The background of the slide is a close-up photograph of numerous water droplets of various sizes on a light blue, reflective surface. The droplets are in sharp focus, showing their spherical shape and the way they reflect light. The overall color palette is cool, dominated by blues and whites.

Glass Engineering and Science

Jane Lindstrom

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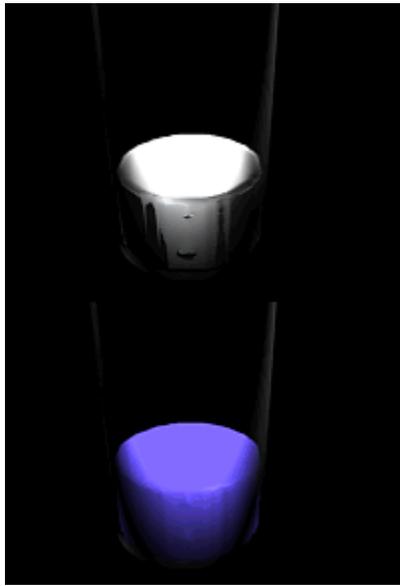
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Chapter 1

Viscosity

Viscosity



Clear liquid above has lower viscosity than the substance below

SI symbol: μ, η

SI unit: $\text{Pa}\cdot\text{s} = \text{kg}/(\text{s}\cdot\text{m})$

Derivations from other quantities: $\mu = G\cdot t$

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress. In everyday terms (and for fluids only), viscosity is "thickness" or "internal friction". Thus, water is "thin", having a lower viscosity, while honey is "thick", having a higher viscosity. Put simply, the less viscous the fluid is, the greater its ease of movement (fluidity).

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. For example, high-viscosity felsic magma will create a tall, steep stratovolcano, because it cannot flow far before it cools, while low-viscosity mafic

lava will create a wide, shallow-sloped shield volcano. All real fluids (except superfluids) have some resistance to stress and therefore are **viscous**, but a fluid which has no resistance to shear stress is known as an **ideal fluid** or **inviscid fluid**.

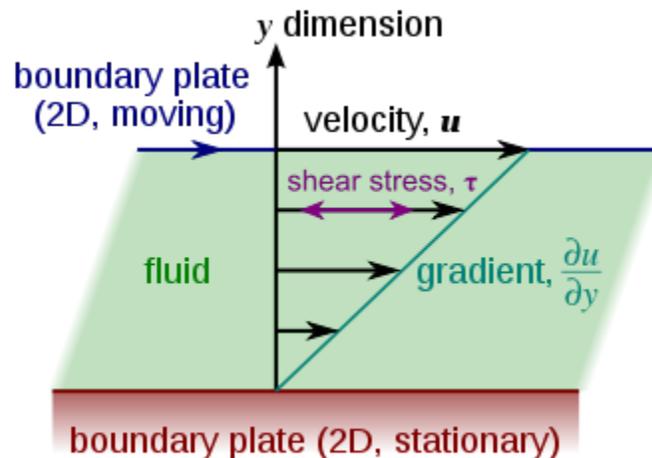
The study of flowing matter is known as rheology, which includes viscosity and related concepts.

Etymology

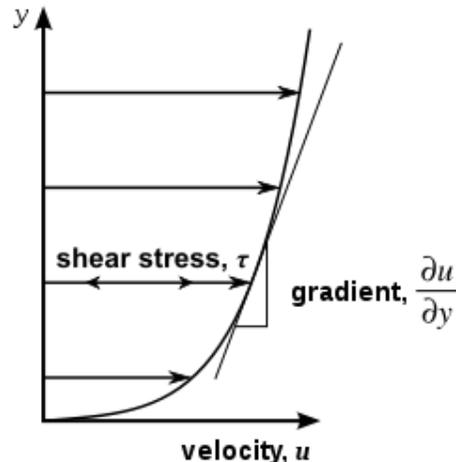
The word "viscosity" derives from the Latin word "viscum alba" for mistletoe. A viscous glue called birdlime was made from mistletoe berries and used for lime-twigs to catch birds.

Properties and behavior

Overview



Laminar shear of fluid between two plates. Friction between the fluid and the moving boundaries causes the fluid to shear. The force required for this action is a measure of the fluid's viscosity. This type of flow is known as a Couette flow.



Laminar shear, the non-constant gradient, is a result of the geometry the fluid is flowing through (e.g. a pipe).

In general, in any flow, layers move at different velocities and the fluid's viscosity arises from the shear stress between the layers that ultimately opposes any applied force.

The relationship between the shear stress and the velocity gradient can be obtained by considering two plates closely spaced at a distance y , and separated by a homogeneous substance. Assuming that the plates are very large, with a large area A , such that edge effects may be ignored, and that the lower plate is fixed, let a force F be applied to the upper plate. If this force causes the substance between the plates to undergo shear flow with a velocity gradient u (as opposed to just shearing elastically until the shear stress in the substance balances the applied force), the substance is called a fluid.

The applied force is proportional to the area and velocity gradient in the fluid and inversely proportional to the distance between the plates. Combining these three relations results in the equation:

$$F = \mu A \frac{u}{y},$$

where μ is the proportionality factor called *viscosity*.

This equation can be expressed in terms of shear stress $\tau = \frac{F}{A}$. Thus as expressed in differential form by Isaac Newton for straight, parallel and uniform flow, the shear stress between layers is proportional to the velocity gradient in the direction perpendicular to the layers:

$$\tau = \mu \frac{\partial u}{\partial y}$$

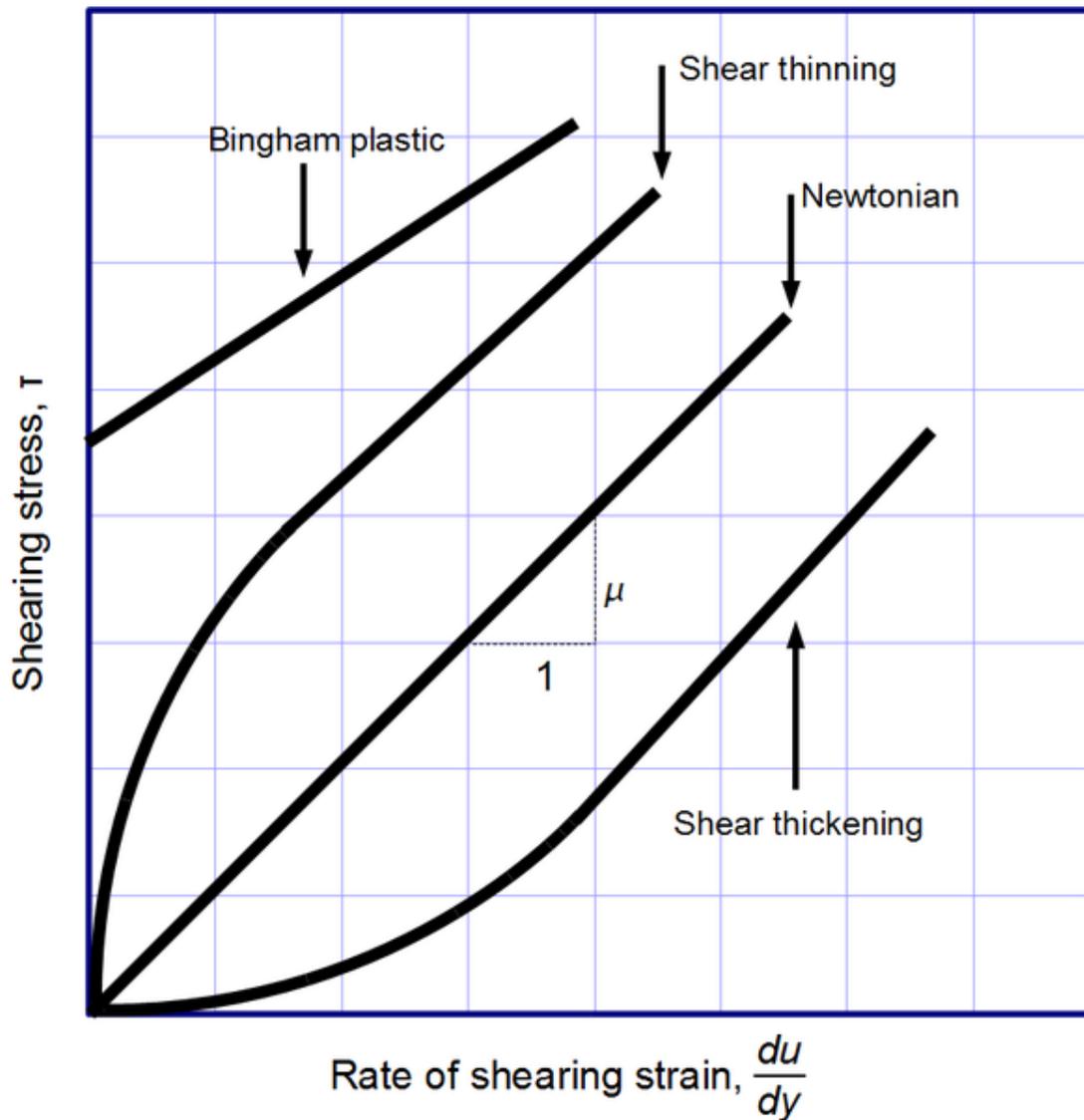
Hence, through this method, the relation between the shear stress and the velocity gradient can be obtained.

$$\frac{u}{y}$$

Note that the *rate of shear deformation* is $\frac{u}{y}$ which can be also written as a *shear velocity*, $\frac{du}{dy}$.

James Clerk Maxwell called viscosity *fugitive elasticity* because of the analogy that elastic deformation opposes shear stress in solids, while in viscous fluids, shear stress is opposed by *rate* of deformation.

Types of viscosity



Viscosity, the slope of each line, varies among materials

Newton's law of viscosity, given above, is a constitutive equation (like Hooke's law, Fick's law, Ohm's law). It is not a fundamental law of nature but an approximation that holds in some materials and fails in others. Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient than simple linearity. Thus there exist a number of forms of viscosity:

- **Newtonian:** fluids, such as water and most gases which have a constant viscosity.
- **Shear thickening:** viscosity *increases* with the rate of shear.
- **Shear thinning:** viscosity *decreases* with the rate of shear. Shear thinning liquids are very commonly, but misleadingly, described as thixotropic.
- **Thixotropic:** materials which become *less* viscous over time when shaken, agitated, or otherwise stressed.

- **Rheopectic**: materials which become *more* viscous over time when shaken, agitated, or otherwise stressed.
- A **Bingham plastic** is a material that behaves as a solid at low stresses but flows as a viscous fluid at high stresses.
- A **magnetorheological fluid** is a type of "smart fluid" which, when subjected to a magnetic field, greatly increases its apparent viscosity, to the point of becoming a viscoelastic solid.

Viscosity coefficients

Viscosity coefficients can be defined in two ways:

- **Dynamic viscosity**, also **absolute viscosity**, the more usual one (typical units Pa·s, Poise, P);
- **Kinematic viscosity** is the *dynamic viscosity* divided by the density (typical units m²/s, Stokes, St).

Viscosity is a tensorial quantity that can be decomposed in different ways into two independent components. The most usual decomposition yields the following viscosity coefficients:

- **Shear viscosity**, the most important one, often referred to as simply **viscosity**, describing the reaction to applied shear stress; simply put, it is the ratio between the pressure exerted on the surface of a fluid, in the lateral or horizontal direction, to the change in velocity of the fluid as you move down in the fluid (this is what is referred to as a velocity gradient).
- **Volume viscosity** (also called **bulk viscosity** or **second viscosity**) becomes important only for such effects where fluid compressibility is essential. Examples would include shock waves and sound propagation. It appears in the Stokes' law (sound attenuation) that describes propagation of sound in Newtonian liquid.

Alternatively,

- **Extensional viscosity**, a linear combination of shear and bulk viscosity, describes the reaction to elongation, widely used for characterizing polymers. For example, at room temperature, water has a dynamic shear viscosity of about 1.0×10^{-3} Pa·s and motor oil of about 250×10^{-3} Pa·s.

Viscosity measurement

Viscosity is measured with various types of viscometers and rheometers. A rheometer is used for those fluids which cannot be defined by a single value of viscosity and therefore require more parameters to be set and measured than is the case for a viscometer. Close temperature control of the fluid is essential to accurate measurements, particularly in materials like lubricants, whose viscosity can double with a change of only 5 °C.

For some fluids, viscosity is a constant over a wide range of shear rates (Newtonian fluids). The fluids without a constant viscosity (non-Newtonian fluids) cannot be described by a single number. Non-Newtonian fluids exhibit a variety of different correlations between shear stress and shear rate.

One of the most common instruments for measuring kinematic viscosity is the glass capillary viscometer.

In paint industries, viscosity is commonly measured with a Zahn cup, in which the efflux time is determined and given to customers. The efflux time can also be converted to kinematic viscosities (centistokes, cSt) through the conversion equations.

Also used in paint, a Stormer viscometer uses load-based rotation in order to determine viscosity. The viscosity is reported in Krebs units (KU), which are unique to Stormer viscometers.

A Ford viscosity cup measures the rate of flow of a liquid. This, under ideal conditions, is proportional to the kinematic viscosity.

Vibrating viscometers can also be used to measure viscosity. These models such as the *Dynatrol* use vibration rather than rotation to measure viscosity.

Extensional viscosity can be measured with various rheometers that apply extensional stress.

Volume viscosity can be measured with an acoustic rheometer.

Apparent viscosity is a calculation derived from tests performed on drilling fluid used in oil or gas well development. These calculations and tests help engineers develop and maintain the properties of the drilling fluid to the specifications required.

Units

Dynamic viscosity

The usual symbol for dynamic viscosity used by mechanical and chemical engineers — as well as fluid dynamicists — is the Greek letter mu (μ). The symbol η is also used by chemists, physicists, and the IUPAC.

The SI physical unit of dynamic viscosity is the pascal-second (Pa·s), (equivalent to N·s/m², or kg/(m·s)). If a fluid with a viscosity of one Pa·s is placed between two plates, and one plate is pushed sideways with a shear stress of one pascal, it moves a distance equal to the thickness of the layer between the plates in one second.

The cgs physical unit for dynamic viscosity is the *poise* (P), named after Jean Louis Marie Poiseuille. It is more commonly expressed, particularly in ASTM standards, as *centipoise* (cP). Water at 20 °C has a viscosity of 1.0020 cP or 0.001002 kg/(m·s).

$$1 \text{ P} = 1 \text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}.$$

$$1 \text{ Pa}\cdot\text{s} = 1 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1} = 10 \text{ P}.$$

The relation to the SI unit is

$$1 \text{ P} = 0.1 \text{ Pa}\cdot\text{s},$$

$$1 \text{ cP} = 1 \text{ mPa}\cdot\text{s} = 0.001 \text{ Pa}\cdot\text{s}.$$

Kinematic viscosity

In many situations, we are concerned with the ratio of the inertial force to the viscous force (i.e. the Reynolds number, $Re = VD / \nu$), the former characterized by the fluid density ρ . This ratio is characterized by the *kinematic viscosity* (Greek letter nu, ν), defined as follows:

$$\nu = \frac{\mu}{\rho}$$

The SI unit of ν is m^2/s . The SI unit of ρ is kg/m^3 .

The cgs physical unit for kinematic viscosity is the *stokes* (St), named after George Gabriel Stokes. It is sometimes expressed in terms of *centiStokes* (cSt). In U.S. usage, *stoke* is sometimes used as the singular form.

$$1 \text{ St} = 1 \text{ cm}^2\cdot\text{s}^{-1} = 10^{-4} \text{ m}^2\cdot\text{s}^{-1}.$$

$$1 \text{ cSt} = 1 \text{ mm}^2\cdot\text{s}^{-1} = 10^{-6} \text{ m}^2\cdot\text{s}^{-1}.$$

Water at 20 °C has a kinematic viscosity of about 1 cSt.

The kinematic viscosity is sometimes referred to as **diffusivity of momentum**, because it has the same unit as and is comparable to diffusivity of heat and diffusivity of mass. It is therefore used in dimensionless numbers which compare the ratio of the diffusivities.

Fluidity

The reciprocal of viscosity is *fluidity*, usually symbolized by $\phi = 1 / \mu$ or $F = 1 / \mu$, depending on the convention used, measured in *reciprocal poise* ($\text{cm}\cdot\text{s}\cdot\text{g}^{-1}$), sometimes called the *rhe*. *Fluidity* is seldom used in engineering practice.

The concept of fluidity can be used to determine the viscosity of an ideal solution. For two components a and b , the fluidity when a and b are mixed is

$$F \approx \chi_a F_a + \chi_b F_b,$$

which is only slightly simpler than the equivalent equation in terms of viscosity:

$$\mu \approx \frac{1}{\chi_a/\mu_a + \chi_b/\mu_b},$$

where χ_a and χ_b is the mole fraction of component a and b respectively, and μ_a and μ_b are the components pure viscosities.

Non-standard units

The Reyn is a British unit of dynamic viscosity.

Viscosity index is a measure for the change of kinematic viscosity with temperature. It is used to characterise lubricating oil in the automotive industry.

At one time the petroleum industry relied on measuring kinematic viscosity by means of the Saybolt viscometer, and expressing kinematic viscosity in units of *Saybolt Universal Seconds* (SUS). Other abbreviations such as SSU (*Saybolt Seconds Universal*) or SUV (*Saybolt Universal Viscosity*) are sometimes used. Kinematic viscosity in centistoke can be converted from SUS according to the arithmetic and the reference table provided in ASTM D 2161.

Molecular origins



Pitch has a viscosity approximately 230 billion (2.3×10^{11}) times that of water.

The viscosity of a system is determined by how molecules constituting the system interact. There are no simple but correct expressions for the viscosity of a fluid. The simplest exact expressions are the Green–Kubo relations for the linear shear viscosity or the Transient Time Correlation Function expressions derived by Evans and Morriss in 1985. Although these expressions are each exact in order to calculate the viscosity of a dense fluid, using these relations requires the use of molecular dynamics computer simulations.

Gases

Viscosity in gases arises principally from the molecular diffusion that transports momentum between layers of flow. The kinetic theory of gases allows accurate prediction of the behavior of gaseous viscosity.

Within the regime where the theory is applicable:

- Viscosity is independent of pressure and
- Viscosity increases as temperature increases.

James Clerk Maxwell published a famous paper in 1866 using the kinetic theory of gases to study gaseous viscosity. To understand why the viscosity is independent of pressure consider two adjacent boundary layers (A and B) moving with respect to each other. The internal friction (the viscosity) of the gas is determined by the probability a particle of layer A enters layer B with a corresponding transfer of momentum. Maxwell's calculations showed him that the viscosity coefficient is proportional to both the density, the mean free path and the mean velocity of the atoms. On the other hand, the *mean free path* is inversely proportional to the density. So an increase of pressure doesn't result in any change of the viscosity.

Relation to mean free path of diffusing particles

In relation to diffusion, the kinematic viscosity provides a better understanding of the behavior of mass transport of a dilute species. Viscosity is related to shear stress and the rate of shear in a fluid, which illustrates its dependence on the mean free path, λ , of the diffusing particles.

From fluid mechanics, for a Newtonian fluid, the shear stress, τ , on a unit area moving parallel to itself, is found to be proportional to the rate of change of velocity with distance perpendicular to the unit area:

$$\tau = \mu \frac{du_x}{dy}$$

for a unit area parallel to the x-z plane, moving along the x axis. We will derive this formula and show how μ is related to λ .

Interpreting shear stress as the time rate of change of momentum, p , per unit area A (rate of momentum flux) of an arbitrary control surface gives

$$\tau = \frac{\dot{p}}{A} = \frac{\dot{m}\langle u_x \rangle}{A}$$

where $\langle u_x \rangle$ is the average velocity along x of fluid molecules hitting the unit area, with respect to the unit area.

Further manipulation will show

$$\dot{m} = \rho \bar{u} A$$

$$\langle u_x \rangle = \frac{1}{2} \lambda \frac{du_x}{dy}, \text{ assuming that molecules hitting the unit area come from all distances between 0 and } \lambda \text{ (equally distributed), and that their average velocities change linearly with distance (always true for small enough } \lambda \text{). From this follows:}$$

$$\tau = \underbrace{\frac{1}{2} \rho \bar{u} \lambda}_{\mu} \cdot \frac{du_x}{dy} \Rightarrow \nu = \frac{\mu}{\rho} = \frac{1}{2} \bar{u} \lambda,$$

where

\dot{m} is the rate of fluid mass hitting the surface,
 ρ is the density of the fluid,

\bar{u} is the average molecular speed ($\bar{u} = \sqrt{\langle u^2 \rangle}$),
 μ is the dynamic viscosity.

Effect of temperature on the viscosity of a gas

Sutherland's formula can be used to derive the dynamic viscosity of an ideal gas as a function of the temperature:

$$\mu = \mu_0 \frac{T_0 + C}{T + C} \left(\frac{T}{T_0} \right)^{3/2}$$

This in turn is equal to

$$\lambda \cdot \frac{T^{3/2}}{T + C}, \text{ where } \lambda = \frac{\mu_0(T_0 + C)}{T_0^{3/2}} \text{ which is a constant.}$$

in Sutherland's formula:

- μ = dynamic viscosity in (Pa·s) at input temperature T ,
- μ_0 = reference viscosity in (Pa·s) at reference temperature T_0 ,
- T = input temperature in kelvins,
- T_0 = reference temperature in kelvins,
- C = Sutherland's constant for the gaseous material in question.

Valid for temperatures between $0 < T < 555$ K with an error due to pressure less than 10% below 3.45 MPa.

Sutherland's constant and reference temperature for some gases

Gas	C [K]	T_0 [K]	μ_0 [$\mu\text{Pa s}$]
air	120	291.15	18.27
nitrogen	111	300.55	17.81
oxygen	127	292.25	20.18
carbon dioxide	240	293.15	14.8
carbon monoxide	118	288.15	17.2
hydrogen	72	293.85	8.76
ammonia	370	293.15	9.82
sulfur dioxide	416	293.65	12.54
helium	79.4	273	19

Viscosity of a dilute gas

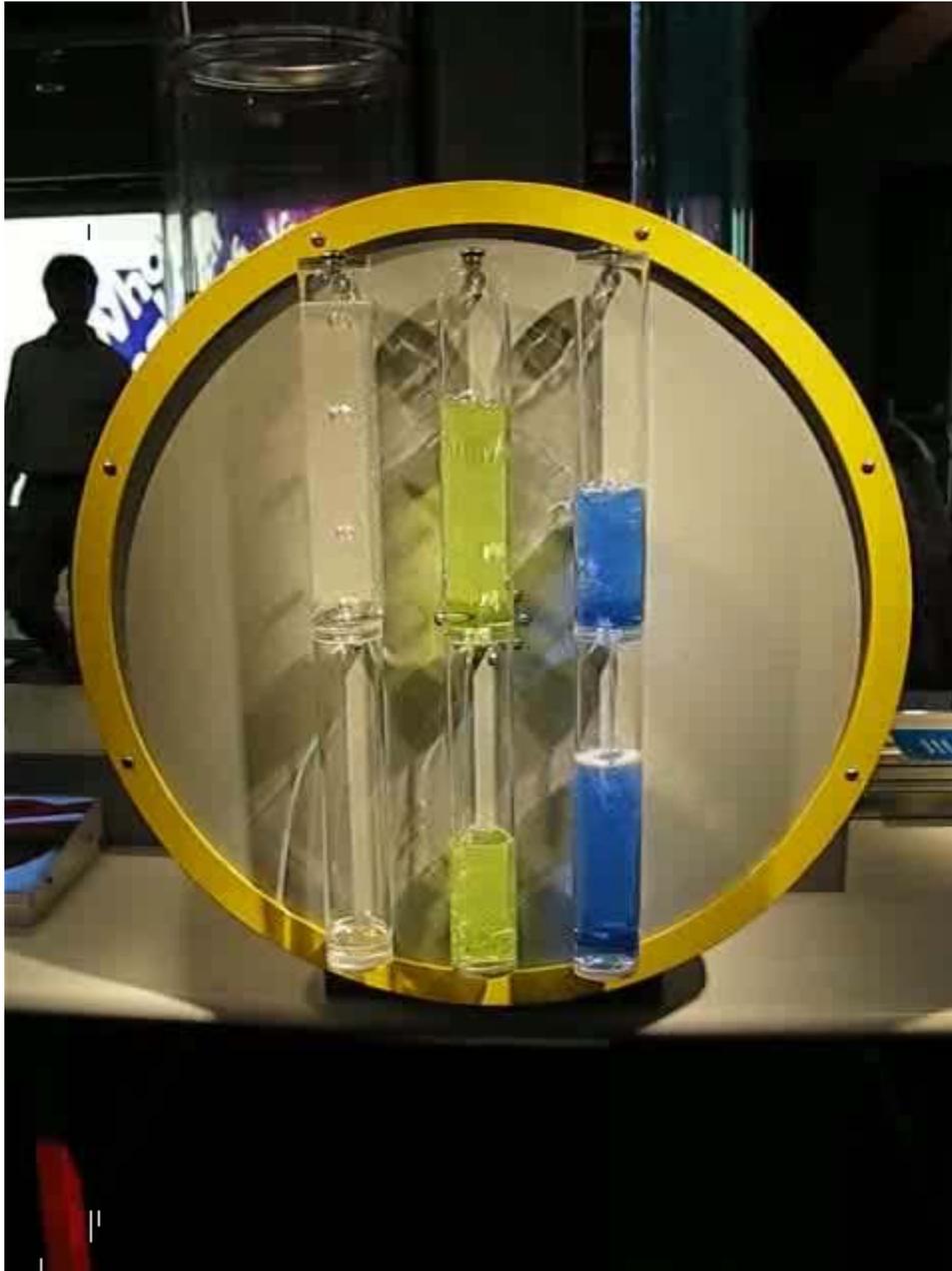
The Chapman-Enskog equation may be used to estimate viscosity for a dilute gas. This equation is based on a semi-theoretical assumption by Chapman and Enskog. The equation requires three empirically determined parameters: the collision diameter (σ), the maximum energy of attraction divided by the Boltzmann constant (ϵ/κ) and the collision integral ($\omega(T^*)$).

$$\mu_0 \times 10^6 = 2.6693 \frac{(MT)^{1/2}}{\sigma^2 \omega(T^*)},$$

with

- $T^* = \kappa T / \epsilon$ — reduced temperature (dimensionless),
- μ_0 = viscosity for dilute gas ($\mu\text{Pa.s}$),
- M = molecular mass (g/mol),
- T = temperature (K),
- σ = the collision diameter (\AA),
- ϵ / κ = the maximum energy of attraction divided by the Boltzmann constant (K),
- ω_μ = the collision integral.

Liquids



Three liquids with different Viscosities

In liquids, the additional forces between molecules become important. This leads to an additional contribution to the shear stress though the exact mechanics of this are still controversial. Thus, in liquids:

- Viscosity is independent of pressure (except at very high pressure); and
- Viscosity tends to fall as temperature increases (for example, water viscosity goes from 1.79 cP to 0.28 cP in the temperature range from 0 °C to 100 °C).

The dynamic viscosities of liquids are typically several orders of magnitude higher than dynamic viscosities of gases.

Viscosity of blends of liquids

The viscosity of the blend of two or more liquids can be estimated using the Refutas equation. The calculation is carried out in three steps.

The first step is to calculate the Viscosity Blending Number (VBN) (also called the Viscosity Blending Index) of each component of the blend:

$$(1) \quad \text{VBN} = 14.534 \times \ln [\ln(v + 0.8)] + 10.975$$

where v is the kinematic viscosity in centistokes (cSt). It is important that the kinematic viscosity of each component of the blend be obtained at the same temperature.

The next step is to calculate the VBN of the blend, using this equation:

$$(2) \quad \text{VBN}_{\text{Blend}} = [x_A \times \text{VBN}_A] + [x_B \times \text{VBN}_B] + \dots + [x_N \times \text{VBN}_N]$$

where x_X is the mass fraction of each component of the blend.

Once the viscosity blending number of a blend has been calculated using equation (2), the final step is to determine the kinematic viscosity of the blend by solving equation (1) for v :

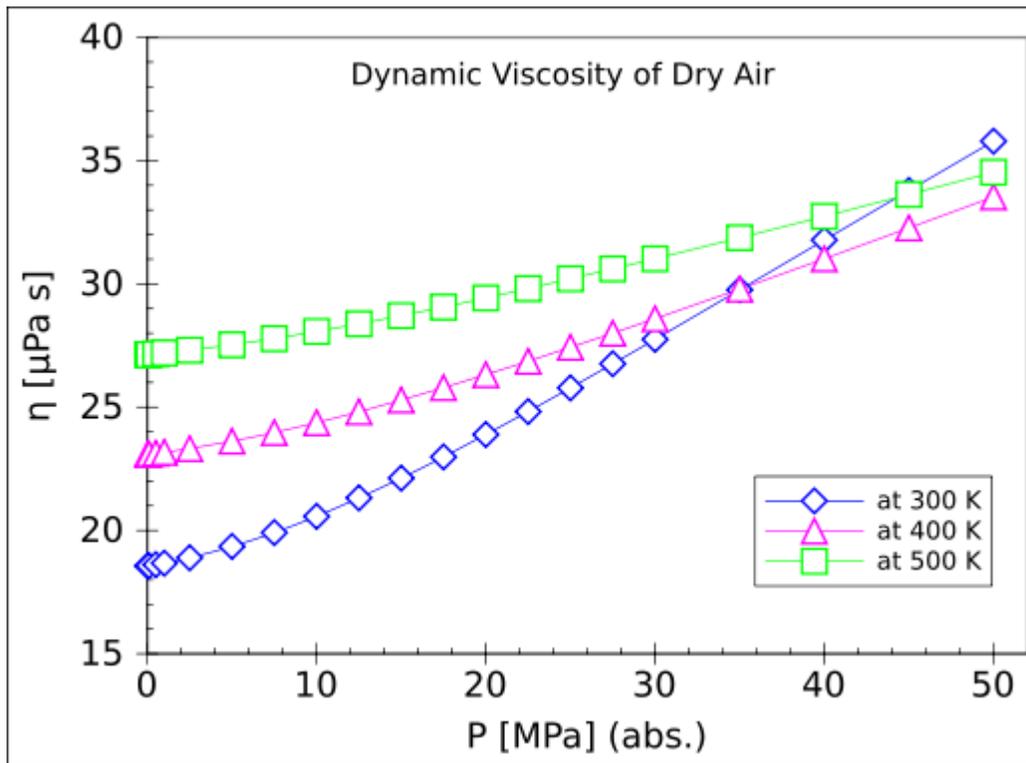
$$(3) \quad v = \exp \left(\exp \left(\frac{\text{VBN}_{\text{Blend}} - 10.975}{14.534} \right) \right) - 0.8,$$

where $\text{VBN}_{\text{Blend}}$ is the viscosity blending number of the blend.

