### 5.2.5 Not so Perfect Materials

**Specular and Diffuse Reflection**

A piece of paper has a fairly flat surface but you can see it from all directions. Why? Clouds are formed by condensed water in the atmosphere and you can cleary see them radiantly white against a blue sky. Why? Before you answer, consider that you can't see the *uncondensed* water vapor even so the water concentration is about the same as in the cloud. And why, exactly, is the sky blue? Why is milk (= water with a few percent of fat) white but water with a few percent of alcohol colorless and transparent? Even if it contains far more than a few percent of e.g. alcohol?

- The answer to the first question should be obvious. Even if the reflection law is fully valid for white paper, i.e. $\alpha_{in} = \alpha_{out}$, every pixel of it is normally hit by light coming from *all* direction so some of it will always be reflected right into your eye.
- Sure. Now go and shine a Laser beam on a piece of paper in an otherwised completely dark room and you will *still* see the paper, no matter from which direction you look at it. Obviously some of the Laser light is still *scattered* into your eyes even so the beam reflected from its general surface goes somewhere else. Why? Because the paper is not *really* or *optically* flat. Some parts of it always reflect light in the direction you are looking.

We are now looking at the interaction of light with matter of not-so-perfect properties, especially at matter with properties that change on a small length scale.


The paper, for example, is not perfectly flat but has a roughness on some length scale far larger than the wavelength of light, but smaller than what your eye can easily resolve as shown in the picture. Some parts of it thus are always reflecting the light into your eye.

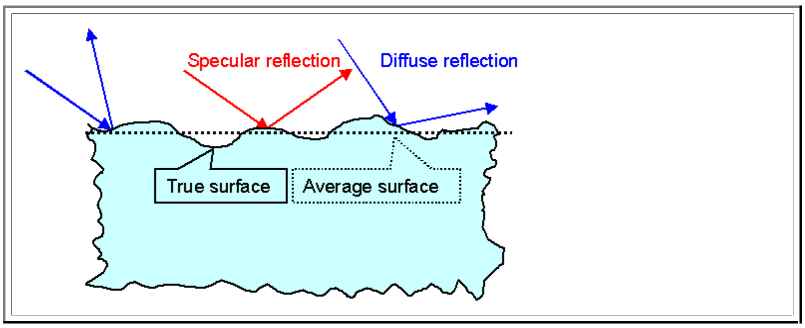
- Condensed water vapor means you have small water droplets suspended in the atmosphere (if they're too big, they fall down and we call it rain); milk means you have some small emulgated grease particles in the water.
- Light is *scattered* at those small things in all directions and the **scattering of light** is one topic we encounter if we look at not-so-perfect materials

Since "small"and "large"are relative values we must use the obvious natural length scale when dealing with light as our ruler and that is of course the wave length $\lambda \approx$ **1 µm**. We then distinguish three cases depending on the length scale $l_{mat}$ inherent to our material

- **$l_{mat} << \lambda$:** The extreme case would be scattering at single atoms or molecules. Proper **nanoparticles** also belong into this group. This kind of scattering is called **Rayleigh scattering**.
- **$l_{mat} >> \lambda$:** No problem, we covered that already. Just look at any part of the sample by itself, apply what we discussed before, and then add up across the sample
- **$l_{mat} \approx \lambda$:** Now we have a problem. What will happen in this case is difficult to deal with and no general rules apply. This kind of scattering is called **Mie scattering**.

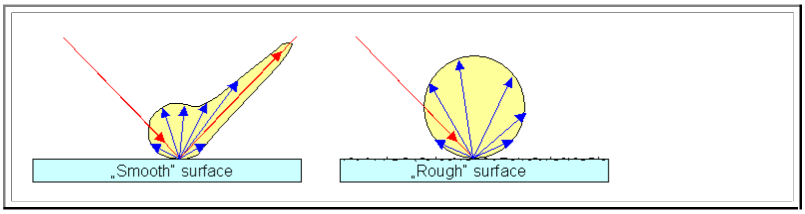
Let's look at the easy stuff first and define some terms.

- **Specular reflection** is the new word for the $\alpha_{in} = \alpha_{out}$ "normal" reflection. The only difference is that now we take the **α's** with respect to the "*average*" surface as shown below.




- **Diffuse reflection** is reflection in all other directions. It is easily conceived as "proper" reflection from those parts of the surface that deviate from the average.

