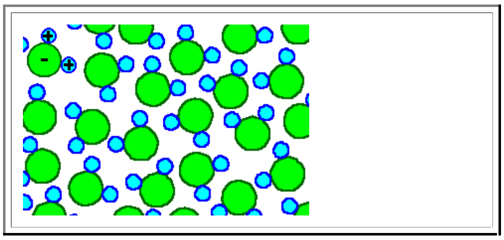
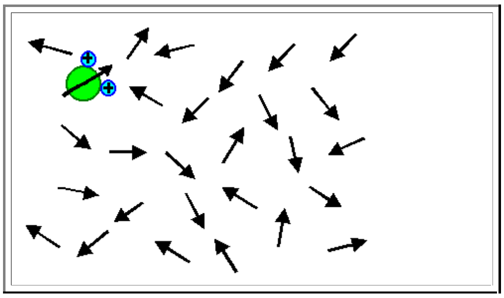
3.2.4 Orientation Polarization

- In the case of **orientation polarization** we have a material with *built-in dipoles* that are *independent of each other*, i.e. they can *rotate freely* - in sharp contrast to ionic polarization.
    - The prime example is *liquid water*, where every water molecule is a little dipole that can have any orientation with respect to the other molecules. Moreover, the orientation changes *all the time* because the *molecules moves*! Orientation polarization for dielectric dipoles thus is pretty much limited to liquids - but we will encounter it in a major way again for *magnetic dipoles*.
    - A two-dimensional "piece of water" may - very graphically - look somewhat like the picture below that captures *one particular moment in time*. It is like a snapshot with a very, very short exposure time. A few nanoseconds later the same piece of water may look totally different in detail, but pretty much the same in general.
    - In a three-dimensional piece of water the blue and red circles would not have to be in the same plane; but that is easy to imagine and difficult to draw.

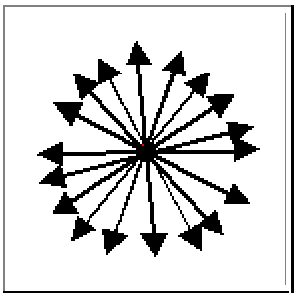


- Shown is a bunch of water molecules that form natural dipoles because the negatively charged oxygen atom and the two positively charged **H** - atoms have different centers of charge. Each molecule carries a dipole moment which can be drawn as a vector of constant length. If we only draw a vector denoting the dipole moment, we get - in two dimensions - a picture like this:



- Again, remember that both pictures are "*snap shots*" that only appear unblurred for very small exposure times, say picoseconds, because the dipoles wiggle, rotate, and move around rather fast, and that in *three* dimensions the vectors would also point out of the drawing plane.

- The total dipole moment is the *vector sum* of the individual dipole moments.



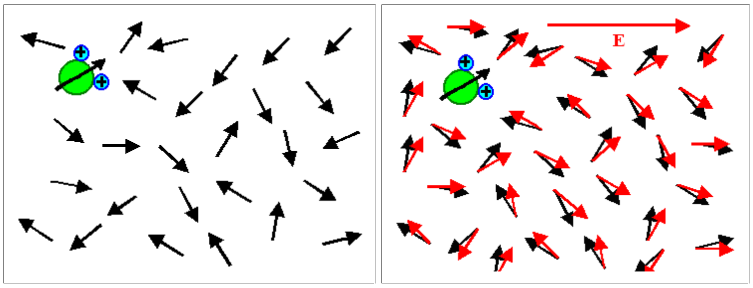
- For dipoles oriented *at random*, at any given moment this looks like the picture below if we draw all vectors from a common origin: The sum of all dipole moments will be zero, if the dipoles are randomly oriented.
- We can see this most easily if we have all dipoles start at the same origin. The picture, of course, is two-dimensional and crossly simplified. There would be a lot more (like $\mathbf{10^{20}}$) dipoles for any appreciable amount of water - you really will average them to zero pretty well.