Viscosity of selected substances

The viscosity of air and water are by far the two most important materials for aviation aerodynamics and shipping fluid dynamics. Temperature plays the main role in determining viscosity.

Viscosity of air

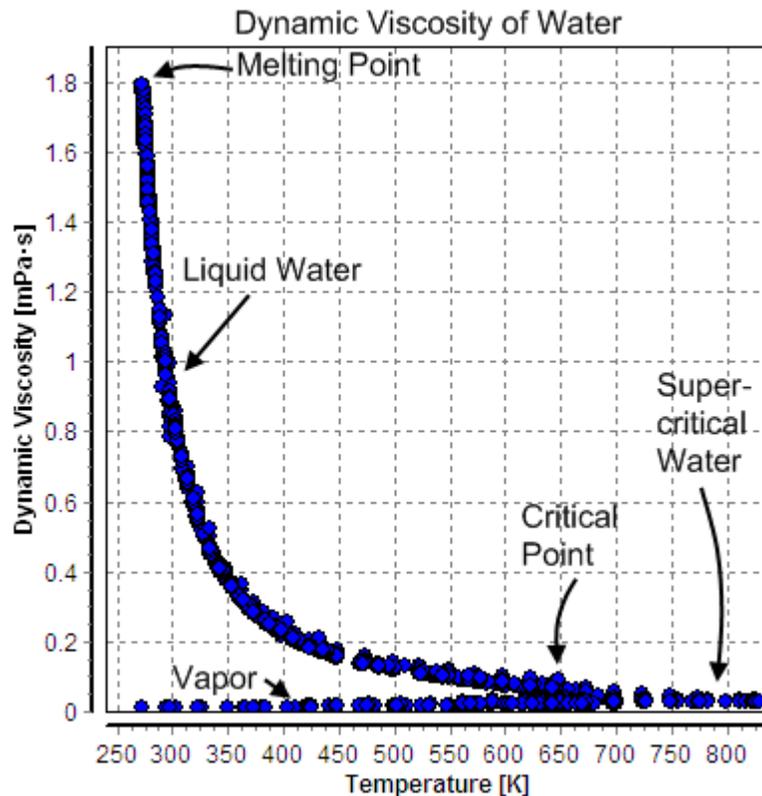


Pressure dependence of the dynamic viscosity of dry air at the temperatures of 300, 400 and 500 K

The viscosity of air depends mostly on the temperature. At 15.0 °C, the viscosity of air is 1.78×10^{-5} kg/(m·s), 17.8 $\mu\text{Pa}\cdot\text{s}$ or 1.78×10^{-5} Pa·s. One can get the viscosity of air as a function of temperature from the Gas Viscosity Calculator

Viscosity of water

Experimental Data Points from Dortmund Data Bank



Dynamic Viscosity of Water

The dynamic viscosity of water is 8.90×10^{-4} Pa·s or 8.90×10^{-3} dyn·s/cm² or 0.890 cP at about 25 °C.

Water has a viscosity of 0.0091 poise at 25 °C, or 1 centipoise at 20 °C.

As a function of temperature T (K): $(\text{Pa}\cdot\text{s}) = A \times 10^{B/(T-C)}$
 where $A=2.414 \times 10^{-5}$ Pa·s ; $B = 247.8$ K ; and $C = 140$ K.

Viscosity of liquid water at different temperatures up to the normal boiling point is listed below.

Temperature	Viscosity
[°C]	[mPa·s]
10	1.308
20	1.002
30	0.7978
40	0.6531
50	0.5471
60	0.4668

70	0.4044
80	0.3550
90	0.3150
100	0.2822

Viscosity of various materials



Example of the viscosity of milk and water. Liquids with higher viscosities will not make such a splash when poured at the same velocity.



Honey being drizzled.



Peanut butter is a semi-solid and can therefore hold peaks.

Some dynamic viscosities of Newtonian fluids are listed below:

Viscosity of selected gases at 100 kPa, [$\mu\text{Pa}\cdot\text{s}$]		
Gas	at 0 °C (273 K)	at 27 °C (300 K)
air	17.4	18.6
hydrogen	8.4	9.0
helium		20.0
argon		22.9
xenon	21.2	23.2
carbon dioxide		15.0
methane		11.2
ethane		9.5

Viscosity of liquids at 25 °C		
Liquid ():	Viscosity	Viscosity
	[Pa·s]	[cP=mPa.s]
acetone	3.06×10^{-4}	0.306
benzene	6.04×10^{-4}	0.604
blood (37 °C)	$(3-4) \times 10^{-3}$	3-4
castor oil	0.985	985
corn syrup	1.3806	1380.6
ethanol	1.074×10^{-3}	1.074
ethylene glycol	1.61×10^{-2}	16.1
glycerol	1.2 (at 20 °C)	1200
HFO-380	2.022	2022
mercury	1.526×10^{-3}	1.526
methanol	5.44×10^{-4}	0.544
Motor oil SAE 10 (20 °C)	0.065	65
Motor oil SAE 40 (20 °C)	0.319	319
nitrobenzene	1.863×10^{-3}	1.863
liquid nitrogen @ 77K	1.58×10^{-4}	0.158
propanol	1.945×10^{-3}	1.945
olive oil	.081	81
pitch	2.3e8	2.3e11
quark-gluon plasma	5e11	5e14
sulfuric acid	2.42×10^{-2}	24.2
water	8.94×10^{-4}	0.894

Viscosity of fluids with variable compositions

Fluid	Viscosity	Viscosity
	[Pa·s]	[cP]
honey	2-10	2,000-10,000
molasses	5-10	5,000-10,000
molten glass	10-1,000	10,000-1,000,000
chocolate syrup	10-25	10,000-25,000
molten chocolate*	45-130	45,000-130,000
ketchup*	50-100	50,000-100,000
peanut butter*	c. 250	c. 250,000
shortening*	c. 250	250,000

* These materials are highly non-Newtonian.

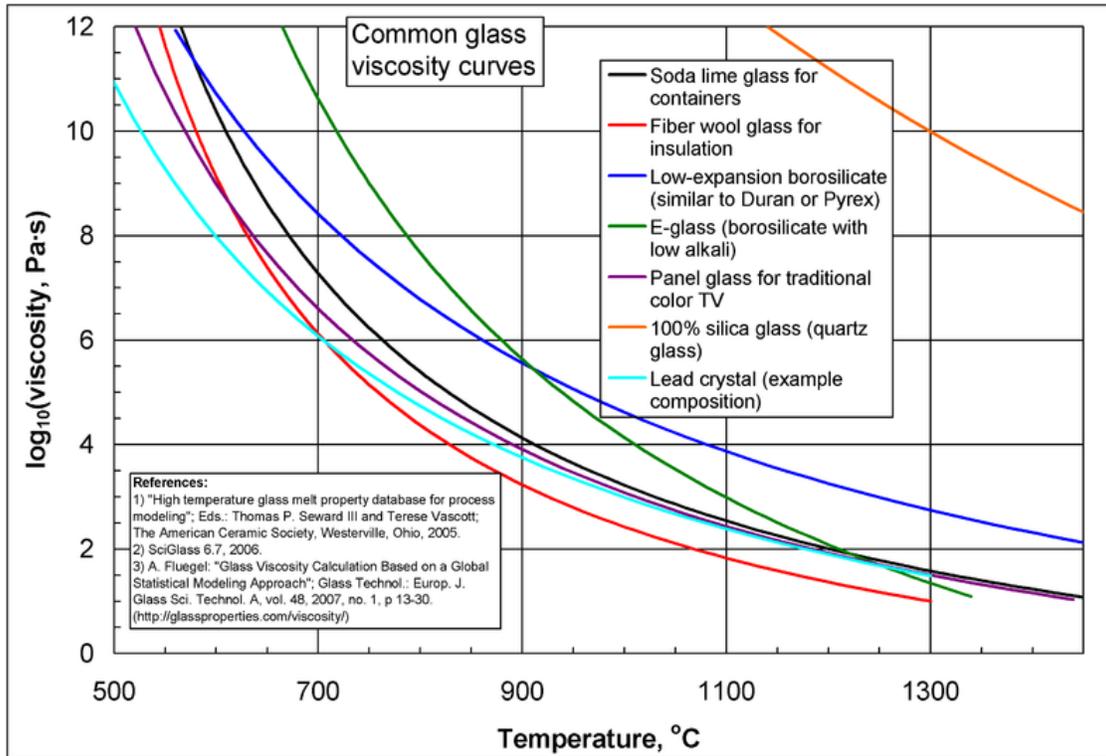
Viscosity of solids

On the basis that all solids such as granite flow to a small extent in response to small shear stress, some researchers have contended that substances known as amorphous solids, such as glass and many polymers, may be considered to have viscosity. This has led some to the view that solids are simply "liquids" with a very high viscosity, typically greater than 10^{12} Pa·s. This position is often adopted by supporters of the widely held misconception that glass flow can be observed in old buildings. This distortion is the result of the undeveloped glass making process of earlier eras, and not due to the viscosity of glass.

However, others argue that solids are, in general, elastic for small stresses while fluids are not. Even if solids flow at higher stresses, they are characterized by their low-stress behavior. This distinction is muddled if measurements are continued over long time periods, such as the Pitch drop experiment. Viscosity may be an appropriate characteristic for solids in a plastic regime. The situation becomes somewhat confused as the term *viscosity* is sometimes used for solid materials, for example Maxwell materials, to describe the relationship between stress and the rate of change of strain, rather than rate of shear.

These distinctions may be largely resolved by considering the constitutive equations of the material in question, which take into account both its viscous and elastic behaviors. Materials for which both their viscosity and their elasticity are important in a particular range of deformation and deformation rate are called *viscoelastic*. In geology, earth materials that exhibit viscous deformation at least three times greater than their elastic deformation are sometimes called rheids.

Viscosity of amorphous materials



Common glass viscosity curves.

Viscous flow in amorphous materials (e.g. in glasses and melts) is a thermally activated process:

$$\mu = A \cdot e^{Q/RT},$$

where Q is activation energy, T is temperature, R is the molar gas constant and A is approximately a constant.

The viscous flow in amorphous materials is characterized by a deviation from the Arrhenius-type behavior: Q changes from a high value Q_H at low temperatures (in the glassy state) to a low value Q_L at high temperatures (in the liquid state). Depending on this change, amorphous materials are classified as either

- strong when: $Q_H - Q_L < Q_L$ or
- fragile when: $Q_H - Q_L \geq Q_L$.

The fragility of amorphous materials is numerically characterized by the Doremus' fragility ratio:

$$R_D = \frac{Q_H}{Q_L}$$

and strong material have $R_D < 2$ whereas fragile materials have $R_D \geq 2$.

The viscosity of amorphous materials is quite exactly described by a two-exponential equation:

$$\mu = A_1 \cdot T \cdot [1 + A_2 \cdot e^{B/RT}] \cdot [1 + C \cdot e^{D/RT}],$$

with constants A_1, A_2, B, C and D related to thermodynamic parameters of joining bonds of an amorphous material.

Not very far from the glass transition temperature, T_g , this equation can be approximated by a Vogel-Fulcher-Tammann (VFT) equation.

If the temperature is significantly lower than the glass transition temperature, $T < T_g$, then the two-exponential equation simplifies to an Arrhenius type equation:

$$\mu = A_L T \cdot e^{Q_H/RT}$$

with:

$$Q_H = H_d + H_m,$$

where H_d is the enthalpy of formation of broken bonds (termed configuron s) and H_m is the enthalpy of their motion. When the temperature is less than the glass transition temperature, $T < T_g$, the activation energy of viscosity is high because the amorphous materials are in the glassy state and most of their joining bonds are intact.

If the temperature is highly above the glass transition temperature, $T > T_g$, the two-exponential equation also simplifies to an Arrhenius type equation:

$$\mu = A_H T \cdot e^{Q_L/RT},$$

with:

$$Q_L = H_m.$$

When the temperature is higher than the glass transition temperature, $T > T_g$, the activation energy of viscosity is low because amorphous materials are melt and have most of their joining bonds broken which facilitates flow.

Eddy viscosity

In the study of turbulence in fluids, a common practical strategy for calculation is to ignore the small-scale *vortices* (or *eddies*) in the motion and to calculate a large-scale motion with an *eddy viscosity* that characterizes the transport and dissipation of energy in the smaller-scale flow. Values of eddy viscosity used in modeling ocean circulation may be from 5×10^4 to 10^6 Pa·s depending upon the resolution of the numerical grid.

The linear viscous stress tensor

Viscous forces in a fluid are a function of the rate at which the fluid velocity is changing over distance. The velocity at any point \mathbf{r} is specified by the velocity field $\mathbf{v}(\mathbf{r})$. The velocity at a small distance $d\mathbf{r}$ from point \mathbf{r} may be written as a Taylor series:

$$\mathbf{v}(\mathbf{r} + d\mathbf{r}) = \mathbf{v}(\mathbf{r}) + \frac{d\mathbf{v}}{d\mathbf{r}}d\mathbf{r} + \dots,$$

where $d\mathbf{v} / d\mathbf{r}$ is shorthand for the dyadic product of the del operator and the velocity:

$$\frac{d\mathbf{v}}{d\mathbf{r}} = \begin{bmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{bmatrix}.$$

This is just the Jacobian of the velocity field.

Viscous forces are the result of relative motion between elements of the fluid, and so are expressible as a function of the velocity field. In other words, the forces at \mathbf{r} are a function of $\mathbf{v}(\mathbf{r})$ and all derivatives of $\mathbf{v}(\mathbf{r})$ at that point. In the case of linear viscosity, the viscous force will be a function of the Jacobian tensor alone. For almost all practical situations, the linear approximation is sufficient.

If we represent x , y , and z by indices 1, 2, and 3 respectively, the i,j component of the Jacobian may be written as $\partial_i v_j$ where ∂_i is shorthand for $\partial/\partial x_i$. Note that when the first and higher derivative terms are zero, the velocity of all fluid elements is parallel, and there are no viscous forces.

Any matrix may be written as the sum of an antisymmetric matrix and a symmetric matrix, and this decomposition is independent of coordinate system, and so has physical significance. The velocity field may be approximated as:

$$v_j(\mathbf{r} + d\mathbf{r}) = v_j(\mathbf{r}) + \frac{1}{2} (\partial_i v_j - \partial_j v_i) dr_i + \frac{1}{2} (\partial_i v_j + \partial_j v_i) dr_i,$$

where Einstein notation is now being used in which repeated indices in a product are implicitly summed. The second term from the right is the asymmetric part of the first derivative term, and it represents a rigid rotation of the fluid about \mathbf{r} with angular velocity ω where:

$$\omega = \frac{1}{2} \nabla \times \mathbf{v} = \frac{1}{2} \begin{bmatrix} \partial_2 v_3 - \partial_3 v_2 \\ \partial_3 v_1 - \partial_1 v_3 \\ \partial_1 v_2 - \partial_2 v_1 \end{bmatrix}.$$

For such a rigid rotation, there is no change in the relative positions of the fluid elements, and so there is no viscous force associated with this term. The remaining symmetric term is responsible for the viscous forces in the fluid. Assuming the fluid is isotropic (i.e. its properties are the same in all directions), then the most general way that the symmetric term (the rate-of-strain tensor) can be broken down in a coordinate-independent (and therefore physically real) way is as the sum of a constant tensor (the rate-of-expansion tensor) and a traceless symmetric tensor (the rate-of-shear tensor):

$$\frac{1}{2} (\partial_i v_j + \partial_j v_i) = \underbrace{\frac{1}{3} \partial_k v_k \delta_{ij}}_{\text{rate-of-expansion tensor}} + \underbrace{\left(\frac{1}{2} (\partial_i v_j + \partial_j v_i) - \frac{1}{3} \partial_k v_k \delta_{ij} \right)}_{\text{rate-of-shear tensor}},$$

where δ_{ij} is the unit tensor. The most general linear relationship between the stress tensor σ and the rate-of-strain tensor is then a linear combination of these two tensors:

$$\sigma_{\text{visc};ij} = \zeta \partial_k v_k \delta_{ij} + \mu \left(\partial_i v_j + \partial_j v_i - \frac{2}{3} \partial_k v_k \delta_{ij} \right),$$

where ζ is the coefficient of bulk viscosity (or "second viscosity") and μ is the coefficient of (shear) viscosity.

The forces in the fluid are due to the velocities of the individual molecules. The velocity of a molecule may be thought of as the sum of the fluid velocity and the thermal velocity. The viscous stress tensor described above gives the force due to the fluid velocity only. The force on an area element in the fluid due to the thermal velocities of the molecules is just the hydrostatic pressure. This pressure term ($-p \delta_{ij}$) must be added to the viscous stress tensor to obtain the total stress tensor for the fluid.

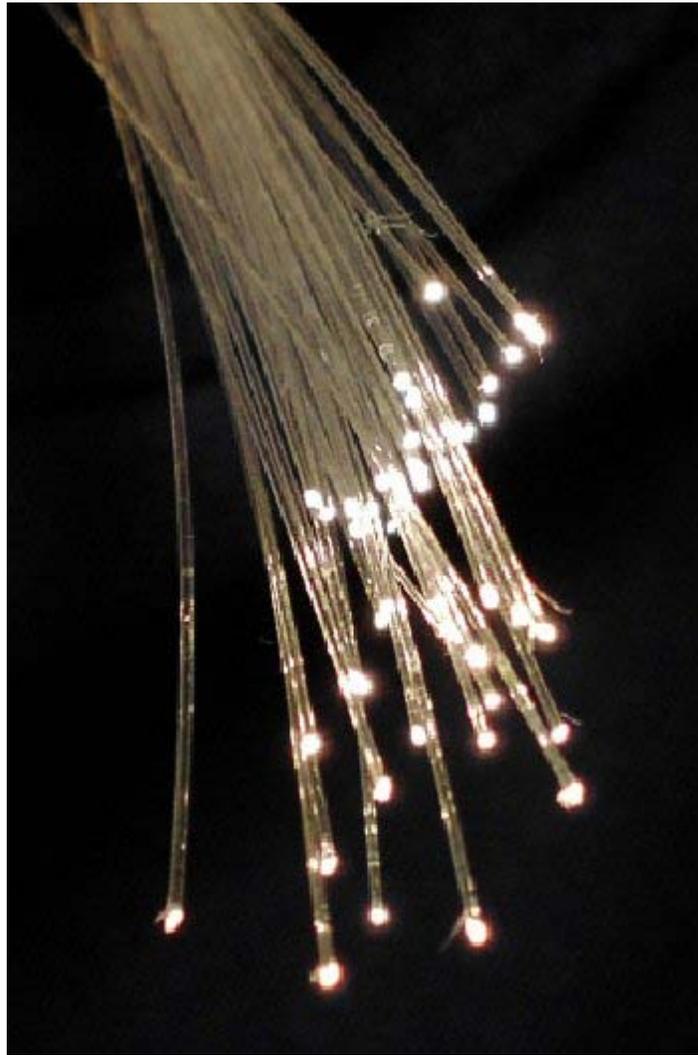
$$\sigma_{ij} = -p \delta_{ij} + \sigma_{\text{visc};ij}.$$

The infinitesimal force dF_i on an infinitesimal area dA_j is then given by the usual relationship:

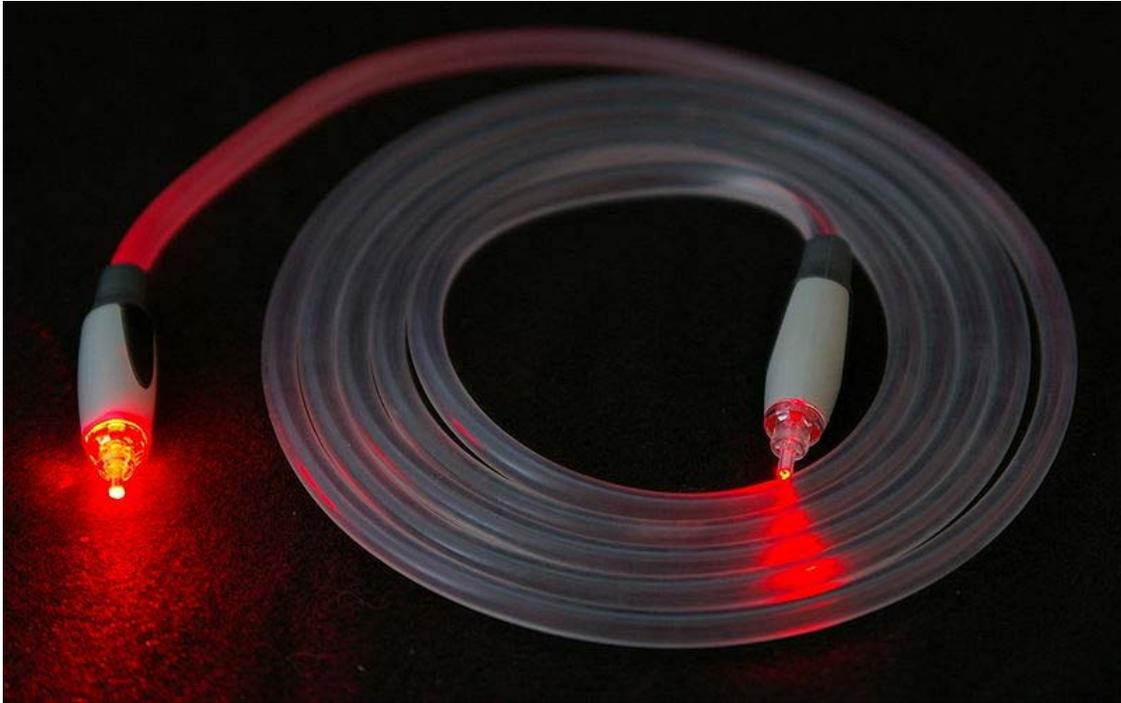
$$dF_i = \sigma_{ij} dA_j.$$

Chapter 2

Optical Fiber



A bundle of optical fibers



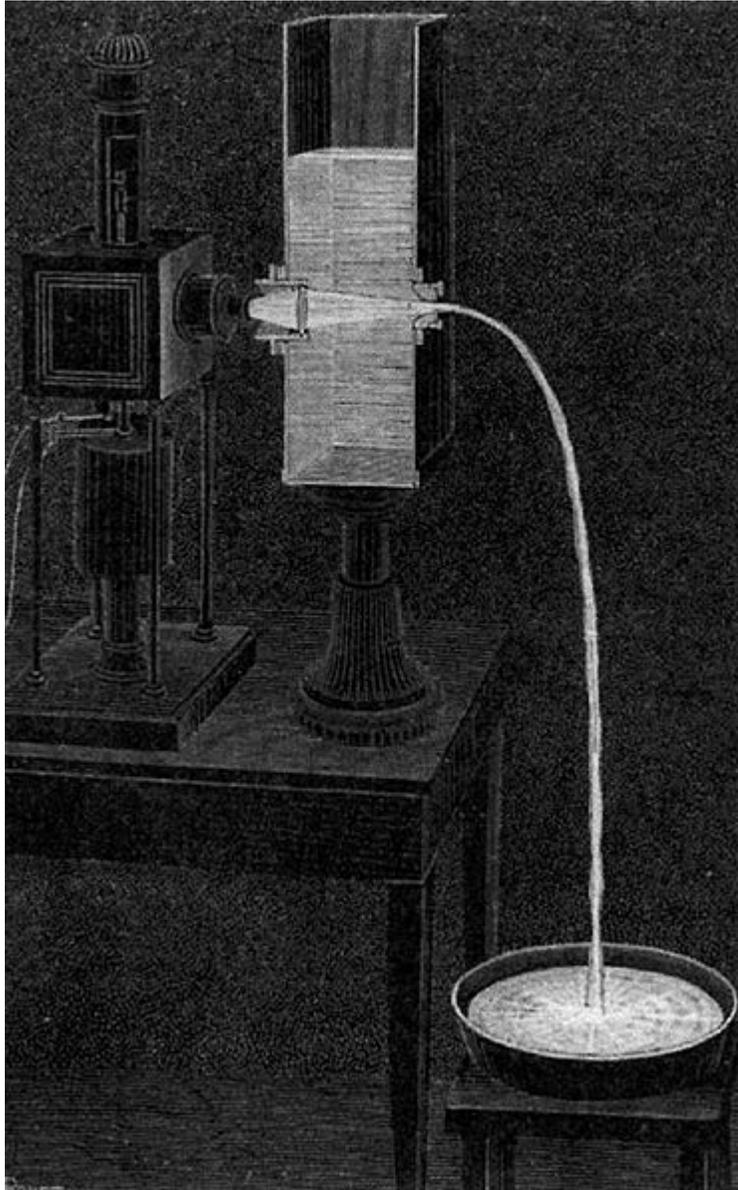
A TOSLINK fiber optic audio cable being illuminated at one end

An **optical fiber** or **optical fibre** is a thin, flexible, transparent fiber that acts as a waveguide, or "light pipe", to transmit light between the two ends of the fiber. The field of applied science and engineering concerned with the design and application of optical fibers is known as **fiber optics**. Optical fibers are widely used in fiber-optic communications, which permits transmission over longer distances and at higher bandwidths (data rates) than other forms of communication. Fibers are used instead of metal wires because signals travel along them with less loss and are also immune to electromagnetic interference. Fibers are also used for illumination, and are wrapped in bundles so they can be used to carry images, thus allowing viewing in tight spaces. Specially designed fibers are used for a variety of other applications, including sensors and fiber lasers.

Optical fiber typically consists of a transparent core surrounded by a transparent cladding material with a lower index of refraction. Light is kept in the core by total internal reflection. This causes the fiber to act as a waveguide. Fibers which support many propagation paths or transverse modes are called multi-mode fibers (MMF), while those which can only support a single mode are called single-mode fibers (SMF). Multi-mode fibers generally have a larger core diameter, and are used for short-distance communication links and for applications where high power must be transmitted. Single-mode fibers are used for most communication links longer than 1,050 meters (3,440 ft).

Joining lengths of optical fiber is more complex than joining electrical wire or cable. The ends of the fibers must be carefully cleaved, and then spliced together either mechanically or by fusing them together with heat. Special optical fiber connectors are used to make removable connections.

History



Daniel Colladon first described this "light fountain" or "light pipe" in an 1842 article titled *On the reflections of a ray of light inside a parabolic liquid stream*. This particular illustration comes from a later article by Colladon, in 1884.

Fiber optics, though used extensively in the modern world, is a fairly simple and old technology. Guiding of light by refraction, the principle that makes fiber optics possible, was first demonstrated by Daniel Colladon and Jacques Babinet in Paris in the early 1840s. John Tyndall included a demonstration of it in his public lectures in London a dozen years later. Tyndall also wrote about the property of total internal reflection in an introductory book about the nature of light in 1870: "When the light passes from air into water, the refracted ray is bent *towards* the perpendicular... When the ray passes from water to air it is bent *from* the perpendicular... If the angle which the ray in water encloses

with the perpendicular to the surface be greater than 48 degrees, the ray will not quit the water at all: it will be *totally reflected* at the surface.... The angle which marks the limit where total reflection begins is called the limiting angle of the medium. For water this angle is $48^{\circ}27'$, for flint glass it is $38^{\circ}41'$, while for diamond it is $23^{\circ}42'$."

Practical applications, such as close internal illumination during dentistry, appeared early in the twentieth century. Image transmission through tubes was demonstrated independently by the radio experimenter Clarence Hansell and the television pioneer John Logie Baird in the 1920s. The principle was first used for internal medical examinations by Heinrich Lamm in the following decade. In 1952, physicist Narinder Singh Kapany conducted experiments that led to the invention of optical fiber. Modern optical fibers, where the glass fiber is coated with a transparent cladding to offer a more suitable refractive index, appeared later in the decade. Development then focused on fiber bundles for image transmission. The first fiber optic semi-flexible gastroscope was patented by Basil Hirschowitz, C. Wilbur Peters, and Lawrence E. Curtiss, researchers at the University of Michigan, in 1956. In the process of developing the gastroscope, Curtiss produced the first glass-clad fibers; previous optical fibers had relied on air or impractical oils and waxes as the low-index cladding material. A variety of other image transmission applications soon followed.