It is clear that the relative magnitudes of both reflection types depends on exactly what the surface looks like at a small scale, and that one could have all kinds of reflected intensity distributions vs. angle. It is thus convenient to characterize a surface (for a given wave length) by polar diagrams as shown below

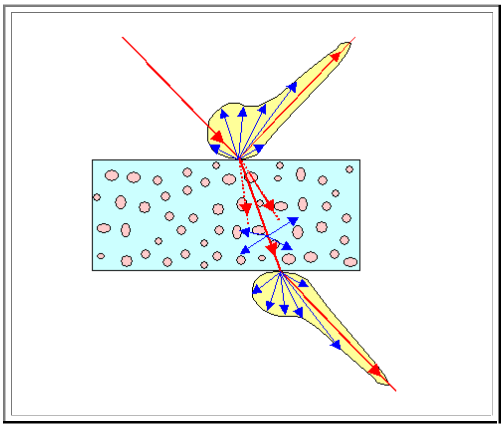



- An **"optically" smooth** surface scatters only little light outside the specular reflection direction, a perfectly rough surface scatters evenly in all directions, producing a polar diagram that can be typically described by $I = I_0 \cos\alpha$.
- It is clear that "optically smooth" means that all deviations from the average perfect surface, i.e. all quantitative roughness parameters, must be substantially smaller than the wavelength of the light considered.
- If we take optics to the extreme, e.g. with **DUV** or **EUV** (= deep or extreme ultraviolet) lithography with wavelengths down to the **20 nm** region, we need to use mirrors for reasons discussed before. Those mirrors need to be large (numerical aperture is important) and flat to *atomic dimensions*! Not so easy to make and calibrate!

## Transparency, Translucency, Opacity

Now let's look at light beams transmitted through a not-so-perfect but basically transparent material. Those materials, by definition, have a small κ value, i.e. a small imaginary part of the complex index of refraction or, same thing, of the dielectric function.

- As shown in the picture, we have
  - Specular and diffuse reflection at the surface the light is impinging on. This is descirbed by the polar diagram characterizing this surface.
  - Scattering of the transmitted light (running in different directions) at defects or imperfections contained in the material (fat droplets in milk, air bubbles in glass, ...).
  - Specular and diffuse reflection at the internal surface the light is coming out off. This is described by a (different) polar diagram characterizing this surface.



- If your material is not fully **transparent** (i.e. looking through it you hardly notice it is there; for example optical glass), light will come out in all directions and we call it **translucent**, for example etched glass or milky glass. If a lot of the light is refelcts and absorbed internally, nothing much will come out at all and we call this material **opaque**, for example china ware or "milky" ice.

Of course we can put some numbers on the properties *transparency*, *translucency*, and *opacity*, but we will not do that here.

- Suffice it to say that good transparency is a rather rare property -even for materials with intrinsically small κ and thus little absorption. Most ionic crystals and oxides, e.g. $\mathbf{Al_2O_3}$ are perfectly transparent as ideal crystals; this is also true for many polymers. Your chinaware and almost everything else made from those materials, however, tends to be rather opaque and at best somewhat translucent if it is thin.
- The reason are imperfections of surface and in the bulk of the material. Any defects not far smaller than the wavelength of the light will make their presence felt by scattering some of the light in unwanted directions.

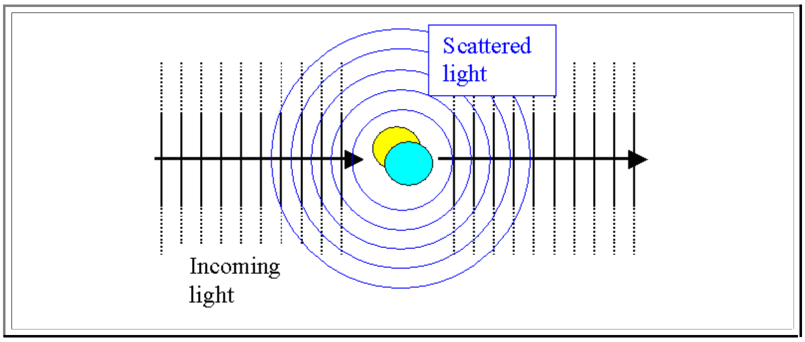
Metals are also rather opaque but for a different reason. Since their free electrons can absorb arbitrary energies and momenta, incoming photons quickly find a suitable electron that will "take" their energy and momentum, "absorbing" the photon within a few nanometers below the surface.

- Scattering or no scattering - nothing will come out on the back surface in either case.

- The picture above contains a small puzzle - did you notice?
  - The main beam is drawn nicely refracted at the air - material boundary. For doing this you need an index of refraction for the material. What is the index of refraction for an **optical compound material**? The question is reminescent to, e.g., Young's modulus for compound materials.
  - The answer, not unexpectedly I hope, is: As long as the constituents of the compond are small enough, it is possible to define a compound index of refraction that is a weighted average of the individual indexes.
  - Eaxtly how you do this might be tricky but there is nothing special here.

