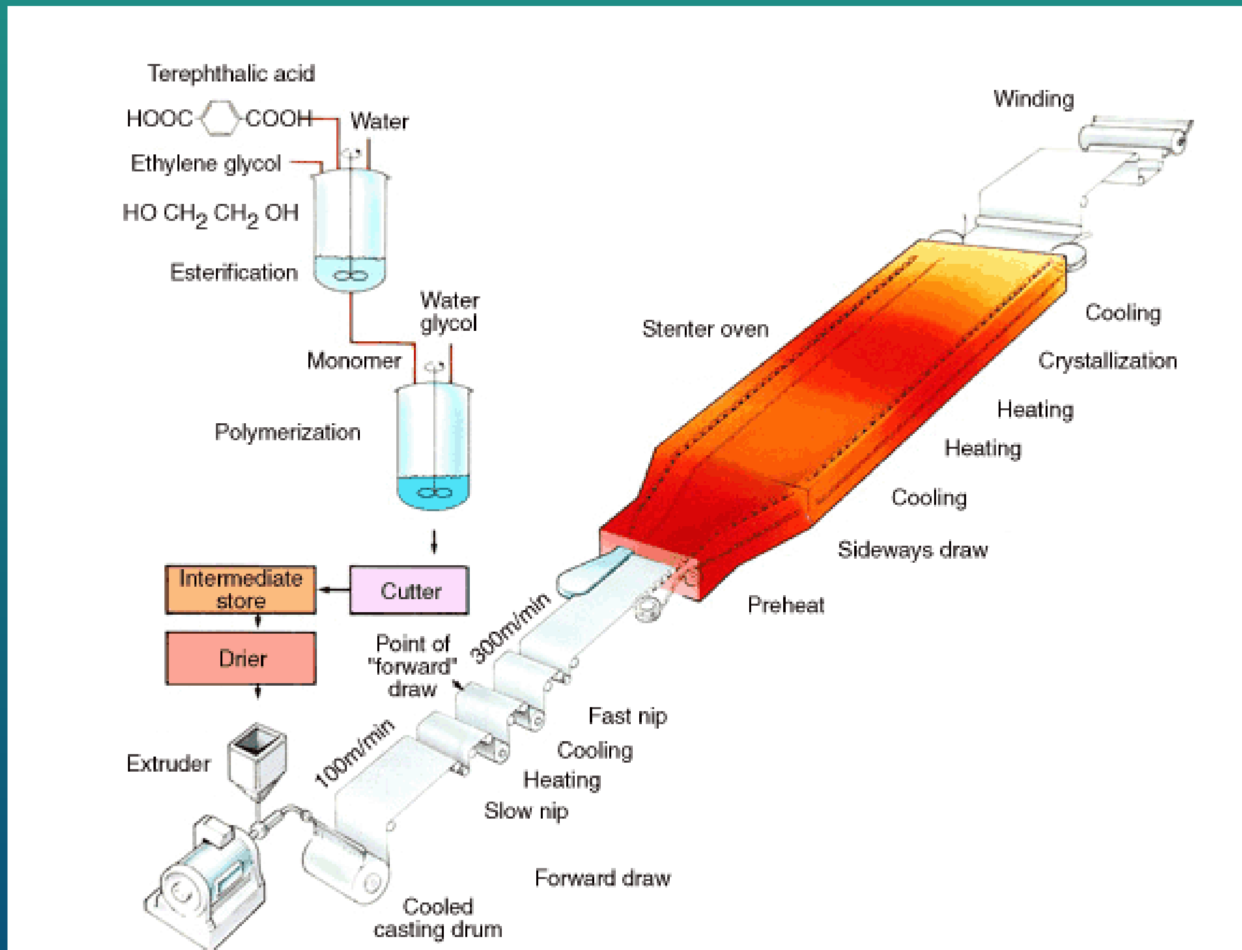
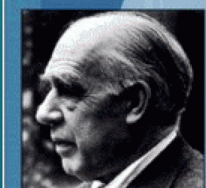