- If we now introduce a field ***E***, the dipoles would have a tendency to turn into the field because that would lower their energy.
    - If you have problems with this statement, just imagine the electrostatic interaction, which will always try to move the positive pole of the dipole towards the negative pole of the field, and vice versa for the negative pole - the dipole would align itself exactly along a field line of the external field for minimum energy.
    - Naively, we would then expect a *perfect orientation into the field* and a ***concomitantly*** large polarization because that would lead to the *minimum of the dipole energy*.
    - Well, water does have a pretty large **DK** of **81**, so there is obviously *some* orientation into the field, but it is easy (not really) to show (in an exercise) that this **DK** is several orders of magnitude too small for *fully* oriented dipole moments at some normal field strengths.

Exercise 3.2-1

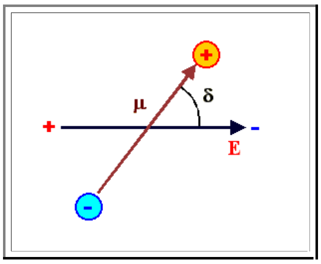
Maximum polarization of water

- In reality, the orientation into the field direction will be *counteracted by random collisions* with other dipoles, and this process is energized by the *thermal energy* "**k*T***" contained in the water.
  - Again, the dipoles are not sitting still, but moving around and rotating all the time - because they contain *thermal energy* and thus also some **entropy**.
  - Whenever two molecules collide, their new orientation is *random* - all memory of an orientation that they might have had in the electrical field is lost. This is analogous to what happens to electrons carrying an electrical current in an electrical field.
  - The electrical field only induces a little bit of *average* orientation in field direction - most of the time an individual dipole points in all kinds of directions. This is the simple truth even so some (undergraduate) text books show pictures to the contrary. The "real" picture (in the sense of a snapshot with a very short exposure time) looks like this:



Without field | **With field**

  - The orientation of all dipoles is just a little bit shifted so that an average orientation in field direction results. In the picture, the effect is even exaggerated!
- In fact, the state of being *liquid* by necessity implies quite a bit of **entropy**, and entropy means *disorder*.
  - Perfectly aligned dipoles would be in *perfect order* without any entropy - this is only possible at extremely low temperatures (and even there quantum theory would not allow it) where we will not have liquids any more, or more generally, dipoles that are able to rotate freely.
  - In other words, we must look for the minimum of the **free enthalpy *G*** and not for the minimum of the **internal energy *U***. At finite temperatures the minimum of the free enthalpy requires some **entropy *S***, i.e. randomness in the dipole orientation, so we should not expect perfect orientation.
- If you are not familiar with the basics of thermodynamics, you have a problem at this point. If you do know your thermodynamics, but are a bit insecure, turn to the basic module "Thermodynamics" (in the "Defects" Hyperscript) to refresh your memory.
- We obviously need to calculate the free enthalpy ***G=U – TS*** to see what kind of average orientation will result in a given field. Note that we use ***U***, the common symbol for the (internal) energy instead of ***H***, the common symbol for the enthalpy, because ***U*** and ***H*** are practically identical for solids and liquids anyway.
  - Moreover, a mix up with the magnetic field strength usually designated by ***H***, too, would be unavoidable otherwise. (The possible mix-up between internal energy ***U*** and voltage ***U*** is not quite so dangerous in this context).
- The internal energy od a dipole is clearly a function of its orientation with respect to the field. It must be minimal, when the dipole is aligned with the field and thedipole moment has the same direction as the electrical field, and maximal if the direction is reversed.
  - This is the easy part: The energy ***U*(δ)** of a dipole with dipole moment μ in a field ***E*** as a function of the angle δ ("delta") between the dipole moment direction and the field direction.