In the late 19th and early 20th centuries, light was guided through bent glass rods to illuminate body cavities. Alexander Graham Bell invented a 'Photophone' to transmit voice signals over an optical beam.

Jun-ichi Nishizawa, a Japanese scientist at Tohoku University, also proposed the use of optical fibers for communications in 1963, as stated in his book published in 2004 in India. Nishizawa invented other technologies which contributed to the development of optical fiber communications, such as the graded-index optical fiber as a channel for transmitting light from semiconductor lasers. Charles K. Kao and George A. Hockham of the British company Standard Telephones and Cables (STC) were the first to promote the idea that the attenuation in optical fibers could be reduced below 20 decibels per kilometer (dB/km), allowing fibers to be a practical medium for communication. They proposed that the attenuation in fibers available at the time was caused by impurities, which could be removed, rather than fundamental physical effects such as scattering. They correctly and systematically theorized the light-loss properties for optical fiber, and pointed out the right material to manufacture such fibers — silica glass with high purity. This discovery led to Kao being awarded the Nobel Prize in Physics in 2009.

NASA used fiber optics in the television cameras sent to the moon. At the time such use in the cameras was 'classified confidential' and only those with the right security clearance or those accompanied by someone with the right security clearance were permitted to handle the cameras.

The crucial attenuation limit of 20 dB/km was first achieved in 1970, by researchers Robert D. Maurer, Donald Keck, Peter C. Schultz, and Frank Zimar working for American glass maker Corning Glass Works, now Corning Incorporated. They demonstrated a fiber with 17 dB/km attenuation by doping silica glass with titanium. A few years later they produced a fiber with only 4 dB/km attenuation using germanium

dioxide as the core dopant. Such low attenuation ushered in optical fiber telecommunication. In 1981, General Electric produced fused quartz ingots that could be drawn into fiber optic strands 25 miles (40 km) long.

Attenuation in modern optical cables is far less than in electrical copper cables, leading to long-haul fiber connections with repeater distances of 70–150 kilometers (43–93 mi). The erbium-doped fiber amplifier, which reduced the cost of long-distance fiber systems by reducing or eliminating optical-electrical-optical repeaters, was co-developed by teams led by David N. Payne of the University of Southampton and Emmanuel Desurvire at Bell Labs in 1986. Robust modern optical fiber uses glass for both core and sheath and is therefore less prone to aging processes. It was invented by Gerhard Bernsee of Schott Glass in Germany in 1973.

The emerging field of photonic crystals led to the development in 1991 of photonic-crystal fiber which guides light by diffraction from a periodic structure, rather than by total internal reflection. The first photonic crystal fibers became commercially available in 2000. Photonic crystal fibers can carry higher power than conventional fibers and their wavelength-dependent properties can be manipulated to improve performance.

Applications

Optical fiber communication

Optical fiber can be used as a medium for telecommunication and networking because it is flexible and can be bundled as cables. It is especially advantageous for long-distance communications, because light propagates through the fiber with little attenuation compared to electrical cables. This allows long distances to be spanned with few repeaters. Additionally, the per-channel light signals propagating in the fiber have been modulated at rates as high as 111 gigabits per second by NTT, although 10 or 40 Gbit/s is typical in deployed systems. Each fiber can carry many independent channels, each using a different wavelength of light (wavelength-division multiplexing (WDM)). The net data rate (data rate without overhead bytes) per fiber is the per-channel data rate reduced by the FEC overhead, multiplied by the number of channels (usually up to eighty in commercial dense WDM systems as of 2008). The current laboratory fiber optic data rate record, held by Bell Labs in Villarsaux, France, is multiplexing 155 channels, each carrying 100 Gbit/s over a 7000 km fiber. Nippon Telegraph and Telephone Corporation have also managed 69.1 Tbit/s over a single 240 km fiber (multiplexing 432 channels, equating to 171 Gbit/s per channel). Bell Labs also broke a 100 Petabit per second *kilometer* barrier (15.5 Tbit/s over a single 7000 km fiber).

For short distance applications, such as creating a network within an office building, fiber-optic cabling can be used to save space in cable ducts. This is because a single fiber can often carry much more data than many electrical cables, such as 4 pair Cat-5 Ethernet cabling. Fiber is also immune to electrical interference; there is no cross-talk between signals in different cables and no pickup of environmental noise. Non-armored fiber cables do not conduct electricity, which makes fiber a good solution for protecting communications equipment located in high voltage environments such as power generation facilities, or metal communication structures prone to lightning strikes. They

can also be used in environments where explosive fumes are present, without danger of ignition. Wiretapping is more difficult compared to electrical connections, and there are concentric dual core fibers that are said to be tap-proof.

Fiber optic sensors

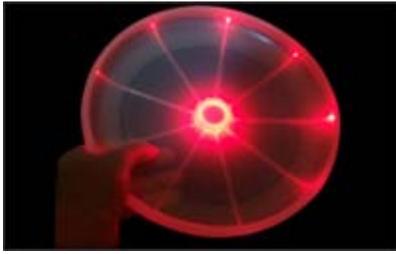
Fibers have many uses in remote sensing. In some applications, the sensor is itself an optical fiber. In other cases, fiber is used to connect a non-fiberoptic sensor to a measurement system. Depending on the application, fiber may be used because of its small size, or the fact that no electrical power is needed at the remote location, or because many sensors can be multiplexed along the length of a fiber by using different wavelengths of light for each sensor, or by sensing the time delay as light passes along the fiber through each sensor. Time delay can be determined using a device such as an optical time-domain reflectometer.

Optical fibers can be used as sensors to measure strain, temperature, pressure and other quantities by modifying a fiber so that the quantity to be measured modulates the intensity, phase, polarization, wavelength or transit time of light in the fiber. Sensors that vary the intensity of light are the simplest, since only a simple source and detector are required. A particularly useful feature of such fiber optic sensors is that they can, if required, provide distributed sensing over distances of up to one meter.

Extrinsic fiber optic sensors use an optical fiber cable, normally a multi-mode one, to transmit modulated light from either a non-fiber optical sensor, or an electronic sensor connected to an optical transmitter. A major benefit of extrinsic sensors is their ability to reach places which are otherwise inaccessible. An example is the measurement of temperature inside aircraft jet engines by using a fiber to transmit radiation into a radiation pyrometer located outside the engine. Extrinsic sensors can also be used in the same way to measure the internal temperature of electrical transformers, where the extreme electromagnetic fields present make other measurement techniques impossible. Extrinsic sensors are used to measure vibration, rotation, displacement, velocity, acceleration, torque, and twisting. A solid state version of the gyroscope using the interference of light has been developed. The fiber optic gyroscope (FOG) has no moving parts and exploits the Sagnac effect to detect mechanical rotation.

A common use for fiber optic sensors are in advanced intrusion detection security systems, where the light is transmitted along the fiber optic sensor cable, which is placed on a fence, pipeline or communication cabling, and the returned signal is monitored and analysed for disturbances. This return signal is digitally processed to identify if there is a disturbance, and if an intrusion has occurred an alarm is triggered by the fiber optic security system.

Other uses of optical fibers



A frisbee illuminated by fiber optics



Light reflected from optical fiber illuminates exhibited model



Fiber optic front sight on a hand gun

Fibers are widely used in illumination applications. They are used as light guides in medical and other applications where bright light needs to be shone on a target without a clear line-of-sight path. In some buildings, optical fibers are used to route sunlight from the roof to other parts of the building. Optical fiber illumination is also used for decorative applications, including signs, art, and artificial Christmas trees. Swarovski boutiques use optical fibers to illuminate their crystal showcases from many different angles while only employing one light source. Optical fiber is an intrinsic part of the light-transmitting concrete building product, LiTraCon.

Optical fiber is also used in imaging optics. A coherent bundle of fibers is used, sometimes along with lenses, for a long, thin imaging device called an endoscope, which is used to view objects through a small hole. Medical endoscopes are used for minimally invasive exploratory or surgical procedures (endoscopy). Industrial endoscopes are used for inspecting anything hard to reach, such as jet engine interiors.

In spectroscopy, optical fiber bundles are used to transmit light from a spectrometer to a substance which cannot be placed inside the spectrometer itself, in order to analyze its composition. A spectrometer analyzes substances by bouncing light off of and through them. By using fibers, a spectrometer can be used to study objects that are too large to fit inside, or gasses, or reactions which occur in pressure vessels.

An optical fiber doped with certain rare earth elements such as erbium can be used as the gain medium of a laser or optical amplifier. Rare-earth doped optical fibers can be used to provide signal amplification by splicing a short section of doped fiber into a regular (undoped) optical fiber line. The doped fiber is optically pumped with a second laser wavelength that is coupled into the line in addition to the signal wave. Both wavelengths of light are transmitted through the doped fiber, which transfers energy from the second pump wavelength to the signal wave. The process that causes the amplification is stimulated emission.

Optical fibers doped with a wavelength shifter are used to collect scintillation light in physics experiments.

Optical fiber can be used to supply a low level of power (around one watt) to electronics situated in a difficult electrical environment. Examples of this are electronics in high-powered antenna elements and measurement devices used in high voltage transmission equipment.

A growing trend in iron sights for arms, is the use of short pieces of optical fiber for contrast enhancement dots, made in such a way that ambient light falling on the length of the fiber is concentrated at the tip, making the dots slightly brighter than the surroundings. This method is most commonly used in front sights, but many makers offer sights that use fiber optics on front and rear sights. Fiber optic sights can now be found on handguns, rifles, and shotguns, both as aftermarket accessories and a growing number of factory guns.

Principle of operation

An optical fiber is a cylindrical dielectric waveguide (nonconducting waveguide) that transmits light along its axis, by the process of total internal reflection. The fiber consists of a *core* surrounded by a cladding layer, both of which are made of dielectric materials. To confine the optical signal in the core, the refractive index of the core must be greater than that of the cladding. The boundary between the core and cladding may either be abrupt, in *step-index fiber*, or gradual, in *graded-index fiber*.

Index of refraction

The index of refraction is a way of measuring the speed of light in a material. Light travels fastest in a vacuum, such as outer space. The speed of light in a vacuum is about 300,000 kilometres (186 thousand miles) per second. Index of refraction is calculated by dividing the speed of light in a vacuum by the speed of light in some other medium. The index of refraction of a vacuum is therefore 1, by definition. The typical value for the cladding of an optical fiber is 1.46. The core value is typically 1.48. The larger the index of refraction, the slower light travels in that medium. From this information, a good rule of thumb is that signal using optical fiber for communication will travel at around 200 million meters per second. Or to put it another way, to travel 1000 kilometers in fiber, the signal will take 5 milliseconds to propagate. Thus a phone call carried by fiber between Sydney and New York, a 12000 kilometer distance, means that there is an absolute minimum delay of 60 milliseconds (or around 1/16th of a second) between when one

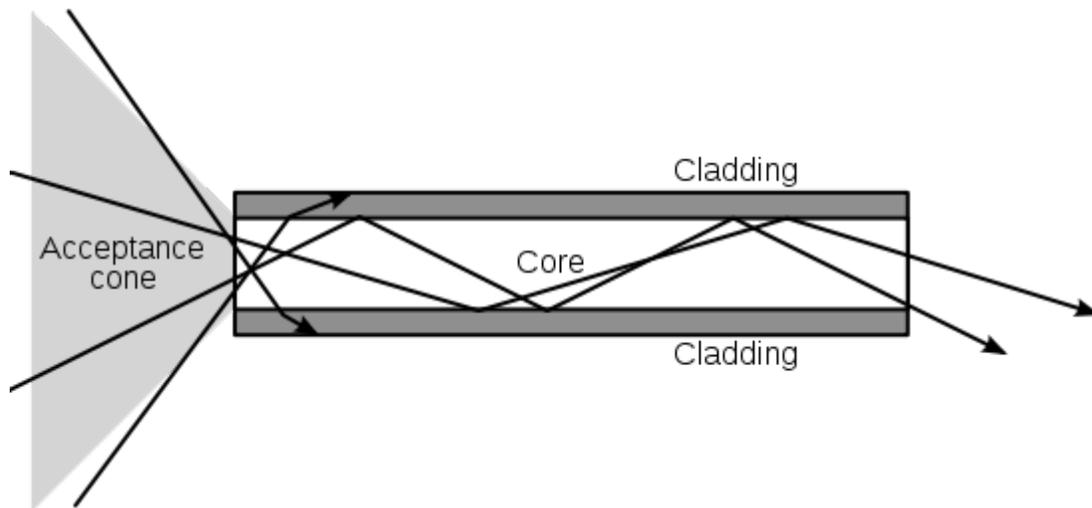
caller speaks to when the other hears. (Of course the fiber in this case will probably travel a longer route, and there will be additional delays due to communication equipment switching and the process of encoding and decoding the voice onto the fiber).

Total internal reflection

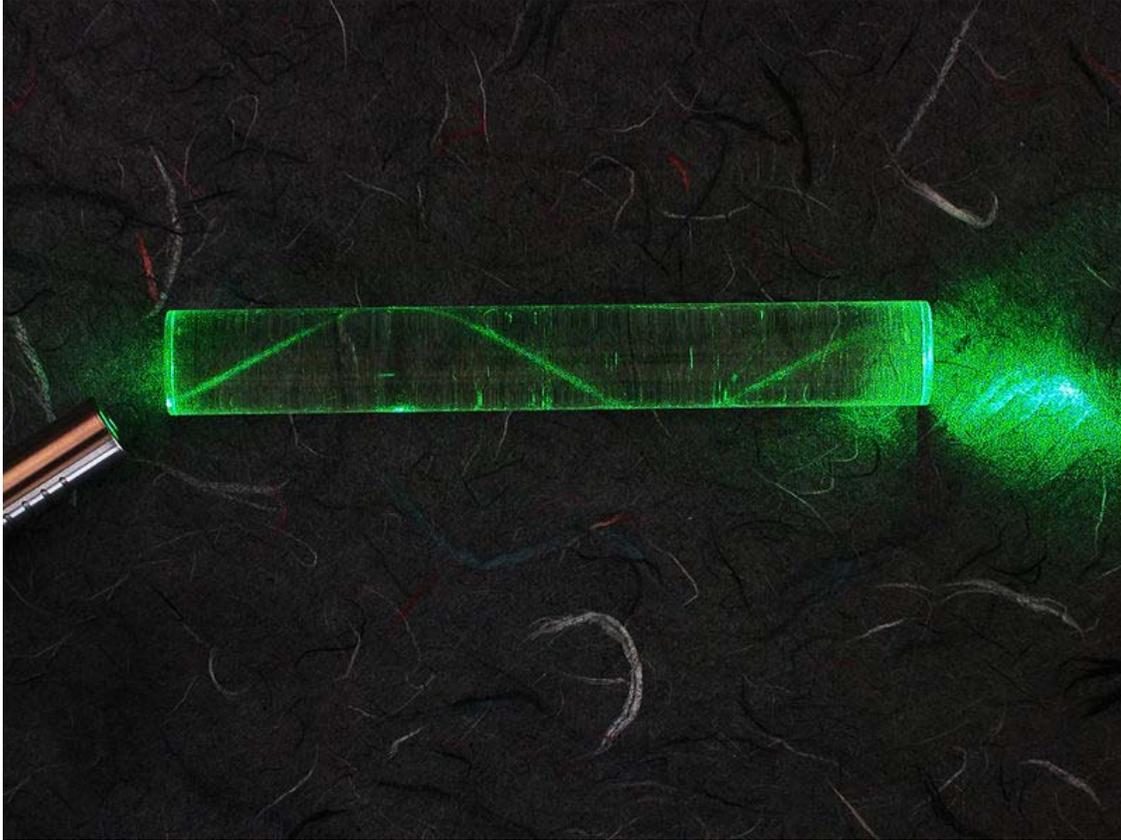
When light traveling in a dense medium hits a boundary at a steep angle (larger than the "critical angle" for the boundary), the light will be completely reflected. This effect is used in optical fibers to confine light in the core. Light travels along the fiber bouncing back and forth off of the boundary. Because the light must strike the boundary with an angle greater than the critical angle, only light that enters the fiber within a certain range of angles can travel down the fiber without leaking out. This range of angles is called the acceptance cone of the fiber. The size of this acceptance cone is a function of the refractive index difference between the fiber's core and cladding.

In simpler terms, there is a maximum angle from the fiber axis at which light may enter the fiber so that it will propagate, or travel, in the core of the fiber. The sine of this maximum angle is the numerical aperture (NA) of the fiber. Fiber with a larger NA requires less precision to splice and work with than fiber with a smaller NA. Single-mode fiber has a small NA.

Multi-mode fiber

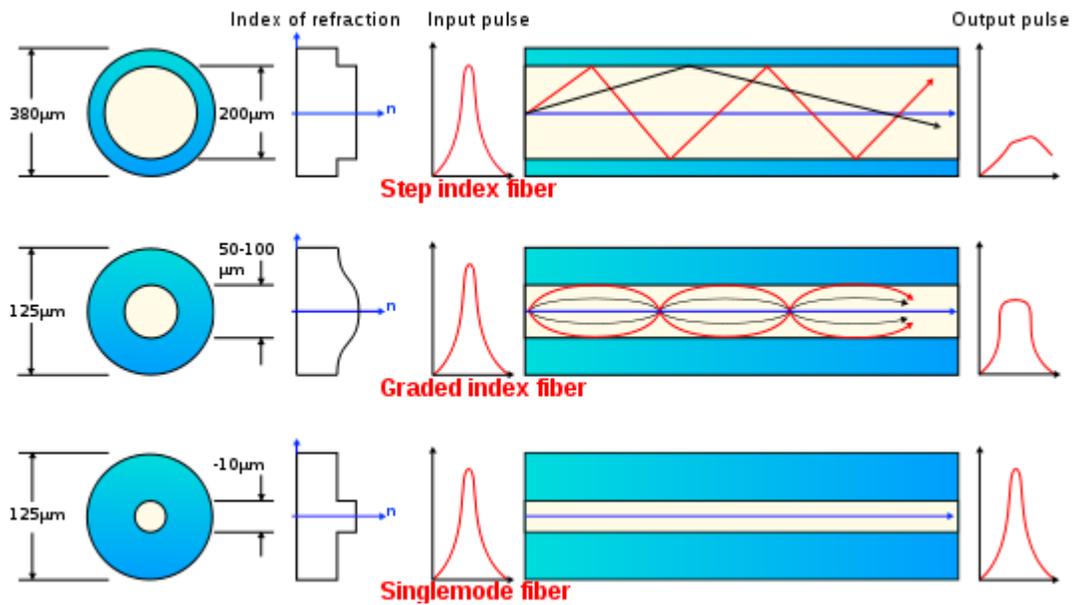


The propagation of light through a multi-mode optical fiber.



A laser bouncing down an acrylic rod, illustrating the total internal reflection of light in a multi-mode optical fiber.

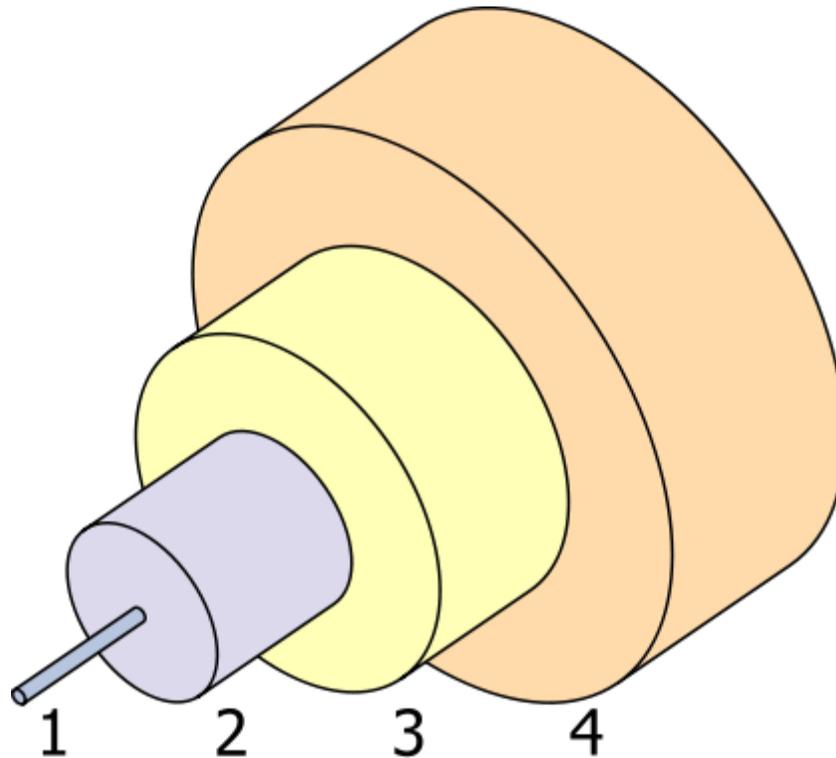
Fiber with large core diameter (greater than 10 micrometers) may be analyzed by geometrical optics. Such fiber is called *multi-mode fiber*, from the electromagnetic analysis. In a step-index multi-mode fiber, rays of light are guided along the fiber core by total internal reflection. Rays that meet the core-cladding boundary at a high angle (measured relative to a line normal to the boundary), greater than the critical angle for this boundary, are completely reflected. The critical angle (minimum angle for total internal reflection) is determined by the difference in index of refraction between the core and cladding materials. Rays that meet the boundary at a low angle are refracted from the core into the cladding, and do not convey light and hence information along the fiber. The critical angle determines the acceptance angle of the fiber, often reported as a numerical aperture. A high numerical aperture allows light to propagate down the fiber in rays both close to the axis and at various angles, allowing efficient coupling of light into the fiber. However, this high numerical aperture increases the amount of dispersion as rays at different angles have different path lengths and therefore take different times to traverse the fiber.



Optical fiber types.

In graded-index fiber, the index of refraction in the core decreases continuously between the axis and the cladding. This causes light rays to bend smoothly as they approach the cladding, rather than reflecting abruptly from the core-cladding boundary. The resulting curved paths reduce multi-path dispersion because high angle rays pass more through the lower-index periphery of the core, rather than the high-index center. The index profile is chosen to minimize the difference in axial propagation speeds of the various rays in the fiber. This ideal index profile is very close to a parabolic relationship between the index and the distance from the axis.

Single-mode fiber



The structure of a typical single-mode fiber.

1. Core: 8 μm diameter
2. Cladding: 125 μm dia.
3. Buffer: 250 μm dia.
4. Jacket: 400 μm dia.

Fiber with a core diameter less than about ten times the wavelength of the propagating light cannot be modeled using geometric optics. Instead, it must be analyzed as an electromagnetic structure, by solution of Maxwell's equations as reduced to the electromagnetic wave equation. The electromagnetic analysis may also be required to understand behaviors such as speckle that occur when coherent light propagates in multi-mode fiber. As an optical waveguide, the fiber supports one or more confined transverse modes by which light can propagate along the fiber. Fiber supporting only one mode is called *single-mode* or *mono-mode fiber*. The behavior of larger-core multi-mode fiber can also be modeled using the wave equation, which shows that such fiber supports more than one mode of propagation (hence the name). The results of such modeling of multi-mode fiber approximately agree with the predictions of geometric optics, if the fiber core is large enough to support more than a few modes.

The waveguide analysis shows that the light energy in the fiber is not completely confined in the core. Instead, especially in single-mode fibers, a significant fraction of the energy in the bound mode travels in the cladding as an evanescent wave.

The most common type of single-mode fiber has a core diameter of 8–10 micrometers and is designed for use in the near infrared. The mode structure depends on the

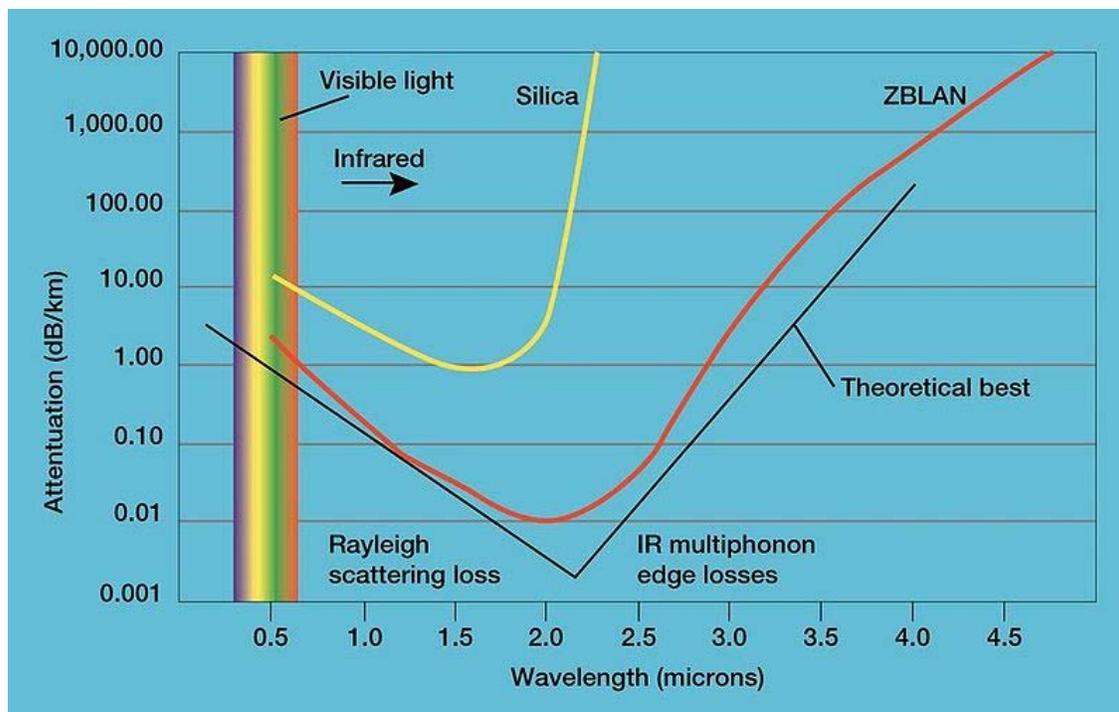
wavelength of the light used, so that this fiber actually supports a small number of additional modes at visible wavelengths. Multi-mode fiber, by comparison, is manufactured with core diameters as small as 50 micrometers and as large as hundreds of micrometers. The normalized frequency V for this fiber should be less than the first zero of the Bessel function J_0 (approximately 2.405).

Special-purpose fiber

Some special-purpose optical fiber is constructed with a non-cylindrical core and/or cladding layer, usually with an elliptical or rectangular cross-section. These include polarization-maintaining fiber and fiber designed to suppress whispering gallery mode propagation.

Photonic-crystal fiber is made with a regular pattern of index variation (often in the form of cylindrical holes that run along the length of the fiber). Such fiber uses diffraction effects instead of or in addition to total internal reflection, to confine light to the fiber's core. The properties of the fiber can be tailored to a wide variety of applications.

Mechanisms of attenuation

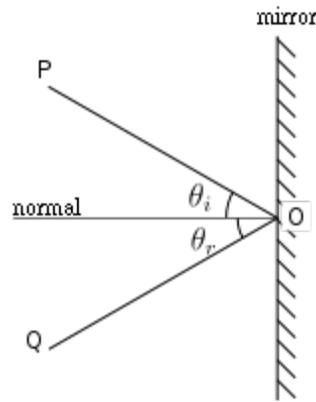


Light attenuation by ZBLAN and silica fibers

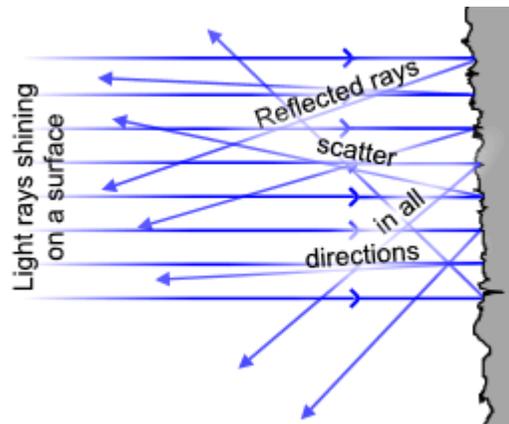
Attenuation in fiber optics, also known as transmission loss, is the reduction in intensity of the light beam (or signal) with respect to distance traveled through a transmission medium. Attenuation coefficients in fiber optics usually use units of dB/km through the medium due to the relatively high quality of transparency of modern optical transmission media. The medium is usually a fiber of silica glass that confines the incident light beam to the inside. Attenuation is an important factor limiting the transmission of a digital

signal across large distances. Thus, much research has gone into both limiting the attenuation and maximizing the amplification of the optical signal. Empirical research has shown that attenuation in optical fiber is caused primarily by both scattering and absorption.

Light scattering



Specular reflection



Diffuse reflection

The propagation of light through the core of an optical fiber is based on total internal reflection of the lightwave. Rough and irregular surfaces, even at the molecular level, can cause light rays to be reflected in random directions. This is called diffuse reflection or scattering, and it is typically characterized by wide variety of reflection angles.

Light scattering depends on the wavelength of the light being scattered. Thus, limits to spatial scales of visibility arise, depending on the frequency of the incident light-wave and the physical dimension (or spatial scale) of the scattering center, which is typically in the form of some specific micro-structural feature. Since visible light has a wavelength of the order of one micrometre (one millionth of a meter) scattering centers will have dimensions on a similar spatial scale.