Terephthalic acid
HOOC COOH
Water
Ethylene glycol
HO CH2 CH2 OH
Esterification
Water glycol
Monomer
Polymerization
Intermediate store
Cutter
Drier
Extruder
Point of "forward" draw
300m/min
100m/min
Fast nip
Cooling
Heating
Slow nip
Forward draw
Cooled casting drum
Stenter oven
Winding
Cooling
Crystallization
Heating
Heating
Cooling
Sideways draw
Preheat

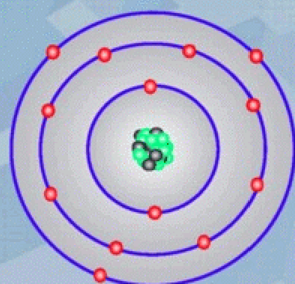
The Bohr Model

Atoms don't really look like this.

We know that the model is incorrect but it is good enough to help us understand many important concepts.



Niels Bohr

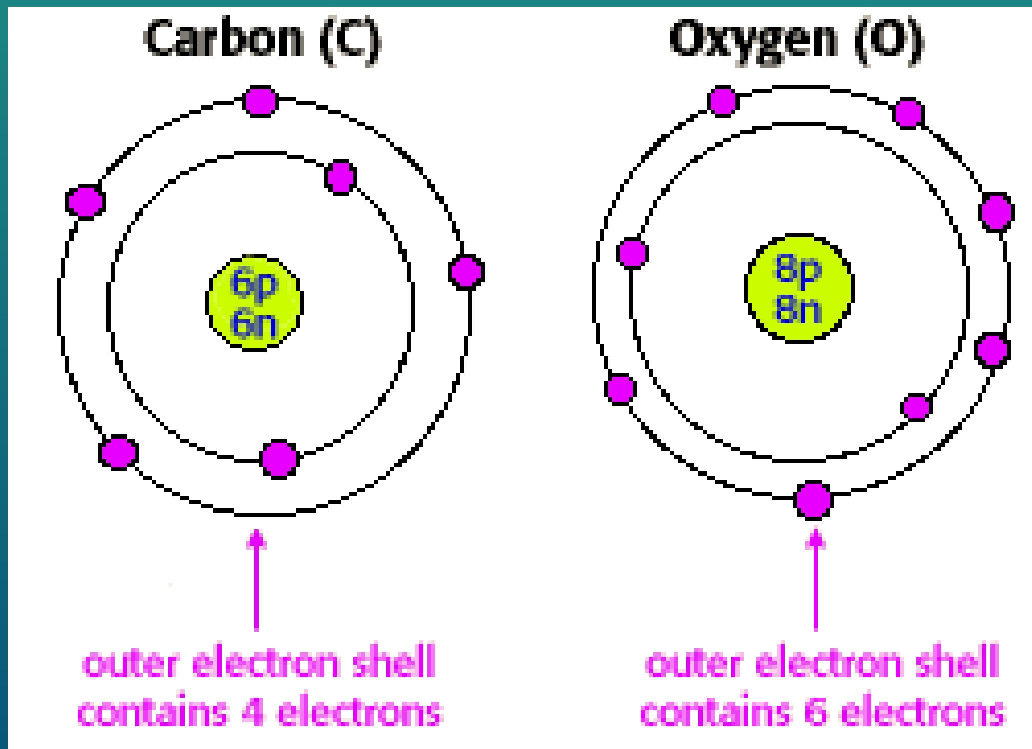


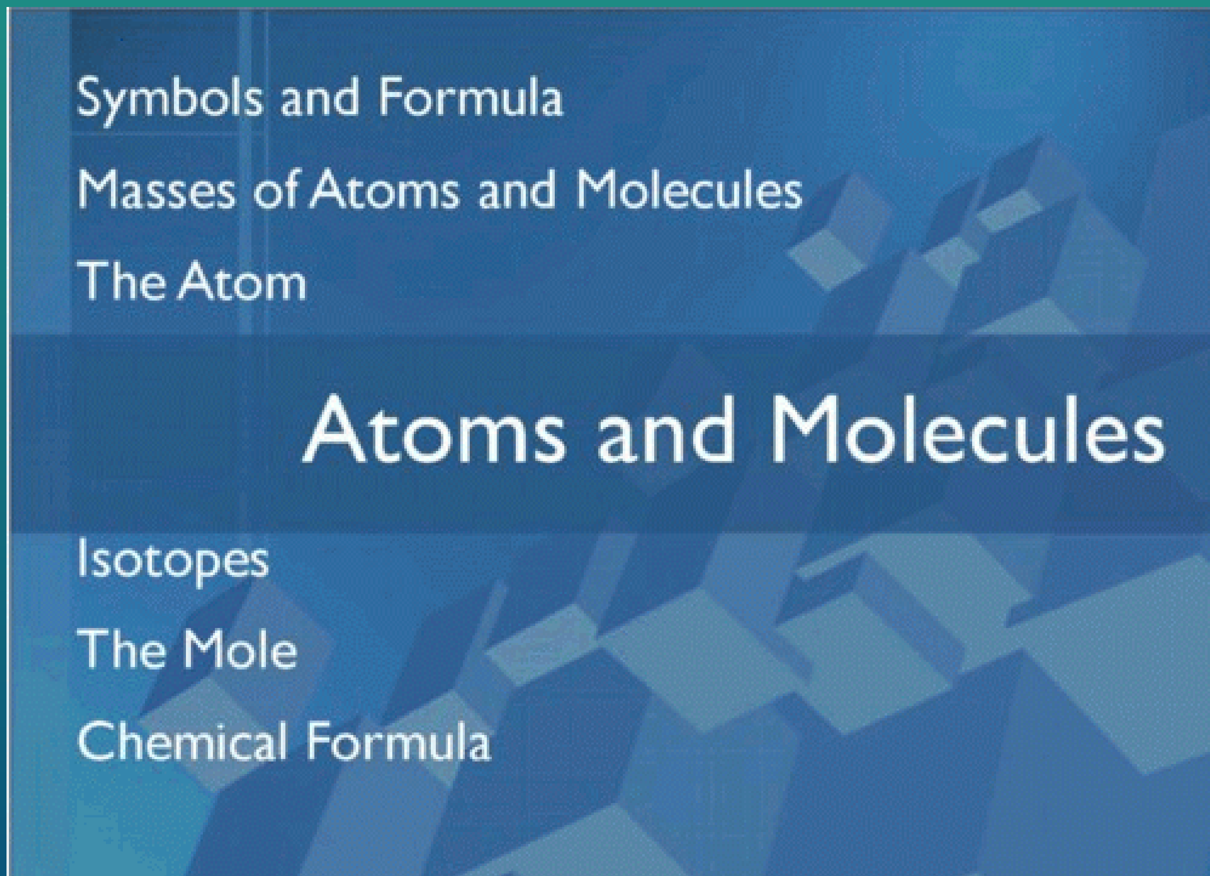
Atom The smallest unit of an element that retains its chemical properties.

Atoms can be split into smaller parts.

Atomic structure

Name	Symbol	Charge	AMU	grams
electron	e^-	-1	$5.4x10^{-4}$	$9.11x10^{-28}$
proton	p	+1	1.0	$1.67x10^{-24}$
neutron	n	0	1.0	$1.67x10^{-24}$


Carbon (C)
6p
6n
outer electron shell
contains 4 electrons
Oxygen (O)
8p
8n
outer electron shell
contains 6 electrons


Symbols and Formula
Masses of Atoms and Molecules
The Atom
Atoms and Molecules
Isotopes
The Mole
Chemical Formula

The atomic symbol

A	- Atomic mass	- Total protons & neutrons
Z	- Atomic number	- # of protons or electrons
C	- Charge	- + or - values
#	- Number	- # of atoms in a formula.

Example - (NH4)2SO4

OK, this example is a little more complicated.

The formula is in a format to show you how the various atoms are hooked up.