- From basic electrostatics we have have

$$U(\delta) = - \underline{\mu} \cdot \underline{E} = - |\underline{\mu}| \cdot |\underline{E}| \cdot \cos\delta$$

- The *minimum energy* ***U*** thus would occur for **δ=0°**, i.e. for perfect alignment in proper field direction (*note the minus sign!*); the maximum energy for **δ=180°**, i.e. for alignment the wrong way around.
- That was for two dimensions - now we must look at this in *three* dimensions.

  - In **3D** we see that all dipoles with the same angle δ between their axis and the field still have the same energy - and this means now all dipoles on a *cone* with opening angle 2δ around the field axis if we consider possible orientations out of the plane of drawing.
  - In order to obtain the *total internal energy* U_total of a *bunch* of dipoles having *all kinds* of angles δ with the field axis, we will have to sum up all cones.
  - This means we take the number of dipoles $N(\delta)$ having a particular orientation δ times the energy belonging to that δ, and integrate the resulting function over δ from 0° to 180°. This is something that we could do - if we would know $N(\delta)$.

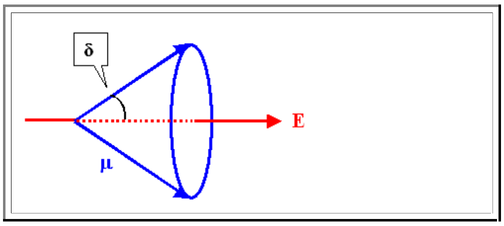
- However, just calcuating U_total will not be of much use. We also *must* consider the entropy term $-TS$, because we do not want to calculate the total *internal energy* U_total, but the total *free enthalpy* $G = U_\text{total} - TS$.
  - We need to consider that term as a function of all possible angle distributions and then see for which distribution we can minimize G.
- *But what is the entropy* $S(N(\delta))$ of an ensemble of dipoles containing $N(\delta)$ members at the angle δ as a function of the many possible distribution $N(\delta)$? Not an easy question to answer from just looking at the dipoles.

Fortunately, we do not have to calculate
S explicitly!

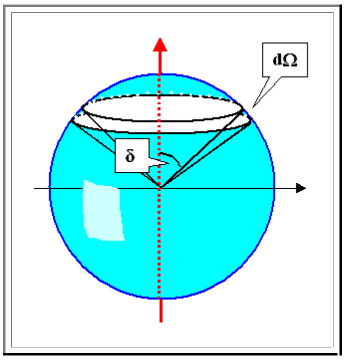
- We *know* a formula for the distribution of (classical) particles on available energy levels that *automatically* gives the minimum of the free enthalpy!
  - We have a *classical* system where a number of independent particles (the dipoles) can occupy a number of energy levels (between U_min and U_max) as defined by $\delta = 0^\circ$ or $\delta = 180^\circ$, respectively.
  - Basic thermodynamics asserts that *in equilibrium*, the distribution of the particles on the available energy levels is given by the proper *distribution function* which is defined in such a way that it *always* gives the minimum of the free enthalpy.
  - Since we deal with classical particles in this approach, we have to use the **Boltzmann distribution**. We obtain for $N(U)$= number of dipoles with the energy U

$$N(U) = A \cdot \exp - \frac{U(\delta)}{kT}$$

  - With a constant A that has yet to be determined.
- This Boltzmann distribution equation gives us the number of dipoles with a certain angle relative to the field direction, i.e. the number of dipoles that have their tips on a circle with an opening angle 2δ relative to the field directions as shown below.



  - We are, however, only interested in the *component of the dipole moment parallel to the field*. For this we look at the ***solid angle*** increment $d\Omega$ defined on the unit sphere as the segment between δ and $\delta + d\delta$.