Thus, attenuation results from the incoherent scattering of light at internal surfaces and interfaces. In (poly)crystalline materials such as metals and ceramics, in addition to

pores, most of the internal surfaces or interfaces are in the form of grain boundaries that separate tiny regions of crystalline order. It has recently been shown that when the size of the scattering center (or grain boundary) is reduced below the size of the wavelength of the light being scattered, the scattering no longer occurs to any significant extent. This phenomenon has given rise to the production of transparent ceramic materials.

Similarly, the scattering of light in optical quality glass fiber is caused by molecular level irregularities (compositional fluctuations) in the glass structure. Indeed, one emerging school of thought is that a glass is simply the limiting case of a polycrystalline solid. Within this framework, "domains" exhibiting various degrees of short-range order become the building blocks of both metals and alloys, as well as glasses and ceramics. Distributed both between and within these domains are micro-structural defects which will provide the most ideal locations for the occurrence of light scattering. This same phenomenon is seen as one of the limiting factors in the transparency of IR missile domes.

At high optical powers, scattering can also be caused by nonlinear optical processes in the fiber.

UV-Vis-IR absorption

In addition to light scattering, attenuation or signal loss can also occur due to selective absorption of specific wavelengths, in a manner similar to that responsible for the appearance of color. Primary material considerations include both electrons and molecules as follows:

- 1) At the electronic level, it depends on whether the electron orbitals are spaced (or "quantized") such that they can absorb a quantum of light (or photon) of a specific wavelength or frequency in the ultraviolet (UV) or visible ranges. This is what gives rise to color.
- 2) At the atomic or molecular level, it depends on the frequencies of atomic or molecular vibrations or chemical bonds, how close-packed its atoms or molecules are, and whether or not the atoms or molecules exhibit long-range order. These factors will determine the capacity of the material transmitting longer wavelengths in the infrared (IR), far IR, radio and microwave ranges.

The design of any optically transparent device requires the selection of materials based upon knowledge of its properties and limitations. The lattice absorption characteristics observed at the lower frequency regions (mid IR to far-infrared wavelength range) define the long-wavelength transparency limit of the material. They are the result of the interactive coupling between the motions of thermally induced vibrations of the constituent atoms and molecules of the solid lattice and the incident light wave radiation. Hence, all materials are bounded by limiting regions of absorption caused by atomic and molecular vibrations (bond-stretching) in the far-infrared ($>10 \mu\text{m}$).

Thus, multi-phonon absorption occurs when two or more phonons simultaneously interact to produce electric dipole moments with which the incident radiation may couple.

These dipoles can absorb energy from the incident radiation, reaching a maximum coupling with the radiation when the frequency is equal to the fundamental vibrational mode of the molecular dipole (e.g. Si-O bond) in the far-infrared, or one of its harmonics.

The selective absorption of infrared (IR) light by a particular material occurs because the selected frequency of the light wave matches the frequency (or an integer multiple of the frequency) at which the particles of that material vibrate. Since different atoms and molecules have different natural frequencies of vibration, they will selectively absorb different frequencies (or portions of the spectrum) of infrared (IR) light.

Reflection and transmission of light waves occur because the frequencies of the light waves do not match the natural resonant frequencies of vibration of the objects. When IR light of these frequencies strikes an object, the energy is either reflected or transmitted.

Manufacturing

Materials

Glass optical fibers are almost always made from silica, but some other materials, such as fluorozirconate, fluoroaluminate, and chalcogenide glasses as well as crystalline materials like sapphire, are used for longer-wavelength infrared or other specialized applications. Silica and fluoride glasses usually have refractive indices of about 1.5, but some materials such as the chalcogenides can have indices as high as 3. Typically the index difference between core and cladding is less than one percent.

Plastic optical fibers (POF) are commonly step-index multi-mode fibers with a core diameter of 0.5 millimeters or larger. POF typically have higher attenuation coefficients than glass fibers, 1 dB/m or higher, and this high attenuation limits the range of POF-based systems.

Silica

Silica exhibits fairly good optical transmission over a wide range of wavelengths. In the near-infrared (near IR) portion of the spectrum, particularly around 1.5 μm , silica can have extremely low absorption and scattering losses of the order of 0.2 dB/km. A high transparency in the 1.4- μm region is achieved by maintaining a low concentration of hydroxyl groups (OH). Alternatively, a high OH concentration is better for transmission in the ultraviolet (UV) region.

Silica can be drawn into fibers at reasonably high temperatures, and has a fairly broad glass transformation range. One other advantage is that fusion splicing and cleaving of silica fibers is relatively effective. Silica fiber also has high mechanical strength against both pulling and even bending, provided that the fiber is not too thick and that the surfaces have been well prepared during processing. Even simple cleaving (breaking) of the ends of the fiber can provide nicely flat surfaces with acceptable optical quality. Silica is also relatively chemically inert. In particular, it is not hygroscopic (does not absorb water).

Silica glass can be doped with various materials. One purpose of doping is to raise the refractive index (e.g. with Germanium dioxide (GeO_2) or Aluminium oxide (Al_2O_3)) or to lower it (e.g. with fluorine or Boron trioxide (B_2O_3)). Doping is also possible with laser-active ions (for example, rare earth-doped fibers) in order to obtain active fibers to be used, for example, in fiber amplifiers or laser applications. Both the fiber core and cladding are typically doped, so that the entire assembly (core and cladding) is effectively the same compound (e.g. an aluminosilicate, germanosilicate, phosphosilicate or borosilicate glass).

Particularly for active fibers, pure silica is usually not a very suitable host glass, because it exhibits a low solubility for rare earth ions. This can lead to quenching effects due to clustering of dopant ions. Aluminosilicates are much more effective in this respect.

Silica fiber also exhibits a high threshold for optical damage. This property ensures a low tendency for laser-induced breakdown. This is important for fiber amplifiers when utilized for the amplification of short pulses.

Because of these properties silica fibers are the material of choice in many optical applications, such as communications (except for very short distances with plastic optical fiber), fiber lasers, fiber amplifiers, and fiber-optic sensors. The large efforts which have been put forth in the development of various types of silica fibers have further increased the performance of such fibers over other materials.

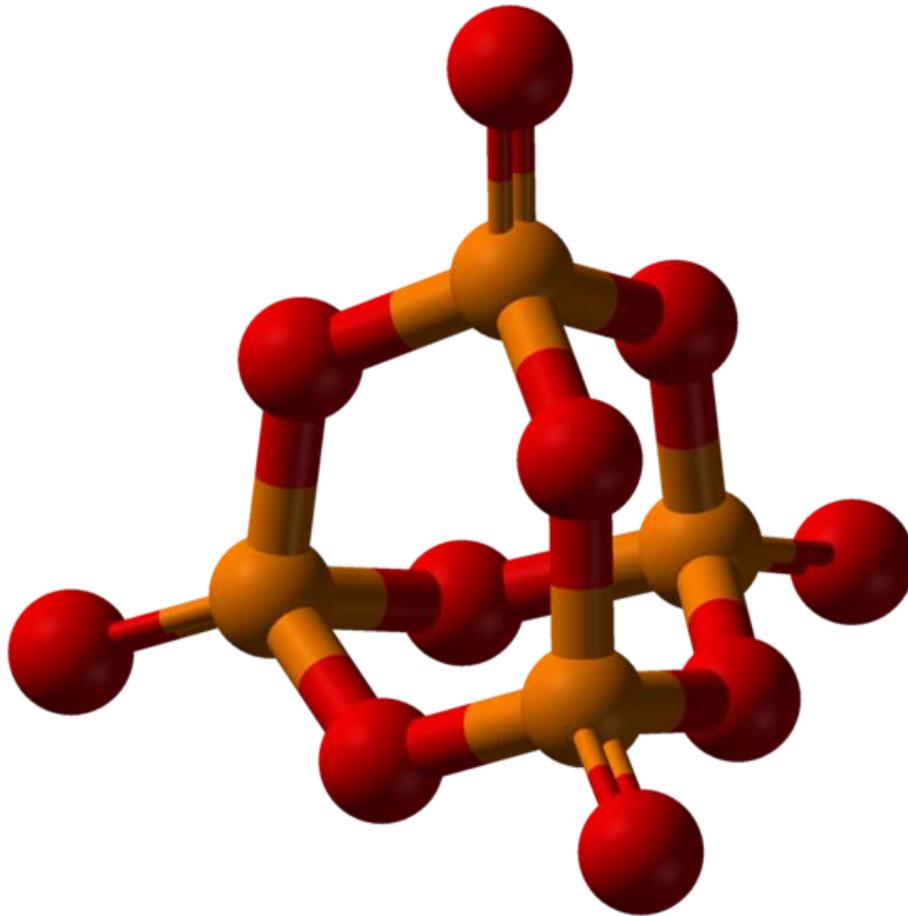
Fluorides

Fluoride glass is a class of non-oxide optical quality glasses composed of fluorides of various metals. Because of their low viscosity, it is very difficult to completely avoid crystallization while processing it through the glass transition (or drawing the fiber from the melt). Thus, although heavy metal fluoride glasses (HMFG) exhibit very low optical attenuation, they are not only difficult to manufacture, but are quite fragile, and have poor resistance to moisture and other environmental attacks. Their best attribute is that they lack the absorption band associated with the hydroxyl (OH) group ($3200\text{--}3600\text{ cm}^{-1}$), which is present in nearly all oxide-based glasses.

An example of a heavy metal fluoride glass is the ZBLAN glass group, composed of zirconium, barium, lanthanum, aluminium, and sodium fluorides. Their main technological application is as optical waveguides in both planar and fiber form. They are advantageous especially in the mid-infrared (2000–5000 nm) range.

HMFGs were initially slated for optical fiber applications, because the intrinsic losses of a mid-IR fiber could in principle be lower than those of silica fibers, which are transparent only up to about $2\text{ }\mu\text{m}$. However, such low losses were never realized in practice, and the fragility and high cost of fluoride fibers made them less than ideal as primary candidates. Later, the utility of fluoride fibers for various other applications was discovered. These include mid-IR spectroscopy, fiber optic sensors, thermometry, and imaging. Also, fluoride fibers can be used for guided lightwave transmission in media such as YAG (yttria-alumina garnet) lasers at $2.9\text{ }\mu\text{m}$, as required for medical applications (e.g. ophthalmology and dentistry).

Phosphates



The P_4O_{10} cage-like structure—the basic building block for phosphate glass.

Phosphate glass constitutes a class of optical glasses composed of metaphosphates of various metals. Instead of the SiO_4 tetrahedra observed in silicate glasses, the building block for this glass former is Phosphorus pentoxide (P_2O_5), which crystallizes in at least four different forms. The most familiar polymorph comprises molecules of P_4O_{10} .

Phosphate glasses can be advantageous over silica glasses for optical fibers with a high concentration of doping rare earth ions. A mix of fluoride glass and phosphate glass is fluorophosphate glass.

Chalcogenides

The chalcogens—the elements in group 16 of the periodic table—particularly sulfur (S), selenium (Se) and tellurium (Te)—react with more electropositive elements, such as silver, to form chalcogenides. These are extremely versatile compounds, in that they can be crystalline or amorphous, metallic or semiconducting, and conductors of ions or electrons.

Process

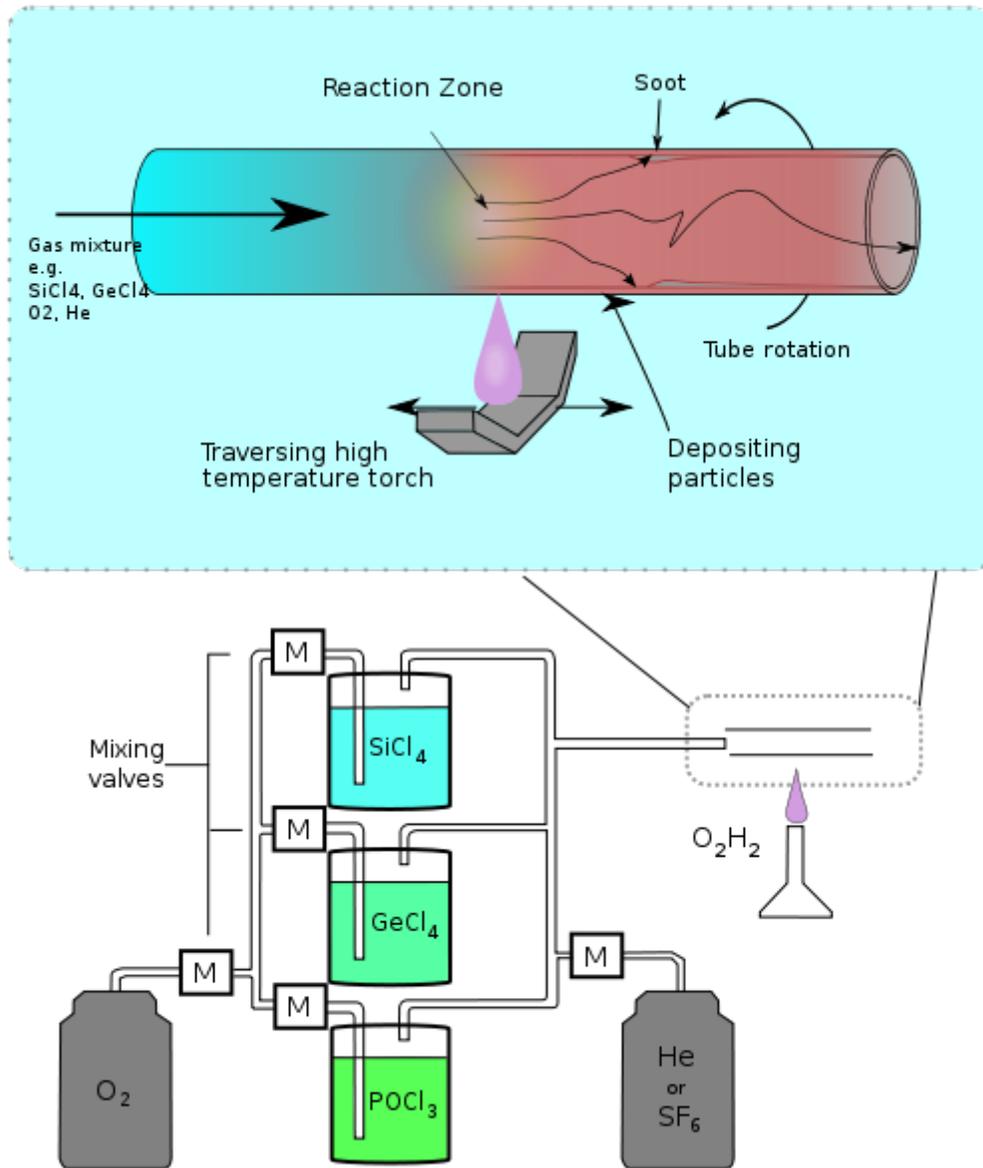


Illustration of the modified chemical vapor deposition (inside) process

Standard optical fibers are made by first constructing a large-diameter *preform*, with a carefully controlled refractive index profile, and then *pulling* the preform to form the long, thin optical fiber. The preform is commonly made by three chemical vapor deposition methods: *inside vapor deposition*, *outside vapor deposition*, and *vapor axial deposition*.

With *inside vapor deposition*, the preform starts as a hollow glass tube approximately 40 centimeters (16 in) long, which is placed horizontally and rotated slowly on a lathe. Gases such as silicon tetrachloride (SiCl₄) or germanium tetrachloride (GeCl₄) are injected with oxygen in the end of the tube. The gases are then heated by means of an external hydrogen burner, bringing the temperature of the gas up to 1900 K (1600 °C,

3000 °F), where the tetrachlorides react with oxygen to produce silica or germania (germanium dioxide) particles. When the reaction conditions are chosen to allow this reaction to occur in the gas phase throughout the tube volume, in contrast to earlier techniques where the reaction occurred only on the glass surface, this technique is called *modified chemical vapor deposition (MCVD)*.

The oxide particles then agglomerate to form large particle chains, which subsequently deposit on the walls of the tube as soot. The deposition is due to the large difference in temperature between the gas core and the wall causing the gas to push the particles outwards (this is known as thermophoresis). The torch is then traversed up and down the length of the tube to deposit the material evenly. After the torch has reached the end of the tube, it is then brought back to the beginning of the tube and the deposited particles are then melted to form a solid layer. This process is repeated until a sufficient amount of material has been deposited. For each layer the composition can be modified by varying the gas composition, resulting in precise control of the finished fiber's optical properties.

In outside vapor deposition or vapor axial deposition, the glass is formed by *flame hydrolysis*, a reaction in which silicon tetrachloride and germanium tetrachloride are oxidized by reaction with water (H₂O) in an oxyhydrogen flame. In outside vapor deposition the glass is deposited onto a solid rod, which is removed before further processing. In vapor axial deposition, a short *seed rod* is used, and a porous preform, whose length is not limited by the size of the source rod, is built up on its end. The porous preform is consolidated into a transparent, solid preform by heating to about 1800 K (1500 °C, 2800 °F).

The preform, however constructed, is then placed in a device known as a drawing tower, where the preform tip is heated and the optic fiber is pulled out as a string. By measuring the resultant fiber width, the tension on the fiber can be controlled to maintain the fiber thickness.

Coatings

The light is "guided" down the core of the fiber by an optical "cladding" with a lower refractive index that traps light in the core through "total internal reflection."

The cladding is coated by a "buffer" that protects it from moisture and physical damage. The buffer is what gets stripped off the fiber for termination or splicing. These coatings are UV-cured urethane acrylate composite materials applied to the outside of the fiber during the drawing process. The coatings protect the very delicate strands of glass fiber—about the size of a human hair—and allow it to survive the rigors of manufacturing, proof testing, cabling and installation.

Today's glass optical fiber draw processes employ a dual-layer coating approach. An inner primary coating is designed to act as a shock absorber to minimize attenuation caused by microbending. An outer secondary coating protects the primary coating against mechanical damage and acts as a barrier to lateral forces. Sometimes a metallic armour layer is added to provide extra protection.

These fiber optic coating layers are applied during the fiber draw, at speeds approaching 100 kilometers per hour (60 mph). Fiber optic coatings are applied using one of two methods: wet-on-dry, in which the fiber passes through a primary coating application, which is then UV cured, then through the secondary coating application which is subsequently cured; and wet-on-wet, in which the fiber passes through both the primary and secondary coating applications and then goes to UV curing.

Fiber optic coatings are applied in concentric layers to prevent damage to the fiber during the drawing application and to maximize fiber strength and microbend resistance. Unevenly coated fiber will experience non-uniform forces when the coating expands or contracts, and is susceptible to greater signal attenuation. Under proper drawing and coating processes, the coatings are concentric around the fiber, continuous over the length of the application and have constant thickness.

Fiber optic coatings protect the glass fibers from scratches that could lead to strength degradation. The combination of moisture and scratches accelerates the aging and deterioration of fiber strength. When fiber is subjected to low stresses over a long period, fiber fatigue can occur. Over time or in extreme conditions, these factors combine to cause microscopic flaws in the glass fiber to propagate, which can ultimately result in fiber failure.

Three key characteristics of fiber optic waveguides can be affected by environmental conditions: strength, attenuation and resistance to losses caused by microbending. External fiber optic coatings protect glass optical fiber from environmental conditions that can affect the fiber's performance and long-term durability. On the inside, coatings ensure the reliability of the signal being carried and help minimize attenuation due to microbending.

Practical issues

Optical fiber cables



An optical fiber cable

In practical fibers, the cladding is usually coated with a tough resin *buffer* layer, which may be further surrounded by a *jacket* layer, usually glass. These layers add strength to

the fiber but do not contribute to its optical wave guide properties. Rigid fiber assemblies sometimes put light-absorbing ("dark") glass between the fibers, to prevent light that leaks out of one fiber from entering another. This reduces cross-talk between the fibers, or reduces flare in fiber bundle imaging applications.

Modern cables come in a wide variety of sheathings and armor, designed for applications such as direct burial in trenches, high voltage isolation, dual use as power lines, installation in conduit, lashing to aerial telephone poles, submarine installation, and insertion in paved streets. The cost of small fiber-count pole-mounted cables has greatly decreased due to the high demand for fiber to the home (FTTH) installations in Japan and South Korea.

Fiber cable can be very flexible, but traditional fiber's loss increases greatly if the fiber is bent with a radius smaller than around 30 mm. This creates a problem when the cable is bent around corners or wound around a spool, making FTTX installations more complicated. "Bendable fibers", targeted towards easier installation in home environments, have been standardized as ITU-T G.657. This type of fiber can be bent with a radius as low as 7.5 mm without adverse impact. Even more bendable fibers have been developed. Bendable fiber may also be resistant to fiber hacking, in which the signal in a fiber is surreptitiously monitored by bending the fiber and detecting the leakage.

Another important feature of cable is cable withstanding against the horizontally applied force. It is technically called max tensile strength defining how much force can be applied to the cable during the installation period.

Telecom Anatolia fiber optic cable versions are reinforced with aramid yarns or glass yarns as intermediary strength member. In commercial terms, usage of the glass yarns are more cost effective while no loss in mechanical durability of the cable. Glass yarns also protect the cable core against rodents and termites.

Termination and splicing



ST connectors on multi-mode fiber.

Optical fibers are connected to terminal equipment by optical fiber connectors. These connectors are usually of a standard type such as *FC*, *SC*, *ST*, *LC*, or *MTRJ*.

Optical fibers may be connected to each other by connectors or by *splicing*, that is, joining two fibers together to form a continuous optical waveguide. The generally accepted splicing method is arc fusion splicing, which melts the fiber ends together with an electric arc. For quicker fastening jobs, a "mechanical splice" is used.

Fusion splicing is done with a specialized instrument that typically operates as follows: The two cable ends are fastened inside a splice enclosure that will protect the splices, and the fiber ends are stripped of their protective polymer coating (as well as the more sturdy

outer jacket, if present). The ends are *cleaved* (cut) with a precision cleaver to make them perpendicular, and are placed into special holders in the splicer. The splice is usually inspected via a magnified viewing screen to check the cleaves before and after the splice. The splicer uses small motors to align the end faces together, and emits a small spark between electrodes at the gap to burn off dust and moisture. Then the splicer generates a larger spark that raises the temperature above the melting point of the glass, fusing the ends together permanently. The location and energy of the spark is carefully controlled so that the molten core and cladding do not mix, and this minimizes optical loss. A splice loss estimate is measured by the splicer, by directing light through the cladding on one side and measuring the light leaking from the cladding on the other side. A splice loss under 0.1 dB is typical. The complexity of this process makes fiber splicing much more difficult than splicing copper wire.

Mechanical fiber splices are designed to be quicker and easier to install, but there is still the need for stripping, careful cleaning and precision cleaving. The fiber ends are aligned and held together by a precision-made sleeve, often using a clear index-matching gel that enhances the transmission of light across the joint. Such joints typically have higher optical loss and are less robust than fusion splices, especially if the gel is used. All splicing techniques involve the use of an enclosure into which the splice is placed for protection afterward.

Fibers are terminated in connectors so that the fiber end is held at the end face precisely and securely. A fiber-optic connector is basically a rigid cylindrical barrel surrounded by a sleeve that holds the barrel in its mating socket. The mating mechanism can be "push and click", "turn and latch" ("bayonet"), or screw-in (threaded). A typical connector is installed by preparing the fiber end and inserting it into the rear of the connector body. Quick-set adhesive is usually used so the fiber is held securely, and a strain relief is secured to the rear. Once the adhesive has set, the fiber's end is polished to a mirror finish. Various polish profiles are used, depending on the type of fiber and the application. For single-mode fiber, the fiber ends are typically polished with a slight curvature, such that when the connectors are mated the fibers touch only at their cores. This is known as a "physical contact" (PC) polish. The curved surface may be polished at an angle, to make an "angled physical contact" (APC) connection. Such connections have higher loss than PC connections, but greatly reduced back reflection, because light that reflects from the angled surface leaks out of the fiber core; the resulting loss in signal strength is known as gap loss. APC fiber ends have low back reflection even when disconnected.

In the 1990s, terminating fiber optic cables was very labor intensive. The number of parts per connector, polishing of the fibers, and the need to oven-bake the epoxy in each connector made terminating fiber optic cables very difficult. Today, many different connectors are on the market and offer an easier, less labor intensive way of terminating the cables. Some of the most popular connectors have already been polished from the factory and include a gel inside the connector and those two steps help save money on labor especially on large projects. A cleave is made at a required length in order to get as close to the polished piece already inside the connector, with the gel surrounding the point where the two piece meet inside the connector very little light loss is exposed.

Free-space coupling

It is often necessary to align an optical fiber with another optical fiber, or with an optoelectronic device such as a light-emitting diode, a laser diode, or a modulator. This can involve either carefully aligning the fiber and placing it in contact with the device, or can use a lens to allow coupling over an air gap. In some cases the end of the fiber is polished into a curved form that is designed to allow it to act as a lens.

In a laboratory environment, a bare fiber end is coupled using a fiber launch system, which uses a microscope objective lens to focus the light down to a fine point. A precision translation stage (micro-positioning table) is used to move the lens, fiber, or device to allow the coupling efficiency to be optimized. Fibers with a connector on the end make this process much simpler: the connector is simply plugged into a pre-aligned fiberoptic collimator, which contains a lens that is either accurately positioned with respect to the fiber, or is adjustable. To achieve the best injection efficiency into single-mode fiber, the direction, position, size and divergence of the beam must all be optimized. With good beams, 70 to 90% coupling efficiency can be achieved.

With properly polished single-mode fibers, the emitted beam has an almost perfect Gaussian shape—even in the far field—if a good lens is used. The lens needs to be large enough to support the full numerical aperture of the fiber, and must not introduce aberrations in the beam. Aspheric lenses are typically used.

Fiber fuse

At high optical intensities, above 2 megawatts per square centimeter, when a fiber is subjected to a shock or is otherwise suddenly damaged, a *fiber fuse* can occur. The reflection from the damage vaporizes the fiber immediately before the break, and this new defect remains reflective so that the damage propagates back toward the transmitter at 1–3 meters per second (4–11 km/h, 2–8 mph). The open fiber control system, which ensures laser eye safety in the event of a broken fiber, can also effectively halt propagation of the fiber fuse. In situations, such as undersea cables, where high power levels might be used without the need for open fiber control, a "fiber fuse" protection device at the transmitter can break the circuit to prevent any damage.

Example

Fiber connections can be used for various types of connections. For example, most high definition televisions offer a digital audio optical connection. This allows the streaming of audio over light, using the TOSLink protocol.

Electric power transmission

Optical fiber can be used to transmit electricity. While the efficiency is not nearly that of traditional copper wire, it is especially useful in situations where it is desirable to not have a metallic conductor as in the case of use near MRI machines which produce strong magnetic currents.

Chapter 3

Radioactive Waste

Radioactive waste is a waste product containing radioactive material. It is usually the product of a nuclear process such as nuclear fission, though industries not directly connected to the nuclear power industry may also produce radioactive waste.

Radioactivity diminishes over time, so in principle the waste needs to be isolated for a period of time until it no longer poses a hazard. This can mean hours to years for some common medical or industrial radioactive wastes, or thousands of years for high-level wastes from nuclear power plants and nuclear weapons reprocessing.

The majority of radioactive waste is "low-level waste", meaning it has low levels of radioactivity per mass or volume.

The main approaches to managing radioactive waste to date have been segregation and storage for short-lived wastes, near-surface disposal for low and some intermediate level wastes, and deep burial or transmutation for the long-lived, high-level wastes.

A summary of the amounts of radioactive wastes and management approaches for most developed countries are presented and reviewed periodically as part of the IAEA Joint Convention on Safety of Spent Fuel Management and the Safety of Radioactive Waste Management.

The nature and significance of radioactive waste

Radioactive waste typically comprises a number of radioisotopes: unstable configurations of elements that decay, emitting ionizing radiation which can be harmful to humans and the environment. Those isotopes emit different types and levels of radiation, which last for different periods of time.

Physics

Long-lived fission products				
Prop:	$t^{1/2}$	Yield	Q *	$\beta\gamma$
Unit:	Ma	%	KeV *	*
⁹⁹ Tc	0.211	6.1385	294	β
¹²⁶ Sn	0.230	0.1084	4050	$\beta\gamma$
⁷⁹ Se	0.327	0.0447	151	β
⁹³ Zr	1.53	5.4575	91	$\beta\gamma$
¹³⁵ Cs	2.3	6.9110	269	β
¹⁰⁷ Pd	6.5	1.2499	33	β
¹²⁹ I	15.7	0.8410	194	$\beta\gamma$

Medium-lived fission products				
Prop:	$t^{1/2}$	Yield	Q *	$\beta\gamma$
Unit:	a	%	KeV *	*
¹⁵⁵ Eu	4.76	.0803	252	$\beta\gamma$
⁸⁵ Kr	10.76	.2180	687	$\beta\gamma$
^{113m} Cd	14.1	.0008	316	β
⁹⁰ Sr	28.9	4.505	2826	β
¹³⁷ Cs	30.23	6.337	1176	$\beta\gamma$
^{121m} Sn	43.9	.00005	390	$\beta\gamma$
¹⁵¹ Sm	90	.5314	77	β

The radioactivity of all nuclear waste diminishes with time. All radioisotopes contained in the waste have a half-life—the time it takes for any radionuclide to lose half of its radioactivity—and eventually all radioactive waste decays into non-radioactive elements. Certain radioactive elements (such as plutonium-239) in “spent” fuel will remain hazardous to humans and other creatures for hundreds of thousands of years. Other radioisotopes remain hazardous for millions of years. Thus, these wastes must be shielded for centuries and isolated from the living environment for millennia. Some elements, such as iodine-131, have a short half-life (around 8 days in this case) and thus they will cease to be a problem much more quickly than other, longer-lived, decay products, but their activity is much greater initially. The two tables show some of the major radioisotopes, their half-lives, and their radiation yield as a proportion of the yield of fission of uranium-235.