$(NH_4)_2SO_4$

We have two (NH_4) units and one SO_4 unit.

Now we can determine the number of atoms.

Example - (NH4)2SO4

Ammonium sulfate contains - 2 nitrogen, 8 hydrogen, 1 sulfur and 4 oxygen.

2 N	x	14.01	=	28.02
8 H	x	1.008	=	8.064
1 S	x	32.06	=	32.06
4 O	x	16.00	=	64.00

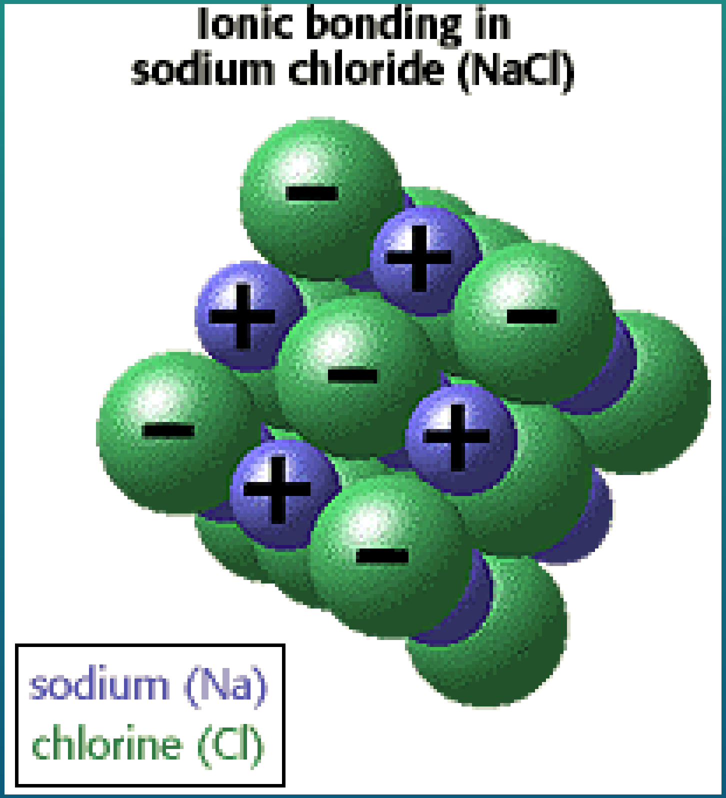
Formula Weight = 132.14

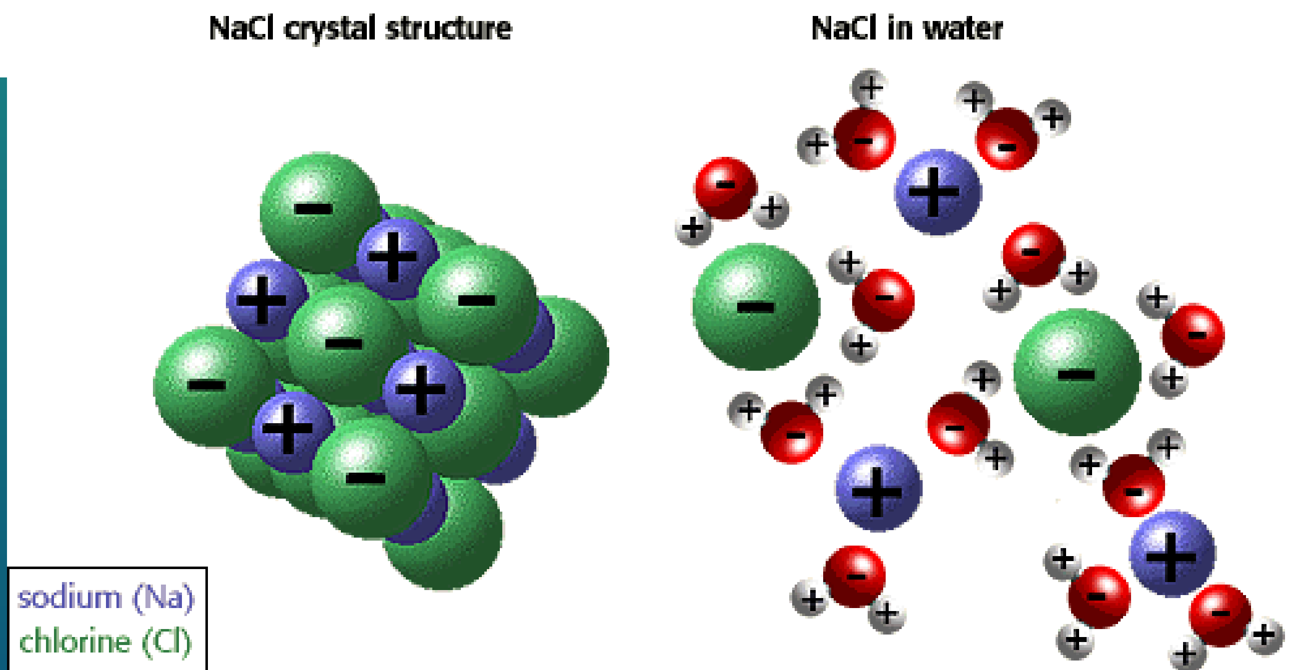
Units are either AMU or grams / mol.