  - The number of dipoles lying in the cone angle increment defined by δ and $\delta + \Delta\delta$ is the same as the number of dipoles with tips ending on the surface of the unit sphere in the incremental angle $d\Omega$. It is given by $N(U(\delta)) \cdot d\Omega$.
  - Note that $d\Omega$ is a measure of an incremental *area*; a kind of ribbon once around the unit sphere.
  - The sum of the components μ_F of the dipole moments *in field direction* is then .

$$\mu_F = (N \cdot d\Omega) \cdot (\mu \cdot \cos \delta)$$

  - If you are not familiar with spherical coordinates, this (and what we will do with it), looks a bit like magic. Since we do not want to learn Math in this lecture, the ***essentials to spherical coordinates*** are explained in detail in a basic module.

- The *average dipole moment*, which is what we want to calculate, will now be obtained by summing up the contributions from all the **d**Ωs

$$\langle \mu_F \rangle = \frac{\displaystyle\int_0^\pi N(U(\delta)) \cdot \mu \cdot \cos\delta \cdot d\Omega}{\displaystyle\int_0^\pi N(U(\delta)) \cdot d\Omega}$$

  - And the integrals have to be taken from the "top" of the sphere to the "bottom" , i.e. from **0** to π.

- **d**Ω and δ are of course closely related, we simply have

$$d\Omega = 2\pi \cdot \sin\delta \cdot d\delta$$

- Putting everything together, we obtain a pretty horrifying integral for μ_F that runs from **0** to π

$$\langle \mu_F \rangle = \frac{\mu \cdot \displaystyle\int_0^\pi \sin\delta \cdot \cos\delta \cdot \exp\frac{\mu \cdot E \cdot \cos\delta}{kT} \cdot d\delta}{\displaystyle\int_0^\pi \sin\delta \cdot \exp\frac{\mu \cdot E \cdot \cos\delta}{kT} \cdot d\delta}$$

- One advantage is that we got rid of the undetermined constant ***A***. The integral, being a determined integral, is now simply a *number* depending on the parameters of the system, i.e. the temperature ***T***, the dipole moment **μ** and the field strength ***E***.
  - *The problem has been reduced to a mathematical exercise in solving integrals*.

- Since we are not interested at doing math, we just show the general direction toward a solution:
  - Use the substitutions

$$\beta = \frac{\mu \cdot E}{kT}$$

$$x = \cos\delta$$

  - The integral reduces to

$$<\mu_F> = \frac{\mu \cdot \int_{+1}^{-1} x \cdot \exp(\beta \cdot x) \cdot dx}{\int_{+1}^{-1} \exp(\beta \cdot x) \cdot dx}$$

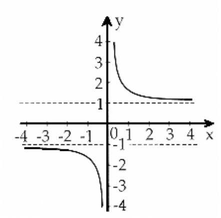
- The final result after quite a bit of fiddling around is

$$<\mu_F> = \mu \cdot L(\beta)$$

  - With **L(β)=Langevin function**, named after Paul Langevin, and defined as
.

$$L(\beta) = \coth(\beta) - \frac{1}{\beta}$$

$$\beta = \frac{\mu \cdot E}{kT}$$



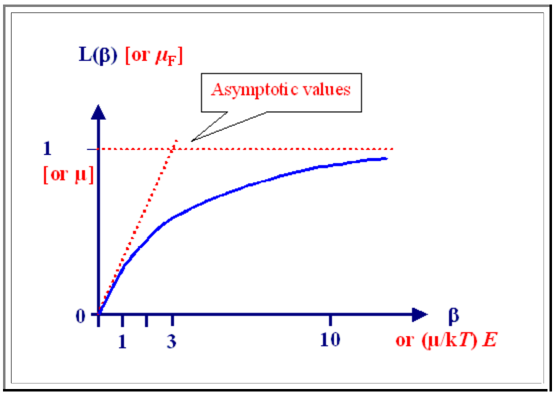
y=**coth** *x*

  - The "**coth**" is the *hyperbolic cotangent*, defined as **coth** $x = (e^x + e^{-x})/(e^x - e^{-x}) = 1/\tanh x$.
  - **L(β)** is a tricky function, because the **coth** *x* part looks pretty much like a hyperbola, from which the real hyperbola **1/*x*** is subtracted. What's left is almost nothing - **L(*x*)** values are between **0** and **1**

- The polarization (always on average, too) is accordingly
.

$$P = N \cdot <\mu>$$

- This is a definite result, but it does not help much. We need to discuss the mathematical construct "*Langevin function* **L(β)**" to get some idea of what we obtained. We look at the graph in general units and in units of the dipole moment and electrical field (in red).