The faster a radioisotope decays, the more radioactive it will be. The energy and the type of the ionizing radiation emitted by a pure radioactive substance are important factors in

deciding how dangerous it is. The chemical properties of the radioactive element will determine how mobile the substance is and how likely it is to spread into the environment and contaminate humans. This is further complicated by the fact that many radioisotopes do not decay immediately to a stable state but rather to a radioactive decay product leading to decay chains.

Pharmacokinetics

Actinides				Half-life	Fission products	
²⁴⁴ Cm	²⁴¹ Pu ^f	²⁵⁰ Cf	²⁴³ Cm ^f	10–30 y	¹³⁷ Cs ⁹⁰ Sr ⁸⁵ Kr	
²³² U ^f		²³⁸ Pu	f is for	69–90 y	¹⁵¹ Sm nc→	
4n	²⁴⁹ Cf ^f	²⁴² Am ^f	fissile	141–351	No fission product has half-life 10 ² to 2×10 ⁵ years	
	²⁴¹ Am		²⁵¹ Cf ^f	431–898		
²⁴⁰ Pu	²²⁹ Th	²⁴⁶ Cm	²⁴³ Am	5–7 ky		
4n	²⁴⁵ Cm ^f	²⁵⁰ Cm	²³⁹ Pu ^f	8–24 ky		
	²³³ U ^f	²³⁰ Th	²³¹ Pa	32–160		
	²³⁴ U			211–290		⁹⁹ Tc ¹²⁶ Sn ⁷⁹ Se
²⁴⁸ Cm	4n+1	²⁴² Pu	4n+3	340–373		Long-lived fission products
	²³⁷ Np			1–2 my		⁹³ Zr ¹³⁵ Cs nc→
²³⁶ U		4n+2	²⁴⁷ Cm ^f	6–23		¹⁰⁷ Pd ¹²⁹ I
²⁴⁴ Pu	4n+1			80 my		>7% >5% >1% >.1%
²³² Th		²³⁸ U	²³⁵ U ^f	0.7–12by	fission product yield	

Exposure to high levels of radioactive waste may cause serious harm or death. Treatment of an adult animal with radiation or some other mutation-causing effect, such as a cytotoxic anti-cancer drug, may cause cancer in the animal. In humans it has been calculated that a 5 sievert dose is usually fatal, and the lifetime risk of dying from radiation induced cancer from a single dose of 0.1 sieverts is 0.8%, increasing by the same amount for each additional 0.1 sievert increment of dosage. Ionizing radiation causes deletions in chromosomes. If a developing organism such as an unborn child is irradiated, it is possible a birth defect may be induced, but it is unlikely this defect will be in a gamete or a gamete forming cell. The incidence of radiation-induced mutations in humans is undetermined, due to flaws in studies done to date.

Depending on the decay mode and the pharmacokinetics of an element (how the body processes it and how quickly), the threat due to exposure to a given activity of a radioisotope will differ. For instance iodine-131 is a short-lived beta and gamma emitter, but because it concentrates in the thyroid gland, it is more able to cause injury than caesium-137 which, being water soluble, is rapidly excreted in urine. In a similar way, the alpha emitting actinides and radium are considered very harmful as they tend to have long biological half-lives and their radiation has a high linear energy transfer value. Because of such differences, the rules determining biological injury differ widely according to the radioisotope, and sometimes also the nature of the chemical compound which contains the radioisotope.

Sources of waste

Radioactive waste comes from a number of sources. The majority of waste originates from the nuclear fuel cycle and nuclear weapons reprocessing. However, other sources include medical and industrial wastes, as well as naturally occurring radioactive materials (NORM) that can be concentrated as a result of the processing or consumption of coal, oil and gas, and some minerals, as discussed below.

Nuclear fuel cycle

Front end

Waste from the front end of the nuclear fuel cycle is usually alpha-emitting waste from the extraction of uranium. It often contains radium and its decay products.

Uranium dioxide (UO_2) concentrate from mining is not very radioactive - only a thousand or so times as radioactive as the granite used in buildings. It is refined from yellowcake (U_3O_8), then converted to uranium hexafluoride gas (UF_6). As a gas, it undergoes enrichment to increase the U-235 content from 0.7% to about 4.4% (LEU). It is then turned into a hard ceramic oxide (UO_2) for assembly as reactor fuel elements.

The main by-product of enrichment is depleted uranium (DU), principally the U-238 isotope, with a U-235 content of ~0.3%. It is stored, either as UF_6 or as U_3O_8 . Some is used in applications where its extremely high density makes it valuable, such as the keels of yachts, and anti-tank shells. It is also used with plutonium for making mixed oxide fuel (MOX) and to dilute, or downblend, highly enriched uranium from weapons stockpiles which is now being redirected to become reactor fuel.

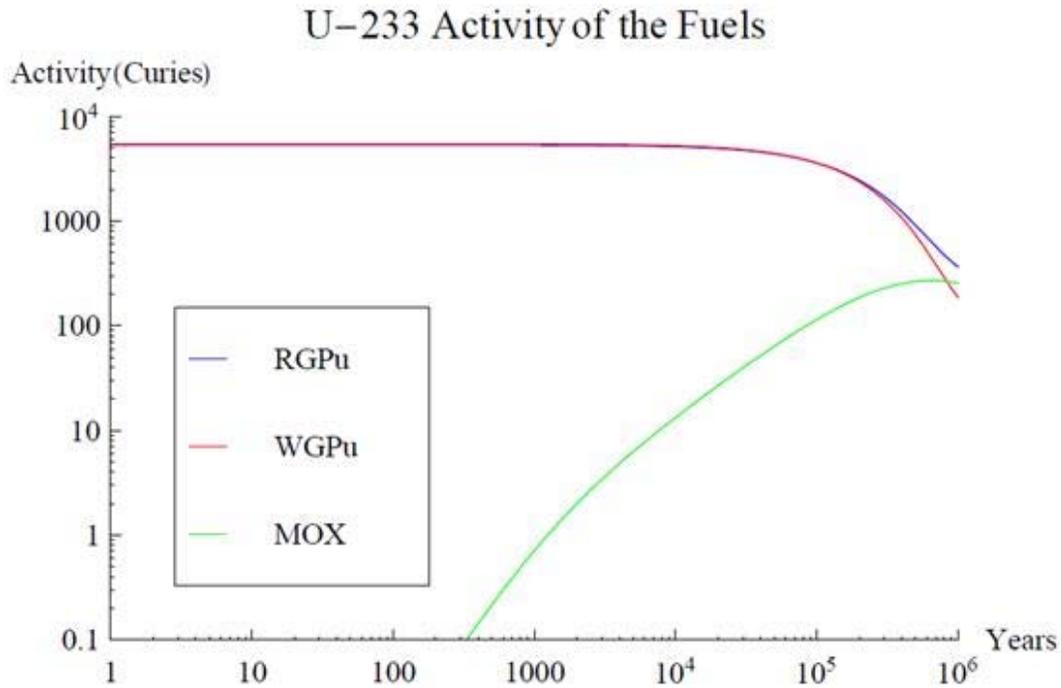
Back end

The back end of the nuclear fuel cycle, mostly spent fuel rods, contains fission products that emit beta and gamma radiation, and actinides that emit alpha particles, such as uranium-234, neptunium-237, plutonium-238 and americium-241, and even sometimes some neutron emitters such as californium (Cf). These isotopes are formed in nuclear reactors.

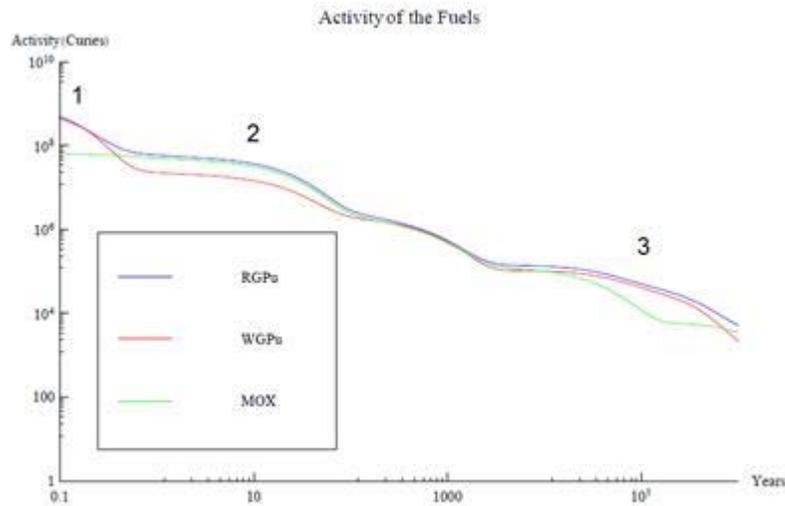
It is important to distinguish the processing of uranium to make fuel from the reprocessing of used fuel. Used fuel contains the highly radioactive products of fission. Many of these are neutron absorbers, called neutron poisons in this context. These eventually build up to a level where they absorb so many neutrons that the chain reaction stops, even with the control rods completely removed. At that point the fuel has to be replaced in the reactor with fresh fuel, even though there is still a substantial quantity of uranium-235 and plutonium present. In the United States, this used fuel is stored, while in countries such as Russia, the United Kingdom, France, Japan and India, the fuel is reprocessed to remove the fission products, and the fuel can then be re-used. This reprocessing involves handling highly radioactive materials, and the fission products removed from the fuel are a concentrated form of high-level waste as are the chemicals used in the process. While these countries reprocess the fuel carrying out single

plutonium cycles, India is the only country known to be planning multiple plutonium recycling schemes.

Fuel composition and long term radioactivity



Activity of U-233 for three fuel types



Total activity for three fuel types

Long-lived radioactive waste from the back end of the fuel cycle is especially relevant when designing a complete waste management plan for spent nuclear fuel (SNF). When

looking at long term radioactive decay, the actinides in the SNF have a significant influence due to their characteristically long half-lives. Depending on what a nuclear reactor is fueled with, the actinide composition in the SNF will be different.

An example of this effect is the use of nuclear fuels with thorium. Th-232 is a fertile material that can undergo a neutron capture reaction and two beta minus decays, resulting in the production of fissile U-233. The SNF of a cycle with thorium will contain U-233, an isotope with a half-life of maximum 20 years. Its radioactive decay will strongly influence the long-term activity curve of the SNF around 1 million years. A comparison of the activity associated to U-233 for three different SNF types can be seen in the figure on the top right.

The burnt fuels are thorium with reactor-grade plutonium (RGPu), thorium with weapons-grade plutonium (WGPu) and Mixed Oxide fuel (MOX). For RGPu and WGPu, the initial amount of U-233 and its decay around 1 million years can be seen. This has an effect in the total activity curve of the three fuel types. The absence of U-233 and its daughter products in the MOX fuel results in a lower activity in region 3 of the figure on the bottom right, whereas for RGPu and WGPu the curve is maintained higher due to the presence of U-233 that has not fully decayed.

The use of different fuels in nuclear reactors results in different SNF composition, with varying activity curves.

Proliferation concerns

Since uranium and plutonium are nuclear weapons materials, there have been proliferations concerns. Ordinarily (in spent nuclear fuel), plutonium is reactor-grade plutonium. In addition to plutonium-239, which is highly suitable for building nuclear weapons, it contains large amounts of undesirable contaminants: plutonium-240, plutonium-241, and plutonium-238. These isotopes are difficult to separate, and more cost-effective ways of obtaining fissile material exist (e.g. uranium enrichment or dedicated plutonium production reactors).

High-level waste is full of highly radioactive fission products, most of which are relatively short-lived. This is a concern since if the waste is stored, perhaps in deep geological storage, over many years the fission products decay, decreasing the radioactivity of the waste and making the plutonium easier to access. The undesirable contaminant Pu-240 decays faster than the Pu-239, and thus the quality of the bomb material increases with time (although its quantity decreases during that time as well). Thus, some have argued, as time passes, these deep storage areas have the potential to become "plutonium mines", from which material for nuclear weapons can be acquired with relatively little difficulty. Critics of the latter idea point out that the half-life of Pu-240 is 6,560 years and Pu-239 is 24,110 years, and thus the relative enrichment of one isotope to the other with time occurs with a half-life of 9,000 years (that is, it takes 9000 years for the *fraction* of Pu-240 in a sample of mixed plutonium isotopes, to spontaneously decrease by half—a typical enrichment needed to turn reactor-grade into weapons-grade Pu). Thus "weapons grade plutonium mines" would be a problem for the

very far future (>9,000 years from now), so that there remains a great deal of time for technology to advance to solve it.

Pu-239 decays to U-235 which is suitable for weapons and which has a very long half life (roughly 10^9 years). Thus plutonium may decay and leave uranium-235. However, modern reactors are only moderately enriched with U-235 relative to U-238, so the U-238 continues to serve as a denaturation agent for any U-235 produced by plutonium decay.

One solution to this problem is to recycle the plutonium and use it as a fuel e.g. in fast reactors. But in the minds of some, the very existence of the nuclear fuel reprocessing plant needed to separate the plutonium from the other elements represents a proliferation concern. In pyrometallurgical fast reactors, the separated plutonium and uranium are contaminated by actinides and cannot be used for nuclear weapons.

Nuclear weapons decommissioning

Waste from nuclear weapons decommissioning is unlikely to contain much beta or gamma activity other than tritium and americium. It is more likely to contain alpha-emitting actinides such as Pu-239 which is a fissile material used in bombs, plus some material with much higher specific activities, such as Pu-238 or Po.

In the past the neutron trigger for an atomic bomb tended to be beryllium and a high activity alpha emitter such as polonium; an alternative to polonium is Pu-238. For reasons of national security, details of the design of modern bombs are normally not released to the open literature.

Some designs might contain a radioisotope thermoelectric generator using Pu-238 to provide a long lasting source of electrical power for the electronics in the device.

It is likely that the fissile material of an old bomb which is due for refitting will contain decay products of the plutonium isotopes used in it, these are likely to include U-236 from Pu-240 impurities, plus some U-235 from decay of the Pu-239; due to the relatively long half-life of these Pu isotopes, these wastes from radioactive decay of bomb core material would be very small, and in any case, far less dangerous (even in terms of simple radioactivity) than the Pu-239 itself.

The beta decay of Pu-241 forms Am-241; the in-growth of americium is likely to be a greater problem than the decay of Pu-239 and Pu-240 as the americium is a gamma emitter (increasing external-exposure to workers) and is an alpha emitter which can cause the generation of heat. The plutonium could be separated from the americium by several different processes; these would include pyrochemical processes and aqueous/organic solvent extraction. A truncated PUREX type extraction process would be one possible method of making the separation.

Legacy waste

Due to historic activities typically related to radium industry, uranium mining, and military programs, there are numerous sites that contain or are contaminated with

radioactivity. In the United States alone, the Department of Energy states there are "millions of gallons of radioactive waste" as well as "thousands of tons of spent nuclear fuel and material" and also "huge quantities of contaminated soil and water." Despite copious quantities of waste, the DOE has stated a goal of cleaning all presently contaminated sites successfully by 2025. The Fernald, Ohio site for example had "31 million pounds of uranium product", "2.5 billion pounds of waste", "2.75 million cubic yards of contaminated soil and debris", and a "223 acre portion of the underlying Great Miami Aquifer had uranium levels above drinking standards." The United States has at least 108 sites designated as areas that are contaminated and unusable, sometimes many thousands of acres. DOE wishes to clean or mitigate many or all by 2025, however the task can be difficult and it acknowledges that some may never be completely remediated. In just one of these 108 larger designations, Oak Ridge National Laboratory, there were for example at least "167 known contaminant release sites" in one of the three subdivisions of the 37,000-acre (150 km²) site. Some of the U.S. sites were smaller in nature, however, cleanup issues were simpler to address, and DOE has successfully completed cleanup, or at least closure, of several sites.

It is a common misconception that nuclear waste has to be stored in a cave after its 20-year decommissioning process.

Medical

Radioactive medical waste tends to contain beta particle and gamma ray emitters. It can be divided into two main classes. In diagnostic nuclear medicine a number of short-lived gamma emitters such as technetium-99m are used. Many of these can be disposed of by leaving it to decay for a short time before disposal as normal waste. Other isotopes used in medicine, with half-lives in parentheses, include:

- Y-90, used for treating lymphoma (2.7 days)
- I-131, used for thyroid function tests and for treating thyroid cancer (8.0 days)
- Sr-89, used for treating bone cancer, intravenous injection (52 days)
- Ir-192, used for brachytherapy (74 days)
- Co-60, used for brachytherapy and external radiotherapy (5.3 years)
- Cs-137, used for brachytherapy, external radiotherapy (30 years)

Industrial

Industrial source waste can contain alpha, beta, neutron or gamma emitters. Gamma emitters are used in radiography while neutron emitting sources are used in a range of applications, such as oil well logging.

Naturally occurring radioactive material (NORM)

Processing of substances containing "natural" radioactivity is often known as NORM. A lot of this waste is alpha particle-emitting matter from the decay chains of uranium and thorium. The main source of radiation in the human body is potassium-40 (⁴⁰K). Most rocks, due to their components, have a certain, but low, level of radioactivity.

Coal

Coal contains a small amount of radioactive uranium, barium, thorium and potassium, but, in the case of pure coal, this is significantly less than the average concentration of those elements in the Earth's crust. The surrounding strata, if shale or mudstone, often contain slightly more than average and this may also be reflected in the ash content of 'dirty' coals. The more active ash minerals become concentrated in the fly ash precisely because they do not burn well. The radioactivity of fly ash is about the same as black shale and is less than phosphate rocks, but is more of a concern because a small amount of the fly ash ends up in the atmosphere where it can be inhaled.

Oil and gas

Residues from the oil and gas industry often contain radium and its daughters. The sulfate scale from an oil well can be very radium rich, while the water, oil and gas from a well often contain radon. The radon decays to form solid radioisotopes which form coatings on the inside of pipework. In an oil processing plant the area of the plant where propane is processed is often one of the more contaminated areas of the plant as radon has a similar boiling point to propane.

Types of radioactive waste



Removal of very low-level waste

Although not significantly radioactive, *uranium mill tailings* are waste. They are byproduct material from the rough processing of uranium-bearing ore. They are sometimes referred to as 11(e)2 wastes, from the section of the U.S. Atomic Energy Act that defines them. Uranium mill tailings typically also contain chemically hazardous heavy metals such as lead and arsenic. Vast mounds of uranium mill tailings are left at many old mining sites, especially in Colorado, New Mexico, and Utah.

Low level waste (LLW) is generated from hospitals and industry, as well as the nuclear fuel cycle. It comprises paper, rags, tools, clothing, filters, etc., which contain small amounts of mostly short-lived radioactivity. Commonly, LLW is designated as such as a precautionary measure if it originated from any region of an 'Active Area', which frequently includes offices with only a remote possibility of being contaminated with radioactive materials. Such LLW typically exhibits no higher radioactivity than one would expect from the same material disposed of in a non-active area, such as a normal office block. Some high activity LLW requires shielding during handling and transport but most LLW is suitable for shallow land burial. To reduce its volume, it is often compacted or incinerated before disposal. Low level waste is divided into four classes, class A, B, C and GTCC, which means "Greater Than Class C".

Intermediate level waste (ILW) contains higher amounts of radioactivity and in some cases requires shielding. ILW includes resins, chemical sludge and metal reactor fuel cladding, as well as contaminated materials from reactor decommissioning. It may be solidified in concrete or bitumen for disposal. As a general rule, short-lived waste (mainly non-fuel materials from reactors) is buried in shallow repositories, while long-lived waste (from fuel and fuel-reprocessing) is deposited in deep underground facilities. U.S. regulations do not define this category of waste; the term is used in Europe and elsewhere.



Spent Fuel Flasks are transported by railway in the United Kingdom. Each flask is constructed of 14 in (360 mm) thick solid steel and weighs in excess of 50 tons

High level waste (HLW) is produced by nuclear reactors. It contains fission products and transuranic elements generated in the reactor core. It is highly radioactive and often thermally hot. HLW accounts for over 95% of the total radioactivity produced in the process of nuclear electricity generation. The amount of HLW worldwide is currently increasing by about 12,000 metric tons every year, which is the equivalent to about 100 double-decker buses or a two-story structure with a footprint the size of a basketball court. A 1000-MWe nuclear power plant produces about 27 tonnes of spent nuclear fuel (unreprocessed) every year.

Transuranic waste (TRUW) as defined by U.S. regulations is, without regard to form or origin, waste that is contaminated with alpha-emitting transuranic radionuclides with half-lives greater than 20 years, and concentrations greater than 100 nCi/g (3.7 MBq/kg), excluding High Level Waste. Elements that have an atomic number greater than uranium are called transuranic ("beyond uranium"). Because of their long half-lives, TRUW is disposed more cautiously than either low level or intermediate level waste. In the US it arises mainly from weapons production, and consists of clothing, tools, rags, residues, debris and other items contaminated with small amounts of radioactive elements (mainly plutonium).

Under US law, transuranic waste is further categorized into "contact-handled" (CH) and "remote-handled" (RH) on the basis of radiation dose measured at the surface of the

waste container. CH TRUW has a surface dose rate not greater than 200 mrem per hour (2 mSv/h), whereas RH TRUW has a surface dose rate of 200 mrem per hour (2 mSv/h) or greater. CH TRUW does not have the very high radioactivity of high level waste, nor its high heat generation, but RH TRUW can be highly radioactive, with surface dose rates up to 1000000 mrem per hour (10000 mSv/h). The US currently permanently disposes of defense-related TRUW at the Waste Isolation Pilot Plant.

Management of waste

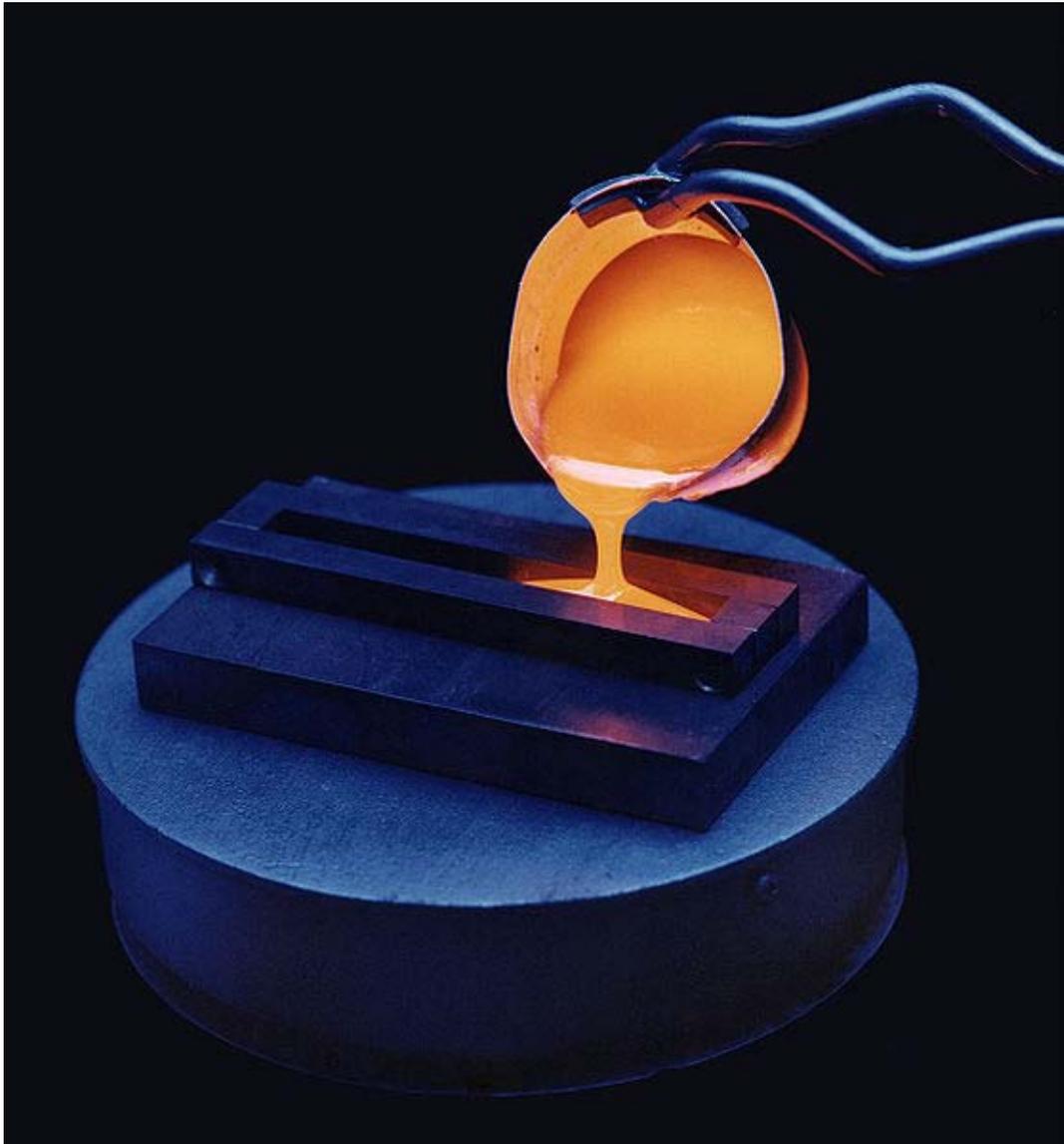


Modern medium to high level transport container for nuclear waste.

Of particular concern in nuclear waste management are two long-lived fission products, Tc-99 (half-life 220,000 years) and I-129 (half-life 17 million years), which dominate spent fuel radioactivity after a few thousand years. The most troublesome transuranic elements in spent fuel are Np-237 (half-life two million years) and Pu-239 (half life 24,000 years). Nuclear waste requires sophisticated treatment and management to successfully isolate it from interacting with the biosphere. This usually necessitates treatment, followed by a long-term management strategy involving storage, disposal or transformation of the waste into a non-toxic form. Governments around the world are considering a range of waste management and disposal options, though there has been limited progress toward long-term waste management solutions.

Initial treatment of waste

Vitrification



A vitrification experiment for the study of nuclear waste disposal

Long-term storage of radioactive waste requires the stabilization of the waste into a form which will neither react nor degrade for extended periods of time. One way to do this is through vitrification. Currently at Sellafield the high-level waste (PUREX first cycle raffinate) is mixed with sugar and then calcined. Calcination involves passing the waste through a heated, rotating tube. The purposes of calcination are to evaporate the water from the waste, and de-nitrate the fission products to assist the stability of the glass produced.

The 'calcine' generated is fed continuously into an induction heated furnace with fragmented glass. The resulting glass is a new substance in which the waste products are bonded into the glass matrix when it solidifies. This product, as a melt, is poured into

stainless steel cylindrical containers ("cylinders") in a batch process. When cooled, the fluid solidifies ("vitrifies") into the glass. Such glass, after being formed, is highly resistant to water.

After filling a cylinder, a seal is welded onto the cylinder. The cylinder is then washed. After being inspected for external contamination, the steel cylinder is stored, usually in an underground repository. In this form, the waste products are expected to be immobilized for a long period of time (many thousands of years).

The glass inside a cylinder is usually a black glossy substance. All this work (in the United Kingdom) is done using hot cell systems. The sugar is added to control the ruthenium chemistry and to stop the formation of the volatile RuO_4 containing radio ruthenium. In the west, the glass is normally a borosilicate glass (similar to Pyrex), while in the former Soviet bloc it is normal to use a phosphate glass. The amount of fission products in the glass must be limited because some (palladium, the other Pt group metals, and tellurium) tend to form metallic phases which separate from the glass. Bulk vitrification uses electrodes to melt soil and wastes, which are then buried underground. In Germany a vitrification plant is in use; this is treating the waste from a small demonstration reprocessing plant which has since been closed down.

Ion exchange

It is common for medium active wastes in the nuclear industry to be treated with ion exchange or other means to concentrate the radioactivity into a small volume. The much less radioactive bulk (after treatment) is often then discharged. For instance, it is possible to use a ferric hydroxide floc to remove radioactive metals from aqueous mixtures. After the radioisotopes are absorbed onto the ferric hydroxide, the resulting sludge can be placed in a metal drum before being mixed with cement to form a solid waste form. In order to get better long-term performance (mechanical stability) from such forms, they may be made from a mixture of fly ash, or blast furnace slag, and Portland cement, instead of normal concrete (made with Portland cement, gravel and sand).

Synroc

The Australian Synroc (synthetic rock) is a more sophisticated way to immobilize such waste, and this process may eventually come into commercial use for civil wastes (it is currently being developed for US military wastes). Synroc was invented by the late Prof Ted Ringwood (a geochemist) at the Australian National University. The Synroc contains pyrochlore and cryptomelane type minerals. The original form of Synroc (Synroc C) was designed for the liquid high level waste (PUREX raffinate) from a light water reactor. The main minerals in this Synroc are hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$), zirconolite ($\text{CaZrTi}_2\text{O}_7$) and perovskite (CaTiO_3). The zirconolite and perovskite are hosts for the actinides. The strontium and barium will be fixed in the perovskite. The caesium will be fixed in the hollandite.