## Rayleigh Scattering

- Why is the sky blue? Because the air **molecules** scatter blue light stonger than red light.
  - So if you don't look at the sun directly, only scattered light scattered somehow in the atmosphere can reach your eye. The more you look in a direction away from the sun, the bluer the light will be. Actually, it should be violet but because the eye is not very sensitive to the shortest still visible wave lengths you are biased towards blue.
- Atoms and molecules are far smaller than the wave length of light so we are talking Rayleigh scattering here. In contrast to Mie scattering occuring for particles with sizes comparable to the wave length, Rayleigh scattering can be treated analytically. Here we only look at the major points of this treatment.
  - The figure shows the basic situation. An incoming light beam in the form of a plane wave with some energy or intensity (per **cm$^2$**) is transmitted to some extent and scattered to some other extent. We assume that scattering happens evenly in all directions, symbolized by the spherical wave emanating from the atom / molecule.
  - In the particle pictures, a stream of photons with some flux density or power per **cm$^2$** and second hits the atom / molecule. A given photon is either not affected at all and just continues going straigtht, or deflected (= scattered) into some other directions with equal probabilities for all directions.




- If we relate the total power (= energy per second) $P_{sc}$ contained in the scattered part to the intensity $I$ = power per **cm$^2$** contained in the incoming beam, i.e. from $P_{sc}/I = \sigma$, the quantity $\sigma$ has the dimension **cm$^2$** and is therefore called the **scattering cross section**.
  - It is easy to understand the meaning of the $\sigma$. The energy or the power contained in the incoming beam that flows through an an area of $\sigma$ **cm$^2$** is what will be scattered out of it.
  - We might expect that $\sigma$ scales roughly with the (two-dimensional) size of the scattering particles, i.e. we expect it very roughly to be found in the **$10^{-19}$ cm$^2$** region.
- Why does an atom / molecule scatter light?
  - Read up chapter 3.3.3 and you know. The electrical field of the incoming wave jiggles the electrons of the particle ("electronic polarization"). Accelerated electrons (that's what jiggled electrons are) emit electromagnetic radiation (= light) with the frequency they are jiggled with, which is the frequency of the incoming light. The total effect is the scattering of the light.
  - Looking a bit deeper into the characteristics of radiation emittance of jiggled electrons (the word "antenna" comes up in this context if we look at it wiht electrical engineers eyes), one finds that the power radiated into space scales with $\omega^4$ or $\lambda^{-4}$. Going through the math for a particle with volume $V$ one obtains

$$\sigma = \frac{P}{I} \approx \frac{\omega^4 V^2}{6\pi c^4}$$

- If we have density of $n$ particles (= atoms / molecules / whatevers) per **cm$^3$**, we can estimate the penetration depth or absorption length $l_{SC}$; i.e. the length after most of the incoming radiation has been scattered off and nothing comes out anymore, to

$$I_{sc} = \frac{1}{n\sigma}$$

- This calls for an exercise

| Exercise 5.2.5 |
|---|
| Rayleigh Scattering |

## A Bit More to Scattering

- We have now dealt with most of the questions from above directly or indirectly:
  - A piece of paper has a fairly flat surface but still you can see it from all directions. Why? Because it is far from being *optically* flat and we have *diffuse* reflection and not just *specular* reflection. On top of that we might have some Mie and Rayleigh scattering at the small and very small inhomogeneities.
  - Clouds are formed by condensed water in the atmosphere and you can clearly see them radiantly white against a blue sky. Why? - considering that you can't see the uncondensed water vapor even so the water concentration is the same.. We have Rayleigh scattering at the small water droplets and since the scattering cross section scales with $V^2$, small water particles containing $n$ water molecules scatter the light far more strongly than $n$ water molecules far apart.
  - Why, exactly, is the sky blue? Because Rayleigh scattering increases sharply (fourth power) with decreasing wave length. It is blue and not violet because the sun emits more blue than violet photons and our eyes are more sensitive to blue than to violet.
  - Why is milk (= water with a few percent of fat) white but water colorless and transparent? Even if it contains far more than a few percent of e.g. alcohol? See above.
- One last point needs to be made. If we consider *large* water droplets or simply a pool of water (huge droplet), it doesn't seem to scatter light very much. If the surface would be perfect (consider a perfect ice crystal for the sake of the argument) there would be some perfectly specular reflection but nothing else. *Why?*
  - The reason is that for Rayleigh scattering from water droplets far smaller than the wavelengths, the electrical fields of the waves coming from each of the $n$ water molecules of a small droplet have all pretty much the same phase. The phases of the scattered waves from randomly distributed molecules then are random, and you know what that means.), so it is small wonder that scattering increase with volume or number of molecules squared.
  - If the droplets get larger we first enter the (difficult) regime of Mie scattering and we don't know off hand what we are going to see. For really large volumes, e.g. a visible ice crystal, we know what we will see. however. What has changed now is that for any wave send out by some atom at the surface via scattering on some direction other than the direction of specular reflection, some other atom at the surface produces an identical wave but with *reversed* phase. So all intensities cancel - except in the specular reflection direction.
  - The transmitted light cannot be scattered at all at the atoms of a perfect crystal (or "liquid"). Only imperfections like small precipitates or voids in crystal or fat globules in milk will scatter.