *Induced dipole moment*  $\mu$  (on top of the existing one)

$$\mu = \frac{q^2 \cdot E}{Y \cdot d_0}$$

- *Polarization*  $P$

$$P = \frac{N \cdot q^2 \cdot E}{Y \cdot d_0}$$

Of course, this is only a very rough approximation for an *idealized* material and just for the case of increasing the distance. Adding up the various moments - some larger, some smaller - will introduce a factor **2** or so; but here we only go for the principle.

For *real* ionic crystals we also may have to consider:

- More complicated geometries (e.g. **CaF<sub>2</sub>**, with ions carrying different amount of charge).
- This example was deliberately chosen: The dielectric constant of **CaF<sub>2</sub>** is of paramount interest to the semiconductor industry of the **21st** century, because **CaF<sub>2</sub>** is pretty much the only usable material with an index of refraction  $n$  ([which is directly tied to the DK](#) via  $\epsilon_r = n^2$ ) that can be used for making lenses for lithography machines enabling dimensions of about **0,1  $\mu\text{m}$** .
- If the field is not parallel to a major axis of the crystal (this is automatically the case in polycrystals), you have to look at the components of  $\mu$  in the field direction and average over the ensemble.

Still, the basic effects is the same and ionic polarization can lead to respectable dielectric constants  $\epsilon_r$  or susceptibilities  $\chi$ .

- Some values are given in the [link](#).

**Questionnaire**

Multiple Choice questions to 3.2.3