Long term management of waste

The time frame in question when dealing with radioactive waste ranges from 10,000 to 1,000,000 years, according to studies based on the effect of estimated radiation doses. Researchers suggest that forecasts of health detriment for such periods should be examined critically. Practical studies only consider up to 100 years as far as effective planning and cost evaluations are concerned. Long term behavior of radioactive wastes remains a subject for ongoing research projects.

Geologic disposal

The process of selecting appropriate deep final repositories for high level waste and spent fuel is now under way in several countries (Schacht Asse II and the Waste Isolation Pilot Plant) with the first expected to be commissioned some time after 2010. The basic concept is to locate a large, stable geologic formation and use mining technology to excavate a tunnel, or large-bore tunnel boring machines (similar to those used to drill the Channel Tunnel from England to France) to drill a shaft 500–1,000 meters below the surface where rooms or vaults can be excavated for disposal of high-level radioactive waste. The goal is to permanently isolate nuclear waste from the human environment. Many people remain uncomfortable with the immediate stewardship cessation of this disposal system, suggesting perpetual management and monitoring would be more prudent.

Because some radioactive species have half-lives longer than one million years, even very low container leakage and radionuclide migration rates must be taken into account. Moreover, it may require more than one half-life until some nuclear materials lose enough radioactivity to cease being lethal to living things. A 1983 review of the Swedish radioactive waste disposal program by the National Academy of Sciences found that country's estimate of several hundred thousand years—perhaps up to one million years—being necessary for waste isolation “fully justified.”

Storing high level nuclear waste above ground for a century or so is considered appropriate by many scientists. This allows the material to be more easily observed and any problems detected and managed, while decay of radionuclides over this time period significantly reduces the level of radioactivity and associated harmful effects to the container material. It is also considered likely that over the next century newer materials will be developed which will not break down as quickly when exposed to a high neutron flux, thus increasing the longevity of the container once it is permanently buried.

Sea-based options for disposal of radioactive waste include burial beneath a stable abyssal plain, burial in a subduction zone that would slowly carry the waste downward into the Earth's mantle, and burial beneath a remote natural or human-made island. While these approaches all have merit and would facilitate an international solution to the problem of disposal of radioactive waste, they would require an amendment of the Law of the Sea.

Article 1 (Definitions), 7., of the 1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, (the London Dumping Convention) states:

“Sea” means all marine waters other than the internal waters of States, as well as the seabed and the subsoil thereof; it does not include sub-seabed repositories accessed only from land.”

The proposed land-based subductive waste disposal method disposes of nuclear waste in a subduction zone accessed from land, and therefore is not prohibited by international agreement. This method has been described as the most viable means of disposing of radioactive waste, and as the state-of-the-art in nuclear waste disposal technology. Another approach termed Remix & Return would blend high-level waste with uranium mine and mill tailings down to the level of the original radioactivity of the uranium ore, then replace it in inactive uranium mines. This approach has the merits of providing jobs for miners who would double as disposal staff, and of facilitating a cradle-to-grave cycle for radioactive materials, but would be inappropriate for spent reactor fuel in the absence of reprocessing, due to the presence in it of highly toxic radioactive elements such as plutonium.

Deep borehole disposal is the concept of disposing of high-level radioactive waste from nuclear reactors in extremely deep boreholes. Deep borehole disposal seeks to place the waste as much as five kilometers beneath the surface of the Earth and relies primarily on the immense natural geological barrier to confine the waste safely and permanently so that it should never pose a threat to the environment.

Transmutation

There have been proposals for reactors that consume nuclear waste and transmute it to other, less-harmful nuclear waste. In particular, the Integral Fast Reactor was a proposed nuclear reactor with a nuclear fuel cycle that produced no transuranic waste and in fact, could consume transuranic waste. It proceeded as far as large-scale tests, but was then canceled by the US Government. Another approach, considered safer but requiring more development, is to dedicate subcritical reactors to the transmutation of the left-over transuranic elements.

An isotope that is found in nuclear waste and that represents a concern in terms of proliferation is Pu-239. The estimated world total of plutonium in the year 2000 was of 1,645 MT, of which 210 MT had been separated by reprocessing. The large stock of plutonium is a result of its production inside uranium-fueled reactors and of the reprocessing of weapons-grade plutonium during the weapons program. An option for getting rid of this plutonium is to use it as a fuel in a traditional Light Water Reactor (LWR). Several fuel types with differing plutonium destruction efficiencies are under study.

Transmutation was banned in the US in April 1977 by President Carter due to the danger of plutonium proliferation, but President Reagan rescinded the ban in 1981. Due to the economic losses and risks, construction of reprocessing plants during this time did not

resume. Due to high energy demand, work on the method has continued in the EU. This has resulted in a practical nuclear research reactor called Myrrha in which transmutation is possible. Additionally, a new research program called ACTINET has been started in the EU to make transmutation possible on a large, industrial scale. According to President Bush's Global Nuclear Energy Partnership (GNEP) of 2007, the US is now actively promoting research on transmutation technologies needed to markedly reduce the problem of nuclear waste treatment.

There have also been theoretical studies involving the use of fusion reactors as so called "actinide burners" where a fusion reactor plasma such as in a tokamak, could be "doped" with a small amount of the "minor" transuranic atoms which would be transmuted (meaning fissioned in the actinide case) to lighter elements upon their successive bombardment by the very high energy neutrons produced by the fusion of deuterium and tritium in the reactor. A study at MIT found that only 2 or 3 fusion reactors with parameters similar to that of the International Thermonuclear Experimental Reactor (ITER) could transmute the entire annual minor actinide production from all of the light water reactors presently operating in the United States fleet while simultaneously generating approximately 1 gigawatt of power from each reactor.

Re-use of waste

Another option is to find applications for the isotopes in nuclear waste so as to re-use them. Already, caesium-137, strontium-90 and a few other isotopes are extracted for certain industrial applications such as food irradiation and radioisotope thermoelectric generators. While re-use does not eliminate the need to manage radioisotopes, it reduces the quantity of waste produced.

The Nuclear Assisted Hydrocarbon Production Method, Canadian patent application 2,659,302, is a method for the temporary or permanent storage of nuclear waste materials comprising the placing of waste materials into one or more repositories or boreholes constructed into an unconventional oil formation. The thermal flux of the waste materials fracture the formation, alters the chemical and/or physical properties of hydrocarbon material within the subterranean formation to allow removal of the altered material. A mixture of hydrocarbons, hydrogen, and/or other formation fluids are produced from the formation. The radioactivity of high-level radioactive waste affords proliferation resistance to plutonium placed in the periphery of the repository or the deepest portion of a borehole.

A 1990 proposed type of breeder reactor called a traveling wave reactor is claimed, if it were to be built, to be able to be fueled by depleted uranium, which is currently considered nuclear waste.

Space disposal

Space disposal is an attractive notion because it permanently removes nuclear waste from the environment. It has significant disadvantages, not least of which is the potential for catastrophic failure of a launch vehicle which would spread radioactive material into the atmosphere and around the world. The high number of launches that would be required

— because no individual rocket would be able to carry very much of the material relative to the material needed to be disposed of—makes the proposal impractical (for both economic and risk-based reasons). To further complicate matters, international agreements on the regulation of such a program would need to be established.

In the future, alternative, non-rocket spacelaunch technologies may provide a solution. It has been suggested that through the use of a stationary launch system many of the risks of catastrophic launch failure could be avoided. A promising concept is the use of high power lasers to launch "indestructible" containers from the ground into space. Such a system would require no rocket propellant, with the launch vehicle's payload making up a near entirety of the vehicle's mass. Without the use of rocket fuel on board there would be little chance of the vehicle exploding.

National management plans

Most countries are considerably ahead of the United States in developing plans for high-level radioactive waste disposal. Sweden and Finland are furthest along in committing to a particular disposal technology, while many others reprocess spent fuel or contract with France or Great Britain to do it, taking back the resulting plutonium and high-level waste. "An increasing backlog of plutonium from reprocessing is developing in many countries... It is doubtful that reprocessing makes economic sense in the present environment of cheap uranium."

In many European countries (e.g., Britain, Finland, the Netherlands, Sweden and Switzerland) the risk or dose limit for a member of the public exposed to radiation from a future high-level nuclear waste facility is considerably more stringent than that suggested by the International Commission on Radiation Protection or proposed in the United States. European limits are often more stringent than the standard suggested in 1990 by the International Commission on Radiation Protection by a factor of 20, and more stringent by a factor of ten than the standard proposed by the US Environmental Protection Agency (EPA) for Yucca Mountain nuclear waste repository for the first 10,000 years after closure. Moreover, the U.S. EPA's proposed standard for greater than 10,000 years is 250 times more permissive than the European limit.

Illegal dumping

Authorities in Italy are investigating a 'Ndrangheta mafia clan accused of trafficking and illegally dumping nuclear waste. According to a turncoat, a manager of the Italy's state energy research agency Enea paid the clan to get rid of 600 drums of toxic and radioactive waste from Italy, Switzerland, France, Germany, and the US, with Somalia as the destination, where the waste was buried after buying off local politicians. Former employees of Enea are suspected of paying the criminals to take waste off their hands in the 1980s and 1990s. Shipments to Somalia continued into the 1990s, while the 'Ndrangheta clan also blew up shiploads of waste, including radioactive hospital waste, and sending them to the sea bed off the Calabrian coast. According to the environmental group Legambiente, former members of the 'Ndrangheta have said that they were paid to sink ships with radioactive material for the last 20 years.

Accidents involving radioactive waste

A number of incidents have occurred when radioactive material was disposed of improperly, shielding during transport was defective, or when it was simply abandoned or even stolen from a waste store. In the Soviet Union, waste stored in Lake Karachay was blown over the area during a dust storm after the lake had partly dried out. At Maxey Flat, a low-level radioactive waste facility located in Kentucky, containment trenches covered with dirt, instead of steel or cement, collapsed under heavy rainfall into the trenches and filled with water. The water that invaded the trenches became radioactive and had to be disposed of at the Maxey Flat facility itself. In other cases of radioactive waste accidents, lakes or ponds with radioactive waste accidentally overflowed into the rivers during exceptional storms. In Italy, several radioactive waste deposits let material flow into river water, thus contaminating water for domestic use. In France, in the summer of 2008 numerous incidents happened; in one, at the Areva plant in Tricastin, it was reported that during a draining operation, liquid containing untreated uranium overflowed out of a faulty tank and about 75 kg of the radioactive material seeped into the ground and, from there, into two rivers nearby; in another case, over 100 staff were contaminated with low doses of radiation.

Scavenging of abandoned radioactive material has been the cause of several other cases of radiation exposure, mostly in developing nations, which may have less regulation of dangerous substances (and sometimes less general education about radioactivity and its hazards) and a market for scavenged goods and scrap metal. The scavengers and those who buy the material are almost always unaware that the material is radioactive and it is selected for its aesthetics or scrap value. Irresponsibility on the part of the radioactive material's owners, usually a hospital, university or military, and the absence of regulation concerning radioactive waste, or a lack of enforcement of such regulations, have been significant factors in radiation exposures. For an example of an accident involving radioactive scrap originating from a hospital see the Goiânia accident.

Transportation accidents involving spent nuclear fuel from power plants are unlikely to have serious consequences due to the strength of the spent nuclear fuel shipping casks.

Chapter 4

Warm Glass



Higgins Glass, fused and slumped ashtray and bowl



Fused glass piece with dichroic glass highlights

Warm glass or **kiln-formed glass** is the working of glass, usually for artistic purposes, by heating it in a kiln. The processes used depend on the temperature reached and range from fusing and slumping to casting.

'Warm' glass is in contrast to the many cold-working glass processes, such as leaded glass. 'Hot' glass, glass blowing or lampworking is the working of glass in a direct flame, such as for laboratory glassware and beadmaking.

Processes

Warm glass working uses a variety of processes, according to the working temperature and the time the glass spends at this temperature. The glass becomes progressively softer, less rigid and less viscous with temperature. Kiln-worked glass (unlike lamp working)

responds slowly though, and so the amount by which this affects the glass depends on the time it spends at working temperature.

There are three main processes, with variations within them. The broad process depends on the temperature, the variation within it depends on the time and also on slight variations of temperature. These processes are:

- Fusing

The glass retains its shape, but becomes sticky and adjacent glass pieces join together.

- Slumping

The glass deforms in shape, becoming flexible but still retaining its approximate solid form.

- Casting

The glass melts, becoming a viscous liquid that takes its shape from that of its containing mould.

It is common for one piece to use several of these processes in turn. Coloured glass may be fused together to make a composite multi-coloured sheet. This glass is then cut cold and re-assembled in pieces, which are then fused back together. The piece is finally slumped into a mould to shape it.

Glass is usually worked for only one process in a heating cycle. Where a piece requires multiple cycles, it is returned to a lower temperature between them.

Fusing



Fused glass platter

Fusing is the use of heat to join the glass by fusion welding, either with or without an associated change in shape, depending on the temperature.

Tack fusing

Tack fusing is the joining together of glass, with as little change to the shape of the pieces as possible. Tack fusing may be used either decoratively, or to assemble a large piece of glass from laminations.

Where tack fusing is used to apply small decorative details to a larger piece, it is often desired to partially melt the small pieces so that they change shape (usually becoming more spherical, under the influence of surface tension), but without changing the shape of the carrier piece. This can be done by using an increased temperature, but only briefly. The large piece, of large thermal mass, heats up more slowly than the small decorations.

Full fusing

Full fusing is like tack fusing, but the temperature is higher so that the fused pieces begin to coalesce. In the complete case, decorative additions to a surface are absorbed entirely into it and the surface becomes flat again. It is usually done for decorative effect.

Slumping



Platter, slumped into a shallow mould

Slumped glass is heated to the temperature at which the glass softens and begins to deform. It may either bend along a single curvature or, if heated sufficiently, may become elastic enough to stretch and curve to follow a compound curvature, such as a bowl.

Mould slumping

Mould slumping begins with a sheet of flat glass placed above a ceramic mould. When heated, the glass slumps into the mould under its own weight.

These moulds are usually commercially made and are offered in a range of standard shapes and sizes: bowls, trays etc. For custom pieces, a glass worker may also make a specialised or temporary mould as a one-off.

To avoid trapped air, the mould is perforated with a small vent hole. The hot glass otherwise forms a good seal with the lip of the mould and an air bubble is trapped. Such a trapped bubble often causes problems - when cooling this air may contract to form a partial vacuum that is enough to break the glass. As the glass is not heated enough to become liquid, this air cannot escape as bubbles and so venting is required.

Kiln wash is used beforehand to prevent the glass sticking to the mould.

Free fall slumping

A mould for free-fall slumping is in the form of a ring with a central opening. When heated, the glass falls through this opening and forms a bowl. Depending on the temperature and time, this bowl may be shallow or deep. If a kiln shelf is placed beneath the ring mould, this catches the falling glass and gives a vessel with a flat base.

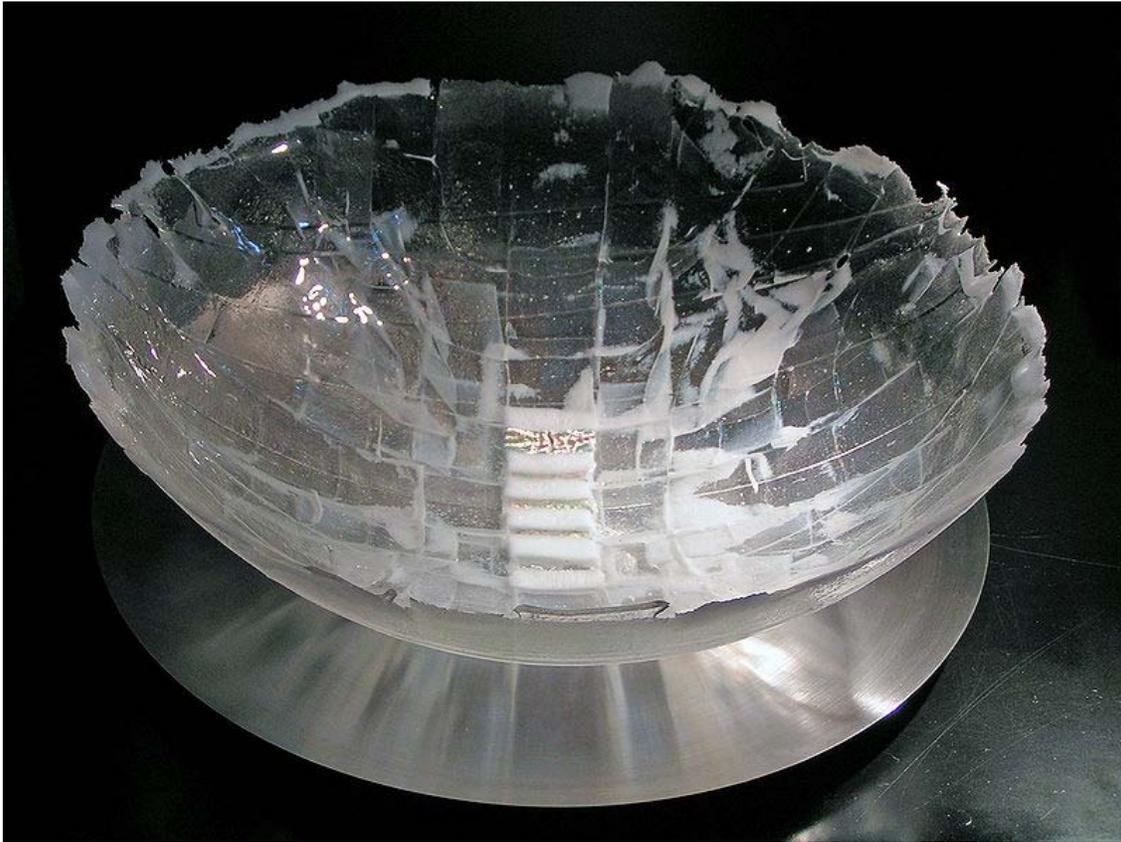
Free fall slumping is used to make taller vessels with steeper sides, such as vases.

Draping

Draping is a variety of free-fall slumping, where the mould former is placed in the centre of the piece and the outer edge falls under the heat. As this outer edge is unconstrained, it tends to fall in large folds. The edge is thus highly uneven, although a carefully draped piece may still retain perfect symmetry. For this reason draped pieces are often used as vases or wavy-edged bowls, but are difficult to use as a more functional vessel.

Draped pieces are sometimes sawn down and smoothed when cold, so as to reduce the unevenness of their edge.

Casting



Cast bowl

Casting is the process where the glass begins to melt and behave as a liquid. Its shape is now constrained entirely by the mould and the previous shape is lost. Glass is viscous though and unlike metal casting, the soft glass does not flow through the mould. Variations in the glass are thus preserved in the final piece, so colours and inclusions present beforehand may still remain in the cast item.

Glass may be cast from either billets (solid ingots), sheet, loosely stacked pieces of glass (these are usually used with a low-temperature casting, so that their boundaries remain deliberately visible afterwards) or frit, ground or powdered glass.

Moulds for casting may be either re-usable ceramic moulds, or else a one-use investment mould of plaster. This mould may in turn have been formed by the lost wax process.

Pâte de Verre



Three pâte de verre vessels.

Pâte de verre (literally *glass paste*) is cast from powdered frit, mixed with a glue binder. This allows the paste to be applied to the sides of a large mould in a thin layer. When fired, a thin-walled vessel is formed. The transparency of the finished casting depends on the size of the frit used: fine powder produces an opaque cast, medium or coarse frit may be used to cast a transparent piece.

Other processes

Fire polishing

Heating the edges to smooth and round them.

Combing

This is one of the few processes that involves manual work on the hot glass while still in the kiln. In a similar manner to slip trailing in ceramics, a pattern is formed on the surface, then trailed into feathers with a pointed metal rake.

Firing

Warm glass working is similar to that for ceramics, in that a piece is assembled, placed into a cold kiln and then heated through a pre-defined cycle, including a slow cooling phase afterwards. Unlike hot glass, warm glass is rarely worked manually whilst hot.

Kilns

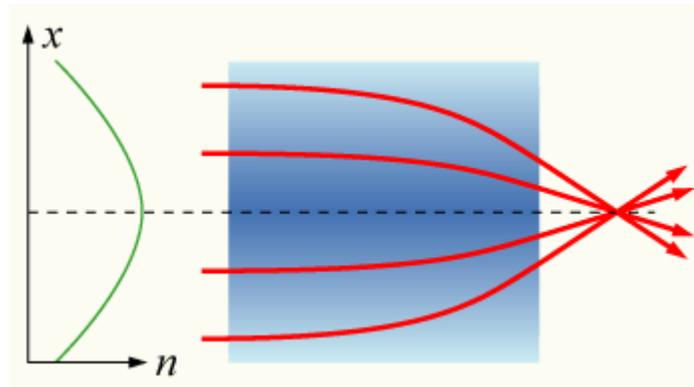
Contemporary warm glass work is almost universally done in an electrically-heated kiln, although some gas or oil-fired kilns are still used. The reason for this is the extra control accuracy and programmability available with electric heating, as well as their lower capital cost and convenient installation.

All kilns for glass work require a pyrometer, usually based on a thermocouple, as knowledge of the kiln temperature is essential for controlling the process.

Electric kilns have controllers with a variety of sophistication: the simplest is the "Infinity Control", a simple open-loop power regulator. As this only controls power, rather than temperature, such a kiln must be manually controlled throughout the cycle. As firing cycles extend over several hours, potentially days for large architectural pieces, automatic unattended control is obviously important. Automatic temperature control uses a PID controller that maintains a constant set temperature. More sophisticated controllers allow the ramp heating and cooling rates to be controlled too, an important factor in glass heating. Controllers dedicated for glass kiln use have their entire heating cycles defined before use with multiple set temperatures, hold times and ramps between them. The most sophisticated controllers of all are dedicated to glass use and allow pre-defined cycles such as "Fuse" or "Slump" to be selected from a simple menu, without their operator needing to be aware of the precise temperatures required.

Chapter 5

Gradient-Index Optics



A gradient-index lens with a parabolic variation of refractive index (n) with radial distance (x). The lens focuses light in the same way as a conventional lens.

Gradient-index optics is the branch of materials science dealing with the production and characterization of gradually changing refractive index lenses. These lenses are able to eliminate the aberrations caused by traditional spherical lenses without requiring variation to the shape of the lens. Gradient index lenses may have a refraction gradient that is spherical, axial, or radial.

Gradient-Index Lenses in Nature

A variety of inhomogeneous lenses exists in nature that allow for different functions. The most obvious lens in nature is the lens present in the eye. Nature progressively varies the refractive index of the lens in order to optimise the optics required for survival. Eagles have the ability to maintain focus and high resolution at large distances. The eyes of an antelope have a broad field of view, which allows them to detect predators. In humans, the lens is able to highly resolve and reduce aberration for both short and long distances (Shirk et al, 2006). The quality of the lens does, however, deteriorate with age with noticeable effects usually occurring after the age of 40 in humans. Another phenomenon related to the varying refractive indexes of materials in nature is the Mirage. Since

refractive index generally increases with density of the material, it is seen that cool air has a higher refractive index than hot air. Therefore, in a desert, light passes from the cool air to the warm air causing the path of the light ray reaching an observer to bend, thus giving them a misconception of the object's spatial displacement, i.e. The object may appear closer to the observer than it actually is.

History

In 1854, J C Maxwell suggested a lens whose refractive index distribution would allow for every region of space to be sharply imaged. Known as the Maxwell Fisheye Lens, it involves a spherical index function and would be expected to be spherical in shape as well (Maxwell, 1854). This lens, however, is impractical to make and has little usefulness since, only points on the surface and within the lens are sharply imaged and extended objects suffer from extreme aberrations. In 1905, R W Wood used a dipping technique creating a gelatin cylinder with a refractive index gradient that varied symmetrically with the radial distance from the axis. Disk shaped slices of the cylinder were later shown to have plane faces with radial index distribution. He showed that even though the faces of the lens were flat, they acted like converging and diverging lens depending on whether the index was a decreasing or increasing relative to the radial distance (Wood, 1905). In 1964, was published a posthumous book of R. K. Luneburg where he discovered a lens that converge all rays of light onto a point which is located on the opposite surface of the lens (Luneburg, 1964). This also limits the applications of the lens, in that it is difficult to be used to focus visual light, however, it was thought to have had some usefulness in microwave applications.

Theory

Yet to upload images and equations.

When considering aberrations, it is necessary to interpret the projections of light in terms of Gaussian Principles. If a ray is emitted from point P, and passes near point P', and Δx and Δy are the deviations from P', then Δx and Δy are measures of the aberration for the rays perceived (Figure 1) (Marchand, 1976). Inhomogeneous GRIN lenses attempt to reduce the aberrations Δx and Δy to zero.

Figure 1: Cartesian Interpretation of Aberrations. Rays of light leaving point P are refracted at the lens plane, and pass through point A. Point P' is the point at which the light rays would ideally converge if an aberration free lens was used. Point A and point P' differ by the values Δx and Δy .

Figure 2: How a Two Dimensional Gradient Index Lens Works. Gradient index lens converge all light rays onto a common point, by refracting light through a changing refractive index (many different refractive indices).

An inhomogeneous gradient-index lens possesses a refractive index whose change follows the function: $n=f(x,y,z)$ of the coordinates of the region of interest in the medium. According to Fermat's principle, the light path integral (L), taken along a ray of light

joining any two points of a medium, is stationary relative to its value for any nearby curve joining the two points. The light path integral is given by the equation:

$$\int_{S_0}^S n dS$$

Where n is the refractive index and S is the arc length of the curve. If Cartesian coordinates are used, this equation is modified to incorporate the change in arc length for a spherical gradient, to each physical dimension:

$$\int_{S_0}^S n(x, y, z) \sqrt{x'^2 + y'^2 + z'^2} dS$$

where prime corresponds to d/ds (Marchand, 1978). The light path integral is able to characterize the path of light through the lens in a qualitative manner, such that the lens may be easily reproduced in the future.

The refractive index gradient of GRIN lenses can be mathematically modelled according to its method of production. For example, GRIN lenses made from a radial gradient index material, such as SELFOC® (Flores-Arias et al, 2006), express a refractive index that varies according to:

$$n_r = n_o \left(1 - \frac{A_r^2}{2} \right)$$

Where, n_r the refractive index at a distance, r , from the optical axis; is the design index on the optical axis and A is a positive constant.

Design and Manufacture of GRIN Lenses

The GRIN lens is designed in two separate phases. In the first phase, the lens is evaluated by analytical techniques. The second phase involves the design of the lens. When considering the manufacturing of GRIN lenses, there are two important features of any technique: the depth of the gradient; and the magnitude of the change in index-of-refraction, Δn , throughout the lens (Moore, 1980). Production techniques involve:

- Neutron Irradiation (Sinai, 1971) – Boron-rich glass is bombarded with neutrons in order to cause a change in the boron concentration, and thus the refractive index of the lens.
- Chemical Vapour Deposition (Keck et al, 1975) – Involving the deposition of different glass with varying refractive indexes, onto a surface to produce a cumulative refractive change.
- Partial Polymerisation (Moore, 1973) – Organic monomer is partially polymerised using UV light at varying intensities in order to give a refractive gradient.
- Ion Exchange (Hensler, 1975) – Ions, such as lithium replace sodium ions already present in a glass substrate. When this technique is modulated spatially, a gradient index lens is formed.
- Ion Stuffing (Mohr, 1979) – Phase separation of a specific glass causes pores to form, which can later be filled using a variety of salts or concentration of salts to give a varying gradient.

Applications

The main uses of GRIN lenses involve applications in telecommunications and optical imaging. In telecommunications, a long fibre many kilometres in length but only a 20-100 μ m diameter have refractive gradients engineered to vary radially from the centre, with refractive index decreasing as distance from the centre increases. This allows for a sinusoidal height distribution of the ray within the fibre, preventing the ray from touching the walls. This differs from the traditional optical fibres which rely on total internal reflection, in that all modes of the GRIN fibres propagate at the same velocity, thus allowing for a higher temporal bandwidth for the fibre (Moore, 1980). Imaging using GRIN lenses is used to mainly reduce the aberrations and increase focus. This involves detailed calculations of aberrations as well as the efficient manufacture of the lenses. Recently, a number of different methods of gradient production have been implemented, such as, optical glasses; plastics; germanium; zinc selenide; and sodium chloride.

Chapter 6

Glass Transition

The **liquid-glass transition** (or **glass transition** for short) is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle state into a molten or rubber-like state. An amorphous solid that exhibits a glass transition is called a glass. Supercooling a viscous liquid into the glass state is called vitrification.

Despite the massive change in the physical properties of a material through its glass transition, the transition is not itself a phase transition of any kind; rather it is a laboratory phenomenon extending over a range of temperature and defined by one of several conventions. Such conventions include a constant cooling rate (20 K/min) and a viscosity threshold of 10^{12} Pa·s, among others. Upon cooling or heating through this glass transition range, the material also exhibits a smooth step in the thermal expansion coefficient and in the specific heat, with the location of these effects again being dependent on the history of the material. However, the question of whether some phase transition *underlies* the glass transition is a matter of continuing research.

T_g is always lower than the melting temperature, T_m , of the crystalline state of the material, if one exists.