  - Since β is proportional to the field strength ***E***, we see that the dipole moment and the polarization increases monotonically with ***E***, eventually saturating and giving $<\mu_F> = \mu$ which is what we must expect.
  - The question is, what *range* of β values is accessible for real materials. i.e. how close to the saturation limit can we get?

- For that we look at some simple approximations.
  - If we develop **L(β)** into a series (consult a math textbook), we get

$$L(\beta) = \frac{\beta}{3} - \frac{\beta^3}{45} + \frac{2\,\beta^5}{945} - \;.....$$

- For large values of β we have **L(β)** ≈ **1**, while for small values of β (β **< 1**), the Langevin function can be approximated by .

$$L(\beta) \approx 1/3 \cdot \beta$$

- The slope thus is **1/3** for β → **0**.
- For "normal" circumstances, we always have β **<< 1** (see below), and we obtain as final result for the **induced dipole moment** the **Langevin - Debye** equation

$$\langle \mu_F \rangle = \frac{\mu^2 \cdot E}{3kT}$$

$$\langle P \rangle = \frac{N \cdot \mu^2 \cdot E}{3kT}$$

- These equations will be rather good approximation for small values of μ and **E** and/or large values of ***T***. For very large fields and very small temperatures the average dipole moment would be equal to the built in dipole moment, i.e. all dipoles would be strictly parallel to the field. This is, however, not observed in "normal" ranges of fields and temperatures.

Lets see that in an example. We take

- $E=10^8$ **V/cm** which is about the highest field strength imaginable before we have electrical breakdown,
  $\mu=10^{-29}$ **Asm**, which is a large dipole moment for a strongly polarized molecule, e.g. for **HCl**, and
  $T=300$ **K**.
- This gives us
  $\beta=0{,}24$ - the approximation is still valid. You may want to consult exercise 3.2-1 again (or for the first time) at this point and look at the same question from a different angle.

At $T=30$ **K**, however, we have $\beta=2{,}4$ and now we must think twice:

- **1.** The approximation would no longer be good. *But*
- **2.** We no longer would have *liquid* **HCl** (or H_2O, or liquid whatever with a dipole moment), but solid **HCl** (or whatever) , and we now look at ionic polarization and no longer at orientation polarization!

You may now feel that this was a rather useless exercise - after all, who is interested in the **DK** of liquids? But consider: This treatment is *not* restricted to electric dipoles. It is valid for all kinds of dipoles that can rotate freely, in particular for the *magnetic dipoles* in paramagnetic materials responding to a magnetic field.

- Again, you may react with stating "Who is interested in paramagnets? Not an electrical engineer!" Right - but the path to *ferromagnets*, which definitely are of interest, starts exactly where orientation polarization ends; you cannot avoid it.

It is important to be aware of the basic condition that we made at the beginning: *there is no interaction between the dipoles*! This will not be true in general.

- Two water molecules coming in close contact will of course "feel" each other and they may have preferred orientations of their dipole moments relative to each other. In this case we will have to modify the calculations; the above equations may no longer be a good approximation.

- On the other hand, if there is a *strong* interaction, we automatically have some bonding and obtain a solid - ice in the case of water. The dipoles most likely cannot orientate themselves freely; we have a different situation (usually ionic polarization). There are, however, some solids where dipoles exist that can rotate to some extent - we will get very special effects, e.g. "ferroelectricity".

Questionaire
Multiple Choice questions to 3.2.4