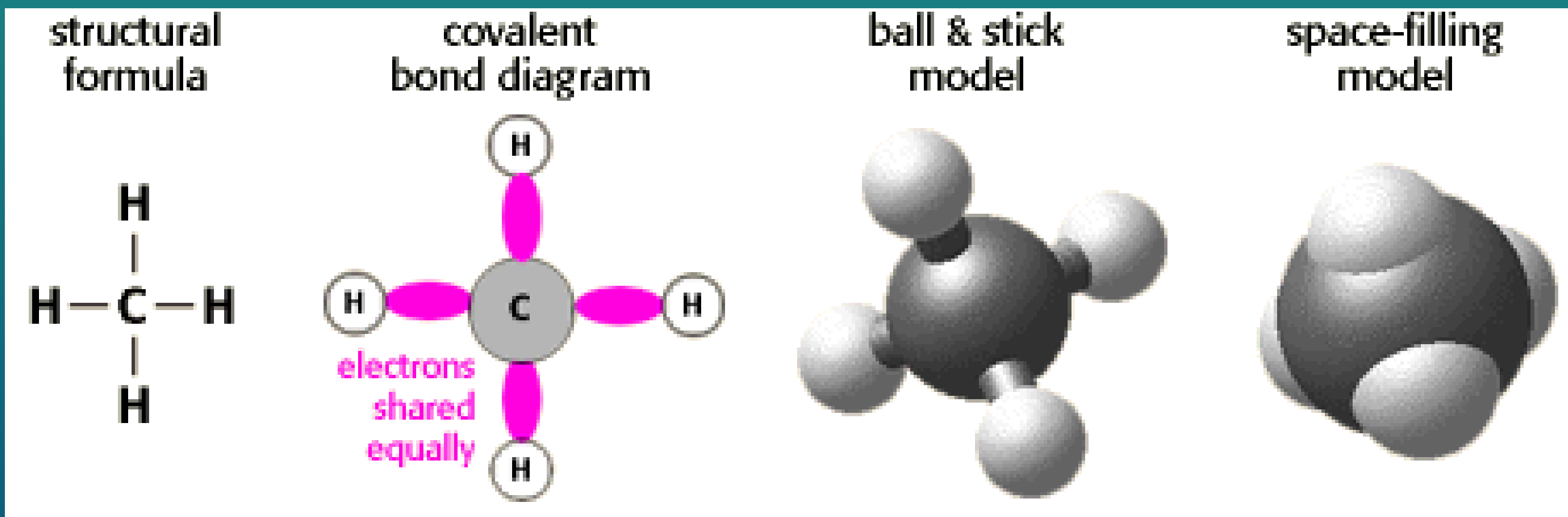
Atomic Symbols

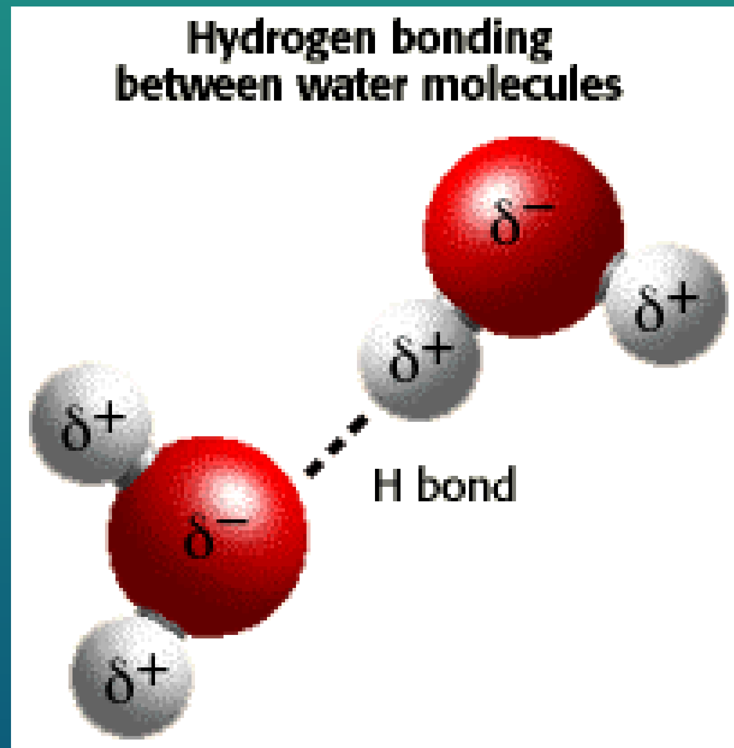
- Each element is assigned a unique symbol.
- Each is 1-2 letters and the first is capitalized.
- Symbol may not match the name - often had a different name to start with.

arsenic	As	potassium	K
barium	Ba	nickel	Ni
carbon	C	nitrogen	N
chlorine	Cl	oxygen	O
hydrogen	H	radon	Rn
helium	He	titanium	Ti
gold	Au	uranium	U


Ionic bonding in
sodium chloride (NaCl)
sodium (Na)
chlorine (Cl)


NaCl crystal structure
NaCl in water
sodium (Na)
chlorine (Cl)


structural formula
covalent bond diagram
ball & stick model
space-filling model
H
H
H
H
C
electrons shared equally