Introduction

The glass transition of a liquid to a solid like state may occur with either cooling or compression. The transition comprises a smooth increase in the viscosity of a material by as much as 17 orders of magnitude without any pronounced change in material structure. The consequence of this dramatic increase is a glass exhibiting solid-like mechanical properties on the timescale of practical observation. This transition is in contrast to the freezing or crystallization transition, which is a first-order phase transition in the Ehrenfest classification and involves discontinuities in thermodynamic and dynamic properties such as volume, energy, and viscosity. In many materials that normally

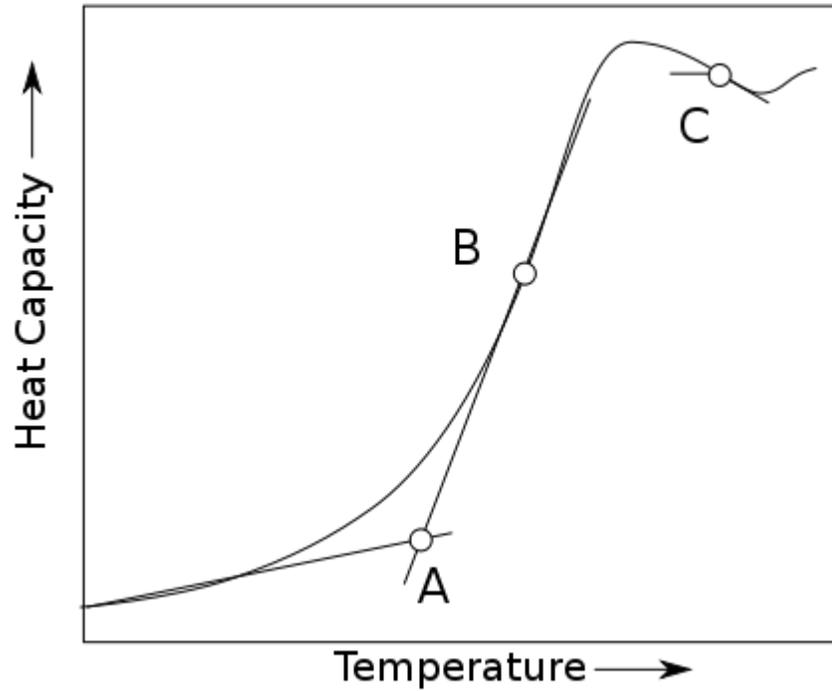
undergo a freezing transition, rapid cooling will avoid this phase transition and instead result in a glass transition at some lower temperature. Other materials, such as many polymers, lack a well defined crystalline state and easily form glasses, even upon very slow cooling or compression.

Below the transition temperature range, the glassy structure does not relax in accordance with the cooling rate used. The expansion coefficient for the glassy state is roughly equivalent to that of the crystalline solid. If slower cooling rates are used, the increased time for structural relaxation (or intermolecular rearrangement) to occur may result in a higher density glass product. Similarly, by annealing (and thus allowing for slow structural relaxation) the glass structure in time approaches an equilibrium density corresponding to the supercooled liquid at this same temperature. T_g is located at the intersection between the cooling curve (volume versus temperature) for the glassy state and the supercooled liquid .

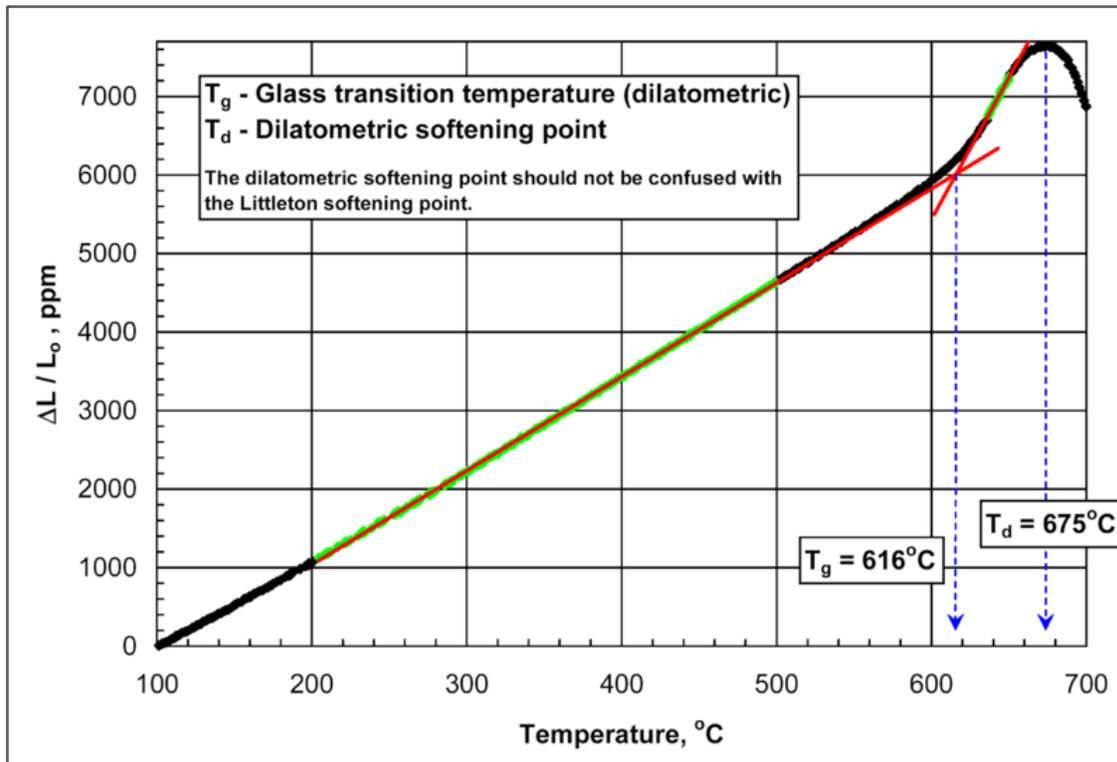
The configuration of the glass in this temperature range changes slowly with time towards the equilibrium structure. The principle of the minimization of the Gibbs free energy provides the thermodynamic driving force necessary for the eventual change. It should be noted here that at somewhat higher temperatures than T_g , the structure corresponding to equilibrium at any temperature is achieved quite rapidly. In contrast, at considerably lower temperatures, the configuration of the glass remains sensibly stable over increasingly extended periods of time.

Thus, the liquid-glass transition is not a transition between states of thermodynamic equilibrium. It is widely believed that the true equilibrium state is always crystalline. Glass is believed to exist in a kinetically locked state, and its entropy, density, and so on, depend on the thermal history. Therefore, the glass transition is primarily a dynamic phenomenon. Time and temperature are interchangeable quantities (to some extent) when dealing with glasses, a fact often expressed in the time-temperature superposition principle. On cooling a liquid, *internal degrees of freedom successively fall out of equilibrium*. However, there is a longstanding debate whether there is an underlying second-order phase transition in the hypothetical limit of infinitely long relaxation times.

Transition temperature T_g



Measurement of T_g by differential scanning calorimetry



Determination of T_g by dilatometry.

Refer to the figure on the right plotting the heat capacity as a function of temperature. In this context, T_g is the temperature corresponding to point A on the curve. The linear sections below and above T_g are colored green. T_g is the temperature at the intersection of the red regression lines.

Different operational definitions of the glass transition temperature T_g are in use, and several of them are endorsed as accepted scientific standards. Nevertheless, all definitions are arbitrary, and all yield different numeric results: at best, values of T_g for a given substance agree within a few kelvins. One definition refers to the viscosity, fixing T_g at a value of 10^{13} poise (or 10^{12} Pa·s). As evidenced experimentally, this value is close to the annealing point of many glasses.

In contrast to viscosity, the thermal expansion, heat capacity, and many other properties of inorganic glasses show a relatively sudden change at the glass transition temperature. Any such step or kink can be used to define T_g . To make this definition reproducible, the cooling or heating rate must be specified.

The most frequently used definition of T_g uses the energy release on heating in differential scanning calorimetry. Typically, the sample is first cooled with 10 K/min and then heated with that same speed.

Yet another definition of T_g uses the kink in dilatometry. Here, heating rates of 3-5 K/min are common. Summarized below are T_g values characteristic of certain classes of materials.

Polymers

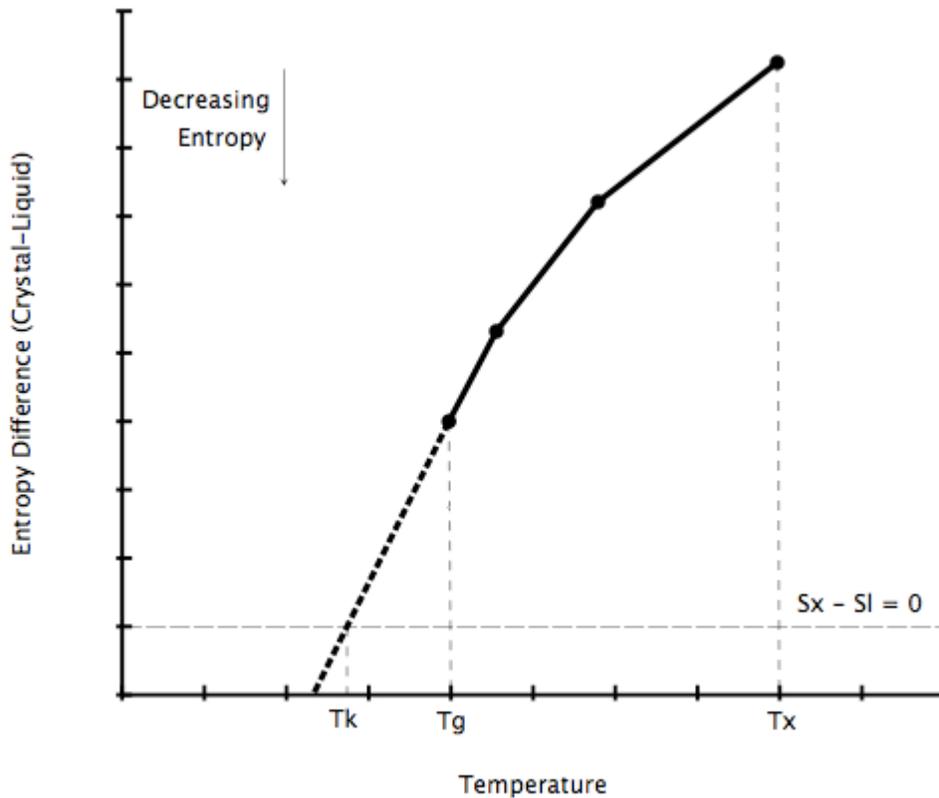
Material	T_g (°C)
Tyre rubber	-70
Polypropylene (atactic)	-20
Polypropylene (isotactic)	0
Poly-3-hydroxybutyrate (PHB)	15
Poly(vinyl acetate) (PVAc)	30
Polyethylene terephthalate (PET)	70
Poly(vinyl chloride) (PVC)	80
Poly(vinyl alcohol) (PVA)	85
Polystyrene	95
Poly(methylmethacrylate) (atactic)	105
Poly(carbonate)	145
Polynorbornene	215

These are only mean values, as the glass transition temperature depends on the cooling rate, molecular weight distribution and could be influenced by additives. Note also that for a semi-crystalline material, such as polyethylene that is 60-80% crystalline at room temperature, the quoted glass transition refers to what happens to the amorphous part of the material upon cooling.

Silicates and other covalent network glasses

Material	T_g (°C)
Chalcogenide GeSbTe	150
Chalcogenide AsGeSeTe	245
ZBLAN fluoride glass	235
Tellurium dioxide	280
Fluoroaluminate	400
Soda-lime glass	520-600
Fused quartz	~1200

Kauzmann's paradox



Entropy difference between crystal and undercooled melt

As a liquid is supercooled, the difference in entropy between the liquid and solid phase decreases. By extrapolating the heat capacity of the supercooled liquid below its glass transition temperature, it is possible to calculate the temperature at which the difference in entropies becomes zero. This temperature has been named the **Kauzmann temperature**.

If a liquid could be supercooled below its Kauzmann temperature, and it did indeed display a lower entropy than the crystal phase, the consequences would be paradoxical.

This **Kauzmann paradox** has been the subject of much debate and many publications since it was first put forward by Walter Kauzmann in 1948.

One resolution of the Kauzmann paradox is to say that there must be a phase change before the entropy of the liquid decreases. In this scenario, the transition temperature is known as the *calorimetric ideal glass transition temperature* T_{0c} . In this view, the glass transition is not merely a kinetic effect, i.e. merely the result of fast cooling of a melt, but there is an underlying thermodynamic basis for glass formation. The glass transition temperature:

$$T_g \rightarrow T_{0c} \text{ as } dT/dt \rightarrow 0.$$

There are at least three other possible resolutions to the Kauzmann paradox. It could be that the heat capacity of the supercooled liquid near the Kauzmann temperature smoothly decreases to a smaller value. It could also be that a first order phase transition to another liquid state occurs before the Kauzmann temperature with the heat capacity of this new state being less than that obtained by extrapolation from higher temperature. Finally, Kauzmann himself resolved the entropy paradox by postulating that all supercooled liquids must crystallize before the Kauzmann temperature is reached.

The glass transition in specific materials

Silica, SiO₂

Silica (the chemical compound SiO₂) has a number of distinct crystalline forms in addition to the quartz structure. Nearly all of the crystalline forms involve tetrahedral SiO₄ units linked together by *shared vertices* in different arrangements. Si-O bond lengths vary between the different crystal forms. For example, in α -quartz the bond length is 161 pm, whereas in α -tridymite it ranges from 154-171 pm. The Si-O-Si bond angle also varies from 140° in α -tridymite to 144° in α -quartz to 180° in β -tridymite. Any deviations from these standard parameters constitute microstructural differences or variations which represent an approach to an amorphous, vitreous or glassy solid.

The transition temperature T_g in silicates is related to the energy required to break and reform covalent bonds in an amorphous (or random network) lattice of covalent bonds. The T_g is clearly influenced by the chemistry of the glass. For example, addition of elements such as B, Na, K or Ca to a silica glass, which have a valency less than 4, helps in breaking up the network structure, thus reducing the T_g . Alternatively, P which has a valency of 5, helps to reinforce an ordered lattice, and thus increases the T_g .

T_g is directly proportional to bond strength, e.g. it depends on quasi-equilibrium thermodynamic parameters of the bonds e.g. on the enthalpy H_d and entropy S_d of configurons – broken bonds: $T_g = H_d / [S_d + R \ln[(1-f_c)/f_c]]$ where R is the gas constant and f_c is the percolation threshold. For strong melts such as SiO₂ the percolation threshold in the above equation is the universal Scher-Zallen critical density in the 3-D space e.g. $f_c = 0.15$, however for fragile materials the percolation thresholds are material-dependent and $f_c \ll 1$. The enthalpy H_d and the entropy S_d of configurons – broken bonds can be found from available experimental data on viscosity.

Polymers

In polymers the glass transition temperature, T_g , is often expressed as the temperature at which the Gibbs free energy is such that the activation energy for the cooperative movement of 50 or so elements of the polymer is exceeded. This allows molecular chains to slide past each other when a force is applied. From this definition, we can see that the introduction of relatively stiff chemical groups (such as benzene rings) will interfere with the flowing process and hence increase T_g .

The stiffness of thermoplastics decreases due to this effect. When the glass temperature has been reached, the stiffness stays the same for a while, i.e., at or near E_2 , until the temperature exceeds T_m , and the material melts. This region is called the rubber plateau.

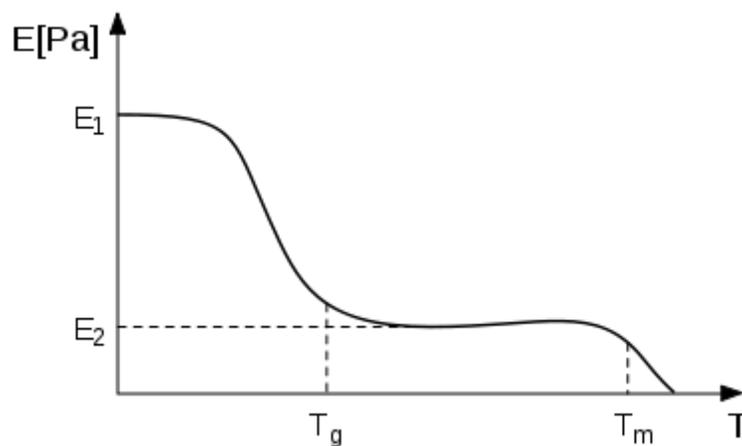


In ironing, a fabric is heated through the glass-rubber transition.

In ironing, a fabric is heated through this transition so that the polymer chains become mobile. The weight of the iron then imposes a preferred orientation. T_g can be significantly decreased by addition of plasticizers into the polymer matrix. Smaller molecules of plasticizer embed themselves between the polymer chains, increasing the spacing and free volume, and allowing them to move past one another even at lower temperatures. The "new-car smell" is due to the initial outgassing of volatile small-molecule plasticizers used to modify interior plastics (e.g., dashboards) to keep them

from cracking in the cold of winter weather. The addition of nonreactive side groups to a polymer can also make the chains stand off from one another, reducing T_g . If a plastic with some desirable properties has a T_g which is too high, it can sometimes be combined with another in a copolymer or composite material with a T_g below the temperature of intended use. Note that some plastics are used at high temperatures, e.g., in automobile engines, and others at low temperatures.

In viscoelastic materials, the presence of liquid-like behavior depends on the properties of and so varies with rate of applied load, i.e., how quickly a force is applied. The silicone toy 'Silly Putty' behaves quite differently depending on the time rate of applying a force: pull slowly and it flows, acting as a heavily viscous liquid; hit it with a hammer and it shatters, acting as a glass.



Stiffness versus temperature

On cooling, rubber undergoes a *liquid-glass transition*, which has also been called a *rubber-glass transition*. For example, the Space Shuttle Challenger disaster was caused by rubber O-rings that were being used well below their glass transition temperature on an unusually cold Florida morning, and thus could not flex adequately to form proper seals between sections of the two solid-fuel rocket boosters.

Mechanics of vitrification

Molecular motion in condensed matter can be represented by a Fourier series whose physical interpretation consists of a superposition of longitudinal and transverse waves of atomic displacement with varying directions and wavelengths. In monatomic systems, we call these waves: *density fluctuations*. (In polyatomic systems, they may also include compositional fluctuations.)

Thus, thermal motion in liquids can be decomposed into elementary longitudinal vibrations (or acoustic phonons) while transverse vibrations (or shear waves) were originally described only in elastic solids exhibiting the highly ordered crystalline state of matter. In other words, simple liquids cannot support an applied force in the form of a shearing stress, and will yield mechanically via macroscopic plastic deformation (or

viscous flow). Furthermore, the fact that a solid deforms locally while retaining its rigidity -- while a liquid yields to macroscopic viscous flow in response to the application of an applied shearing force -- is accepted by many as the mechanical distinction between the two.

The inadequacies of this conclusion, however, were pointed out by Frenkel in his revision of the kinetic theory of solids and the theory of elasticity in liquids. This revision follows directly from the continuous characteristic of the structural transition from the liquid state into the solid one when this transition is not accompanied by crystallization—ergo the supercooled viscous liquid. Thus we see the intimate correlation between transverse acoustic phonons (or shear waves) and the onset of rigidity upon vitrification, as described by Bartenev in his mechanical description of the vitrification process.

The velocities of longitudinal acoustic phonons in condensed matter are directly responsible for the thermal conductivity which levels out temperature differentials between compressed and expanded volume elements. Kittel proposed that the behavior of glasses is interpreted in terms of an approximately constant "mean free path" for lattice phonons, and that the value of the mean free path is of the order of magnitude of the scale of disorder in the molecular structure of a liquid or solid. The thermal phonon mean free paths or relaxation lengths of a number of glass formers have been plotted versus the glass transition temperature, indicating a linear relationship between the two. This has suggested a new criterion for glass formation based on the value of the phonon mean free path.

It has often been suggested that heat transport in dielectric solids occurs through elastic vibrations of the lattice, and that this transport is limited by elastic scattering of acoustic phonons by lattice defects (e.g. randomly spaced vacancies). These predictions were confirmed by experiments on commercial glasses and glass ceramics, where mean free paths were apparently limited by "internal boundary scattering" to length scales of 10 - 100 micrometers. The relationship between these transverse waves and the mechanism of vitrification has been described by several authors who proposed that the onset of correlations between such phonons results in an orientational ordering or "freezing" of local shear stresses in glass-forming liquids, thus yielding the glass transition.

Electronic structure

The influence of thermal phonons and their interaction with electronic structure is a topic which was appropriately introduced in a discussion of the resistance of liquid metals. Lindemann's theory of melting is referenced, and it is suggested that the drop in conductivity in going from the crystalline to the liquid state is due to the increased scattering of conduction electrons as a result of the increased amplitude of atomic vibration. Such theories of localization have been applied to transport in metallic glasses, where the mean free path of the electrons is very small (on the order of the interatomic spacing).

The formation of a non-crystalline form of a gold-silicon alloy by the method of splat quenching from the melt led to further considerations of the influence of electronic structure on glass forming ability, based on the properties of the metallic bond.

Other work indicates that the mobility of localized electrons is enhanced by the presence of dynamic phonon modes. One claim against such a model is that if chemical bonds are important, the nearly free electron models should not be applicable. However, if the model includes the buildup of a charge distribution between all pairs of atoms just like a chemical bond (e.g., silicon, when a band is just filled with electrons) then it should apply to solids.

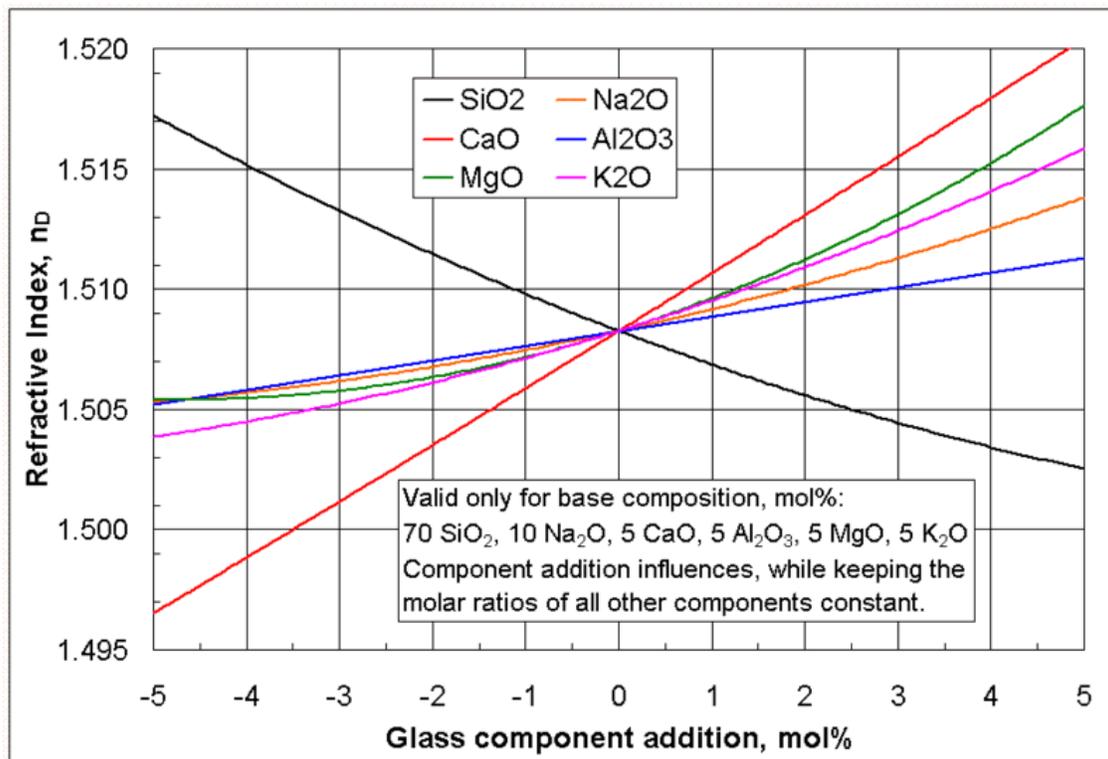
Thus, if the electrical conductivity is low, the mean free path of the electrons is very short. The electrons will only be sensitive to the short-range order in the glass since they do not get a chance to scatter from atoms spaced at large distances. Since the short-range order is similar in glasses and crystals, the electronic energies should be similar in these two states. For alloys with lower resistivity and longer electronic mean free paths, the electrons could begin to sense that there is disorder in the glass, and this would raise their energies and destabilize the glass with respect to crystallization. Thus, the glass formation tendencies of certain alloys may therefore be due in part to the fact that the electron mean free paths are very short, so that only the short-range order is ever important for the energy of the electrons.

It has also been argued that glass formation in metallic systems is related to the "softness" of the interaction potential between unlike atoms. Some authors, emphasizing the strong similarities between the local structure of the glass and the corresponding crystal, suggest that chemical bonding helps to stabilize the amorphous structure.

Other authors have suggested that the electronic structure yields its influence on glass formation through the directional properties of bonds. Non-crystallinity is thus favored in elements with a large number of polymorphic forms and a high degree of bonding anisotropy. Crystallization becomes more unlikely as bonding anisotropy is increased from isotropic metallic to anisotropic metallic to covalent bonding, thus suggesting a relationship between the group number in the periodic table and the glass forming ability in elemental solids.

Chapter 7

Calculation of Glass Properties



The calculation of glass properties allows "fine-tuning" of desired material characteristics, e.g., the refractive index.

The **calculation of glass properties (glass modeling)** is used to predict glass properties of interest or glass behavior under certain conditions (e.g., during production) without experimental investigation, based on past data and experience, with the intention to save time, material, financial, and environmental resources, or to gain scientific insight. It was first practised at the end of the 19th century by A. Winkelmann and O. Schott. The combination of several glass models together with other relevant functions can be used for optimization and six sigma procedures. In the form of statistical analysis glass

modeling can aid with accreditation of new data, experimental procedures, and measurement institutions (glass laboratories).

History

Historically, the calculation of glass properties is directly related to the founding of glass science. At the end of the 19th century the physicist Ernst Abbe developed equations that allow calculating the design of optimized optical microscopes in Jena, Germany, stimulated by co-operation with the optical workshop of Carl Zeiss. Before Ernst Abbe's time the building of microscopes was mainly a work of art and experienced craftsmanship, resulting in very expensive optical microscopes with variable quality. Now Ernst Abbe knew exactly how to construct an excellent microscope, but unfortunately, the required lenses and prisms with specific ratios of refractive index and dispersion did not exist. Ernst Abbe was not able to find answers to his needs from glass artists and engineers; glass making was not based on science at this time.

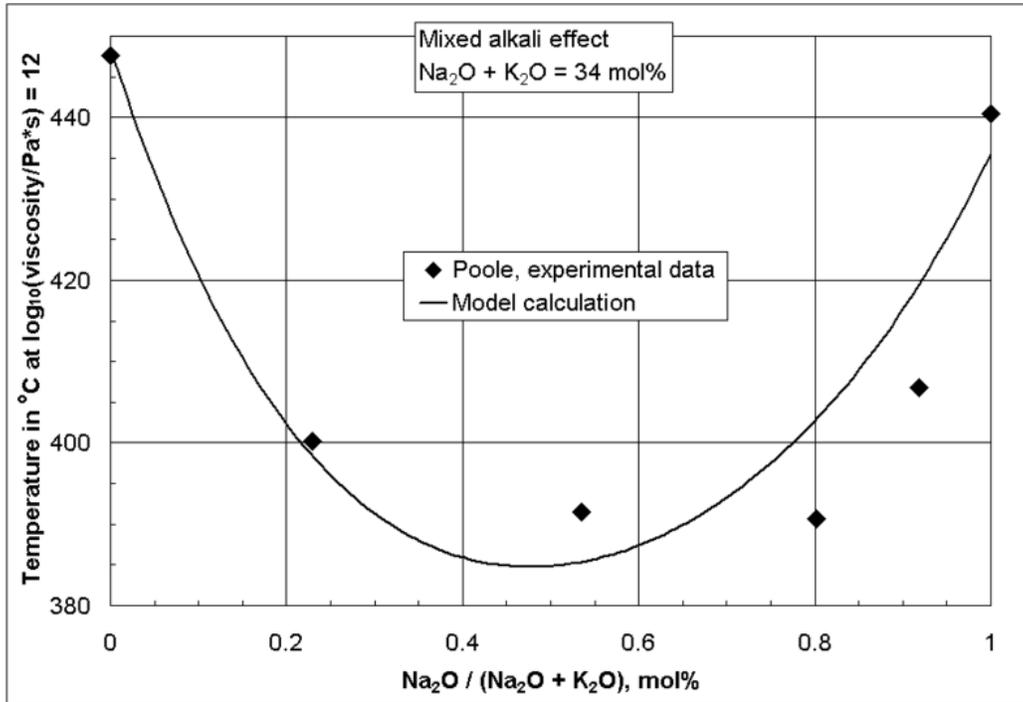
In 1879 the young glass engineer Otto Schott sent Abbe glass samples with a special composition (lithium silicate glass) that he had prepared himself and that he hoped to show special optical properties. Following measurements by Ernst Abbe, Schott's glass samples did not have the desired properties, and they were also not as homogeneous as desired. Nevertheless, Ernst Abbe invited Otto Schott to work on the problem further and to evaluate all possible glass components systematically. Finally, Schott succeeded in producing homogeneous glass samples, and he invented borosilicate glass with the optical properties Abbe needed. These inventions gave rise to the well-known companies Zeiss and Schott Glass. Systematic glass research was born. In 1908, Eugene Sullivan founded glass research also in the United States (Corning, New York).

At the beginning of glass research it was most important to know the relation between the glass composition and its properties. For this purpose Otto Schott introduced the **additivity principle** in several publications for calculation of glass properties. This principle implies that the relation between the glass composition and a specific property is linear to all glass component concentrations, assuming an ideal mixture, with C_i and b_i representing specific glass component concentrations and related coefficients respectively in the equation below. The additivity principle is a simplification and only valid within narrow composition ranges as seen in the displayed diagrams for the refractive index and the viscosity. Nevertheless, the application of the additivity principle lead the way to many of Schott's inventions, including optical glasses, glasses with low thermal expansion for cooking and laboratory ware (Duran), and glasses with reduced freezing point depression for mercury thermometers. Subsequently, English and Gehlhoff *et al.* published similar additive glass property calculation models. Schott's additivity principle is still widely in use today in glass research and technology.

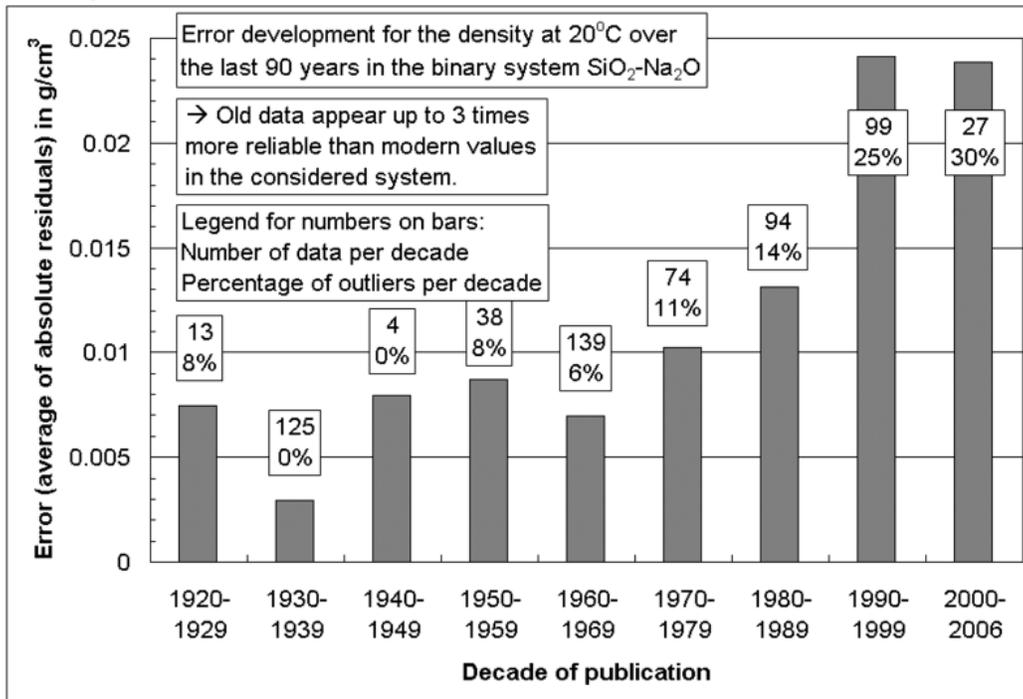
Additivity Principle:

$$\text{Glass Property} = b_0 + \sum_{i=1}^n b_i C_i$$

Global models



The mixed-alkali effect: If a glass contains more than one alkali oxide, some properties show non-additive behavior. The image shows, that the viscosity of a glass is significantly decreased.



Decreasing accuracy of modern glass literature data for the density at 20°C in the binary system SiO₂-Na₂O.

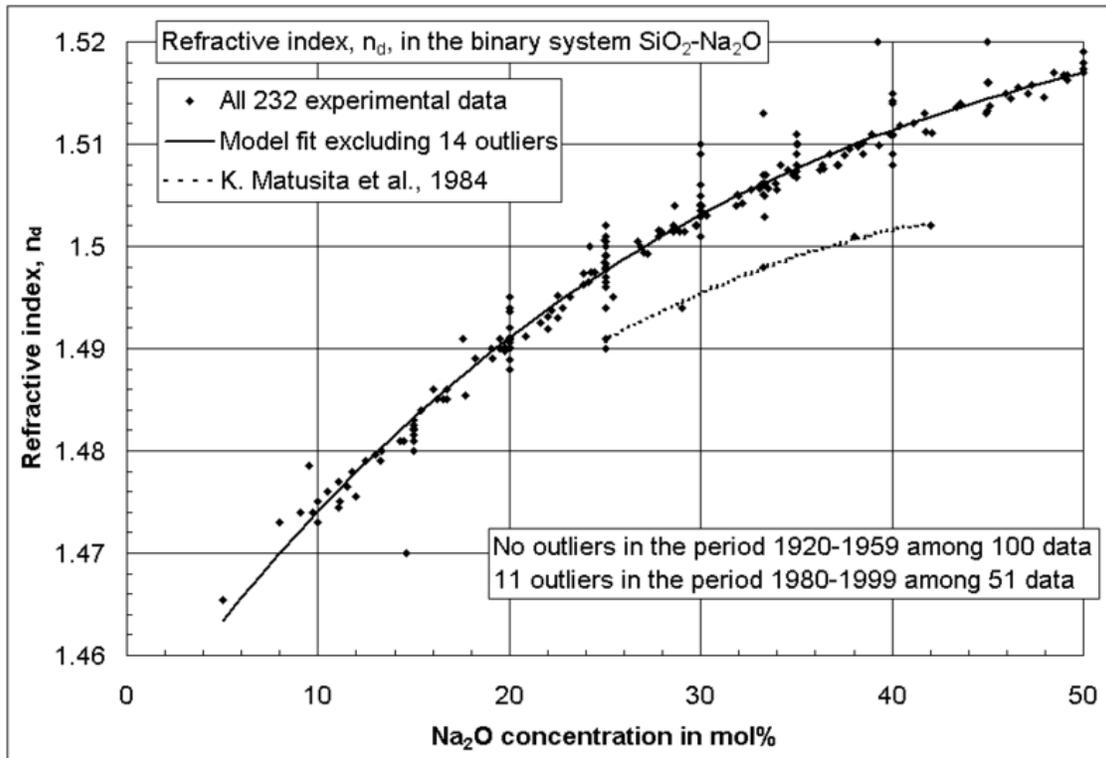
Schott and many scientists and engineers afterwards applied the additivity principle to experimental data measured in their own laboratory within sufficiently narrow composition ranges (**local glass models**). This is most convenient because disagreements between laboratories and non-linear glass component interactions do not need to be considered. In the course of several decades of systematic glass research thousands of glass compositions were studied, resulting in millions of published glass properties, collected in glass databases. This huge pool of experimental data was not investigated as a whole, until Bottinga, Kucuk, Priven, Choudhary, Mazurin, and Fluegel published their **global glass models**, using various approaches. In contrast to the models by Schott the global models consider many independent data sources, making the model estimates more reliable. In addition, global models can reveal and quantify *non-additive* influences of certain glass component combinations on the properties, such as the *mixed-alkali effect* as seen in the diagram on the right, or the *boron anomaly*. Global models also reflect interesting developments of glass property measurement accuracy, e.g., a decreasing accuracy of experimental data in modern scientific literature for some glass properties, shown in the diagram. They can be used for accreditation of new data, experimental procedures, and measurement institutions (glass laboratories). In the following sections (except melting enthalpy) *empirical* modeling techniques are presented, which seem to be a successful way for handling huge amounts of experimental data. The resulting models are applied in contemporary engineering and research for the calculation of glass properties.

Non-empirical (*deductive*) glass models exist. They are often not created to obtain reliable glass property predictions in the first place (except melting enthalpy), but to establish relations among several properties (e.g. atomic radius, atomic mass, chemical bond strength and angles, chemical valency, heat capacity) to gain scientific insight. In future, the investigation of property relations in deductive models may ultimately lead to reliable predictions for all desired properties, provided the property relations are well understood and all required experimental data are available.

Methods

Glass properties and glass behavior during production can be calculated through statistical analysis of glass databases such as GE-SYSTEM SciGlass and Interglad, sometimes combined with the finite element method. For estimating the melting enthalpy thermodynamic databases are used.

Linear regression

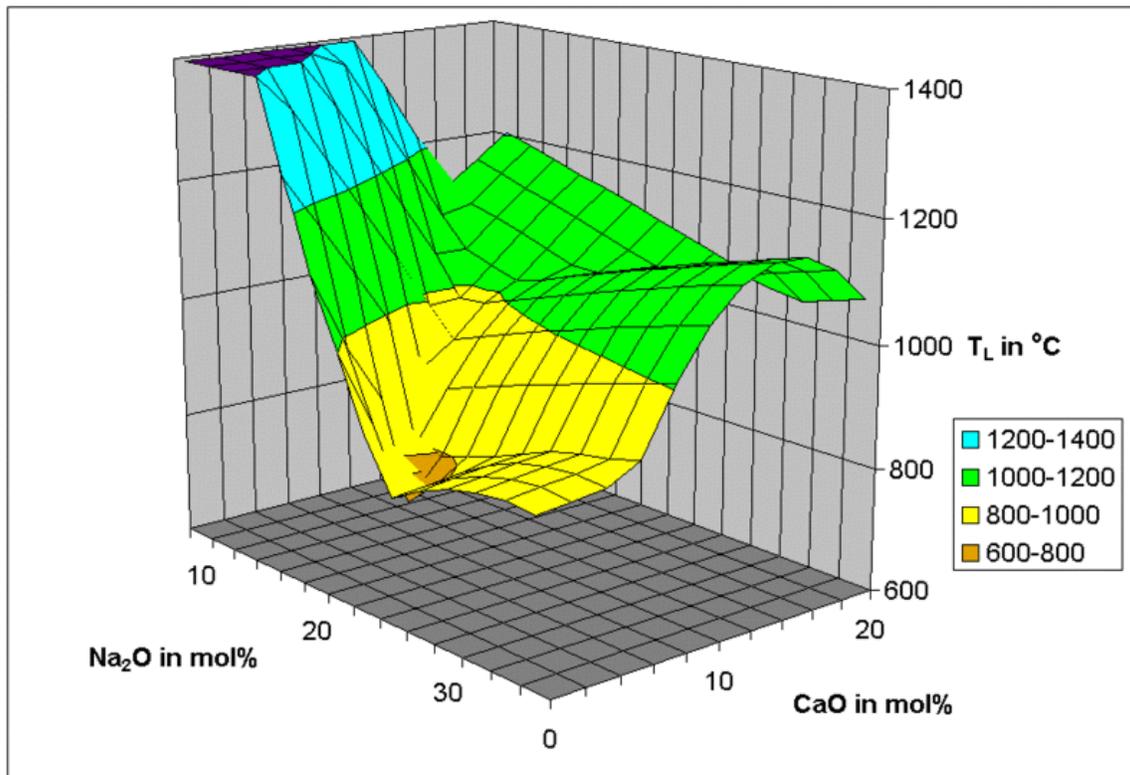


Refractive index in the system $\text{SiO}_2\text{-Na}_2\text{O}$. Dummy variables can be used to quantify systematic differences of whole datasets from one investigator.

If the desired glass property is not related to crystallization (e.g., liquidus temperature) or phase separation, linear regression can be applied using common polynomial functions up to the third degree. Below is an example equation of the second degree. The C -values are the glass component concentrations like Na_2O or CaO in percent or other fractions, the b -values are coefficients, and n is the total number of glass components. The glass main component silica (SiO_2) is excluded in the equation below because of over-parametrization due to the constraint that all components sum up to 100%. Many terms in the equation below can be neglected based on correlation and significance analysis. Systematic errors such as seen in the picture are quantified by dummy variables. Further details and examples are available in an online tutorial by Fluegel.

$$\text{Glass Property} = b_0 + \sum_{i=1}^n \left(b_i C_i + \sum_{k=i}^n b_{ik} C_i C_k \right)$$

Non-linear regression



Liquidus surface in the system SiO₂-Na₂O-CaO using disconnected peak functions based on 237 experimental data from 28 investigators. Error = 15°C.

The liquidus temperature has been modeled by non-linear regression using neural networks and disconnected peak functions. The disconnected peak functions approach is based on the observation that within one primary crystalline phase field linear regression can be applied and at eutectic points sudden changes occur.

Glass melting enthalpy

The glass melting enthalpy reflects the amount of energy needed to convert the mix of raw materials (batch) to a melt glass. It depends on the batch and glass compositions, on the efficiency of the furnace and heat regeneration systems, the average residence time of the glass in the furnace, and many other factors. A pioneering article about the subject was written by Carl Kröger in 1953.

Finite element method

For modeling of the glass flow in a glass melting furnace the finite element method is applied commercially, based on data or models for viscosity, density, thermal conductivity, heat capacity, absorption spectra, and other relevant properties of the glass melt. The finite element method may also be applied to glass forming processes.

Optimization

It is often required to optimize several glass properties simultaneously, including production costs. GE-SYSTEM This can be performed, e.g., by simplex search, or in a spreadsheet as follows:

1. Listing of the desired properties;
2. Entering of models for the reliable calculation of properties based on the glass composition, including a formula for estimating the production costs;
3. Calculation of the squares of the differences (errors) between desired and calculated properties;
4. Reduction of the sum of square errors using the Solver option in Microsoft Excel with the glass components as variables. Other software (e.g. Microcal Origin) can also be used to perform these optimizations.

It is possible to weight the desired properties differently. Basic information about the principle can be found in an article by Huff *et al.* The combination of several glass models together with further relevant technological and financial functions can be used in six sigma optimization.

Chapter 8

Glass-to-Metal Seal



Uranium glass used as lead-in seals in a vacuum capacitor

Glass-to-metal seals are a very important element of the construction of vacuum tubes, electric discharge tubes, incandescent light bulbs, glass encapsulated semiconductor diodes, reed switches, pressure tight glass windows in metal cases, and metal or ceramic packages of electronic components.

Mercury seal

The first technological use of a glass-to-metal seal was the encapsulation of the vacuum in the barometer by Torricelli. The liquid mercury wets the glass and thus provides for a vacuum tight seal. Liquid mercury was also used to seal the metal leads of early mercury arc lamps into the fused silica bulbs.

Platinum wire seal

The next step was to use thin platinum wire. Platinum is easily wetted by glass and has a similar coefficient of thermal expansion as typical soda-lime and lead glass. It is also easy to work with because of its non-oxidibility and high melting point. This type of seal was used in scientific equipment throughout the 19th century and also in the early incandescent lamps and radio tubes.

Dumet wire seal

In 1911 the Dumet-wire seal was invented which is still the common practice to seal copper leads through soda-lime or lead glass. If copper is properly oxidised before it is wetted by molten glass a vacuum tight seal of good mechanical strength can be obtained. After copper is oxidized, it is often dipped in a borax solution, as borating the copper helps prevent over-oxidation when reintroduced to a flame. Simple copper wire is not usable because its coefficient of thermal expansion is much higher than that of the glass. Thus, on cooling a strong tensile force acts on the glass-to-metal interface and it breaks. Glass and glass-to-metal interfaces are especially sensitive to tensile stress. Dumet-wire is a copper clad wire (about 25% of the weight of the wire is copper) with a core of nickel-iron alloy 42, an alloy with a composition of about 42% nickel. The core has a low coefficient of thermal expansion, allowing for a wire with a coefficient of radial thermal expansion which is slightly lower than the linear coefficient of thermal expansion of the glass, so that the glass-to-metal interface is under a low compression stress. It is not possible to adjust the axial thermal expansion of the wire as well. Because of the much higher mechanical strength of the nickel-iron core compared to the copper, the axial thermal expansion of the Dumet-wire is about the same as of the core. Thus, a shear stress builds up which is limited to a safe value by the low tensile strength of the copper. This is also the reason why Dumet is only useful for wire diameters lower than about 0.5 mm. In a typical Dumet seal through the base of a vacuum tube a short piece of Dumet-wire is butt welded to a nickel wire at one end and a copper wire at the other end. When the base is pressed of lead glass the Dumet-wire and a short part of the nickel and the copper wire are enclosed in the glass. Then the nickel wire and the glass around the Dumet-wire are heated by a gas flame and the glass seals to the Dumet-wire. The nickel and copper do not seal vacuum tight to the glass but are mechanically supported. The butt welding also avoids problems with gas-leakages at the interface between the core wire and the copper.

Copper tube seal

Another possibility to avoid a strong tensile stress when sealing copper through glass is the use of a thin walled copper tube instead of a solid wire. Here a shear stress builds up

in the glass-to-metal interface which is limited by the low tensile strength of the copper combined with a low tensile stress. The copper tube is insensitive to high electrical current compared to a Dumet-seal because on heating the tensile stress converts into a compression stress which is again limited by the tensile strength of the copper. Also, it is possible to lead an additional solid copper wire through the copper tube. In a later variant, only a short section of the copper tube has a thin wall and the copper tube is hindered to shrink at cooling by a ceramic tube inside the copper tube.

If large parts of copper are to be fitted to glass like the water cooled copper anode of a high power radio transmitter tube or an x-ray tube historically the Houskeeper knife edge seal is used. Here the end of a copper tube is machined to a sharp knife edge, invented by O. Kruh in 1917. In the method described by W.G. Houskeeper the outside or the inside of the copper tube right to the knife edge is wetted with glass and connected to the glass tube. In later descriptions the knife edge is just wetted several millimeters deep with glass, usually deeper on the inside, and then connected to the glass tube.

If copper is sealed to glass, it is an advantage to get a thin bright red Cu_2O containing layer between copper and glass. This is done by borating. After W.J. Scott a copper plated tungsten wire is immersed for about 30 s in chromic acid and then washed thoroughly in running tap water. Then it is dipped into a saturated solution of borax and heated to bright red heat in the oxidizing part of a gas flame. Possibly followed by quenching in water and drying. Another method is to oxidize the copper slightly in a gas flame and then to dip it into borax solution and let it dry. The surface of the borated copper is black when hot and turns to dark wine red on cooling.

It is also possible to make a bright seal between copper and glass where it is possible to see the blank copper surface through the glass, but this gives less adherence than the seal with the red Cu_2O containing layer. If glass is melted on copper in a reducing hydrogen atmosphere the seal is extremely weak. If copper is to be heated in hydrogen-containing atmosphere e.g. a gas flame it needs to be oxygen-free to prevent hydrogen embrittlement. Copper which is ment to be used as an electrical conductor is not necessarily oxygen-free and contains particles of Cu_2O which react with hydrogen that diffuses into the copper to H_2O which cannot diffuse out-off the copper and thus causes embrittlement. The copper usually used in vacuum applications is of the very pure OFHC (oxygen-free-high-conductivity) quality which is both free of Cu_2O and deoxidising additives which might evaporate at high temperature in vacuum.

Copper disc seal

In the copper disc seal, as proposed by W.G. Houskeeper, the end of a glass tube is closed by a round copper disk. An additional ring of glass on the opposite side of the disc increases the possible thickness of the disk to more than 0.3 mm. Best mechanical strength is obtained if both sides of the disk are fused to the same type of glass tube and both tubes are under vacuum. The disk seal is of special practical interest because it is a simple method to make a seal to low expansion borosilicate glass without the need of special tools or materials. The keys to success are proper borating, heating of the joint to a temperature as close to the melting point of the copper as possible and to slow down the cooling, at least by packing the assembly into glass wool while it is still red hot.

Matched seal

In a matched seal the thermal expansion of metal and glass is matched. Copper-plated tungsten wire can be used to seal through borosilicate glass with a low coefficient of thermal expansion which is matched by tungsten. The tungsten is electrolytically copper plated and heated in hydrogen atmosphere to fill cracks in the tungsten and to get a proper surface to easily seal to glass. The borosilicate glass of usual laboratory glassware has a lower coefficient of thermal expansion than tungsten, thus it is necessary to use an intermediate sealing glass to get a stress-free seal.

There are combinations of glass and iron-nickel-cobalt alloys (Kovar) where even the non-linearity of the thermal expansion is matched. These alloys can be directly sealed to glass, but then the oxidation is critical. Also, their low electrical conductivity is a disadvantage. Thus, they are often gold plated. It is also possible to use silver plating, but then an additional gold layer is necessary as an oxygen diffusion barrier to prevent the formation of iron oxide.

While there are Fe-Ni alloys which match the thermal expansion of tungsten at room temperature, they are not useful to seal to glass because of a too strong increase of their thermal expansion at higher temperatures.

Reed switches use a matched seal between an iron-nickel alloy (NiFe 52) and a matched glass. The glass of reed switches is usually green due to its iron content because the sealing of reed switches is done by heating with infrared radiation and this glass shows a high absorption in the near infrared.

The electrical connections of high-pressure sodium vapour lamps, the yellow lamps for street lighting, are made of niobium alloyed with 1% of zirconium.

Historically, some television cathode ray tubes were made by using ferritic steel for the funnel and glass matched in expansion to ferritic steel. The steel plate used had a diffusion layer enriched with chromium at the surface made by heating the steel together with chromium oxide in a HCl-containing atmosphere. In contrast to copper, pure iron does not bond strongly to silicate glass. Also, technical iron contains some carbon which forms bubbles of CO when it is sealed to glass under oxidizing conditions. Both are a major source of problems for the technical enamel coating of steel and make direct seals between iron and glass unsuitable for high vacuum applications. The oxide layer formed on chromium-containing steel can seal vacuum tight to glass and the chromium strongly reacts with carbon. Silver-plated iron was used in early microwave tubes.

It is possible to make matched seals between copper or austenitic steel and glass, but silicate glass with that high thermal expansion is especially fragile and has a low chemical durability.

Molybdenum foil seal

Another widely used method to seal through glass with low coefficient of thermal expansion is the use of stripes of thin molybdenum foil. This can be done with matched

coefficients of thermal expansion or unmatched after Houskeeper. Then the edges of the strip also have to be knife sharp. The disadvantage here is that the tip of the edge which is a local point of high tensile stress reaches through the wall of the glass container. This can lead to low gas leakages. In the tube to tube knife edge seal the edge is either outside, inside, or buried into the glass wall.

Compression seal

Another possibility of seal construction is the compression seal. This type of glass-to-metal seal can be used to feed through the wall of a metal container. Here the wire is usually matched to the glass which is inside of the bore of a strong metal part with higher coefficient of thermal expansion.

Design aspects

Also the mechanical design of a glass-to-metal seal has an important influence on the reliability of the seal. In practical glass-to-metal seals cracks usually start at the edge of the interface between glass and metal either inside or outside the glass container. If the metal and the surrounding glass are symmetric the crack propagates in an angle away from the axis. So, if the glass envelope of the metal wire extends far enough from the wall of the container the crack will not go through the wall of the container but it will reach the surface on the same side where it started and the seal will not leak despite the crack.

Another important aspect is the wetting of the metal by the glass. If the thermal expansion of the metal is higher than the thermal expansion of the glass like with the Houskeeper seal, a high contact angle (bad wetting) means that there is a high tensile stress in the surface of the glass near the metal. Such seals usually break inside the glass and leave a thin cover of glass on the metal. If the contact angle is low (good wetting) the surface of the glass is everywhere under compression stress like an enamel coating. Ordinary soda-lime glass does not flow on copper at temperatures below the melting point of the copper and, thus, does not give a low contact angle. The solution is to cover the copper with a solder glass which has a low melting point and does flow on copper and then to press the soft soda-lime glass onto the copper. The solder glass must have a coefficient of thermal expansion which is equal or a little lower than that of the soda-lime glass. Classically high lead containing glasses are used, but it is also possible to substitute these by multi-component glasses e.g. based on the system $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{B}_2\text{O}_3-\text{ZnO}-\text{TiO}_2-\text{BaO}-\text{Al}_2\text{O}_3$.

Chapter 9

Optical Lens Design

Optical lens design refers to the calculation of lens construction parameters (variables) that will meet a set of performance requirements and constraints, including cost and schedule limitations.

Construction parameters include surface profile types (spherical, aspheric, holographic, diffractive, etc.), and the parameters for each surface type such as radius of curvature, distance to the next surface, glass type and optionally tilt and decenter.

Design requirements

Performance requirements can include:

1. Optical performance, i.e., image quality: quantified by encircled energy, modulation transfer function, Strehl ratio, ghost reflection control, and pupil performance (size, location and aberration control); the choice of the image quality metric is application specific.
2. Physical requirements such as weight, static volume, dynamic volume, center of gravity and overall configuration requirements.
3. Environmental requirements: ranges for temperature, pressure, vibration and electromagnetic shielding.

Design constraints can include realistic lens element center and edge thicknesses, minimum and maximum air-spaces between lenses, maximum constraints on entrance and exit angles, physically realizable glass index of refraction and dispersion properties.

Manufacturing costs and delivery schedules are also a major part of optical design. The price of an optical glass blank of given dimensions can vary by a factor of fifty or more, depending on the size, glass type, index homogeneity quality, and availability, with BK7 usually being the cheapest. Costs for larger and/or thicker optical blanks of a given material, above 100mm to 150mm or so, usually increase faster than what would be proportional to just the increase in physical volume. This is primarily due to increased blank annealing time required to achieve acceptable index homogeneity and internal

stress birefringence levels throughout the blank volume. Availability of glass blanks is driven by how frequently a particular glass type is mixed and poured by a given manufacturer, and can seriously affect manufacturing cost and schedule.

Process

Lenses can first be designed using paraxial theory to position images and pupils, then real surfaces inserted and optimized. Paraxial theory can be skipped in simpler cases and the lens directly optimized using real surfaces. Lenses are first designed using average index of refraction and dispersion properties published in the glass manufacturer's catalog and through glass model calculations. However, the properties of the real glass blanks will vary from this ideal; index of refraction values can vary by as much as 0.0003 or more from catalog values, and dispersion can either remain about the same or vary slightly. These changes in index and dispersion can sometimes be enough to affect the lens focus location and imaging performance in highly corrected systems.

The lens blank manufacturing process is as follows:

1. The glass batch ingredients for a desired glass type are mixed together in a powder state,
2. the powder mixture is melted together in a furnace,
3. the fluid is further mixed while molten to maximize batch homogeneity,
4. poured into lens blanks and
5. annealed according to empirically determined time-temperature schedules.

The glass blank pedigree, or "melt data", can be determined for a given glass batch by making small precision prisms from various locations in the batch and measuring their index of refraction on a spectrometer, typically at five or more wavelengths. Lens design programs have curve fitting routines that can fit the melt data to a selected dispersion curve, from which the index of refraction at any wavelength within the fitted wavelength range can be calculated. A re-optimization, or "melt re-comp", can then be performed on the lens design using measured index of refraction data where available. When manufactured, the resulting lens performance will more closely match the desired requirements than if average glass catalog values for index of refraction were assumed.

Delivery schedules are impacted by glass and mirror blank availability and lead times to acquire, the amount of tooling a shop must fabricate prior to starting on a project, the manufacturing tolerances on the parts (tighter tolerances mean longer fab times), the complexity of any optical coatings that must be applied to the finished parts, further complexities in mounting or bonding lens elements into cells and in the overall lens system assembly, and any post-assembly alignment and quality control testing and tooling required. Tooling costs and delivery schedules can be reduced by using existing tooling at any given shop wherever possible, and by maximizing manufacturing tolerances to the extent possible.

Lens optimization

Optical design is partly a science because ray paths and wavefront structure can be very accurately calculated anywhere along the propagation path through the lens. Glass and coating optical properties can be measured and modeled with sufficient precision for use in lenses. If tolerances are included during the design, parts can usually be manufactured accurately enough that the resulting lens assembly performs acceptably close to the paper design.

Optical design is also partly an art, though, as the multi-dimensional design space within which a constrained lens design is free to roam is literally beyond human imagination if more than a few construction parameters are free to vary. The number, type and placement of optical elements are partly driven by physical requirements, but are also often based on previous similar designs obtained from published data, patents and textbooks. Skill and intuition in lens design are acquired over years of experience spanning hundreds to thousands of different lens design projects, preferably leading to additional experiences (and headaches) dealing with fabricating and aligning systems.

As an example of the complexity of lens-design space, a simple two-element air-spaced lens has nine variables (four radii of curvature, two thicknesses, one airspace thickness, and two glass types). Even for this simplest case, the design space is thus nine-dimensional, and local or global solutions within this space can at least be imagined as smaller or larger bubbles in a sponge-like 9-D foam-scape. A complex multi-configuration lens corrected over a wide spectral band and field of view, at multiple zoomed focal lengths and over a realistic temperature range, can have an extremely complex design volume, having over a hundred dimensions.

Lens optimization techniques that can navigate this multi-dimensional space and proceed to local minima have been studied since the 1940s, beginning with early work by James G. Baker, and later by D. Feder, Wynne, Glatzel, D. Grey and others. Prior to the advent of digital computers, lens design was an agonizingly slow hand-calculation process requiring high-precision trigonometric and logarithmic tables, reams of paper, plotting 2-D cuts through the multi-dimensional space, and significant patience and understudying from previous masters. Tracing a single ray through a given lens surface could take more than an hour of painstaking calculations and checks, and a lens designer could not design more than a very few complex, high-performance anastigmatic objectives in an entire lifetime.

Modern desktop computers can now raytrace tens to hundreds of millions of rays per second through a lens, and perform hundreds to thousands of optimization cycles per second, rapidly exploring the n-dimensional design volume and even hill-climbing in and out of local minima in the search for the best solution.

However, even with lightning-fast optimizers, seasoned experience is still needed to guide solution trajectories through unacceptably shallow local minima and achieve the desired performance requirements. Experience in the mechanical and physical properties of glass, metals, optical coatings and bonding materials is also needed, especially in

systems required to give high sustained performance over wide temperature ranges and harsh environmental conditions.