Hydrogen bonding
between water molecules
δ−
δ+
δ+
δ+
δ−
δ+
H bond

Formula

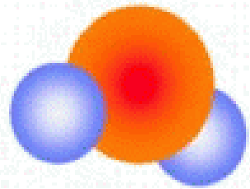
Formula are used to represent the elements in a compound.

- Lists the elements in a compound.
- Tells how many of each element there are.
- May also show how the elements are connected to each other.

H_2O - water
2 hydrogen
1 oxygen

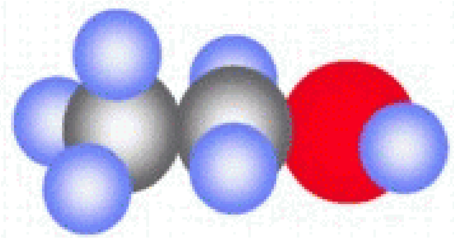
CH_3CH_2OH - ethyl alcohol
2 carbon, 6 hydrogen and 1 oxygen
(shows how atoms are arranged)

Molecular representations

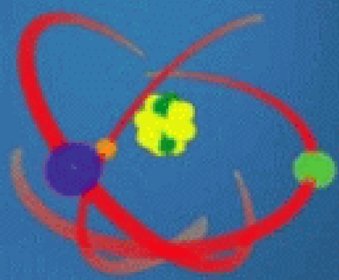


H_2O - water

CH_3CH_2OH - ethyl alcohol



Structure of the atom



Atoms have a specific arrangement.

Nucleus

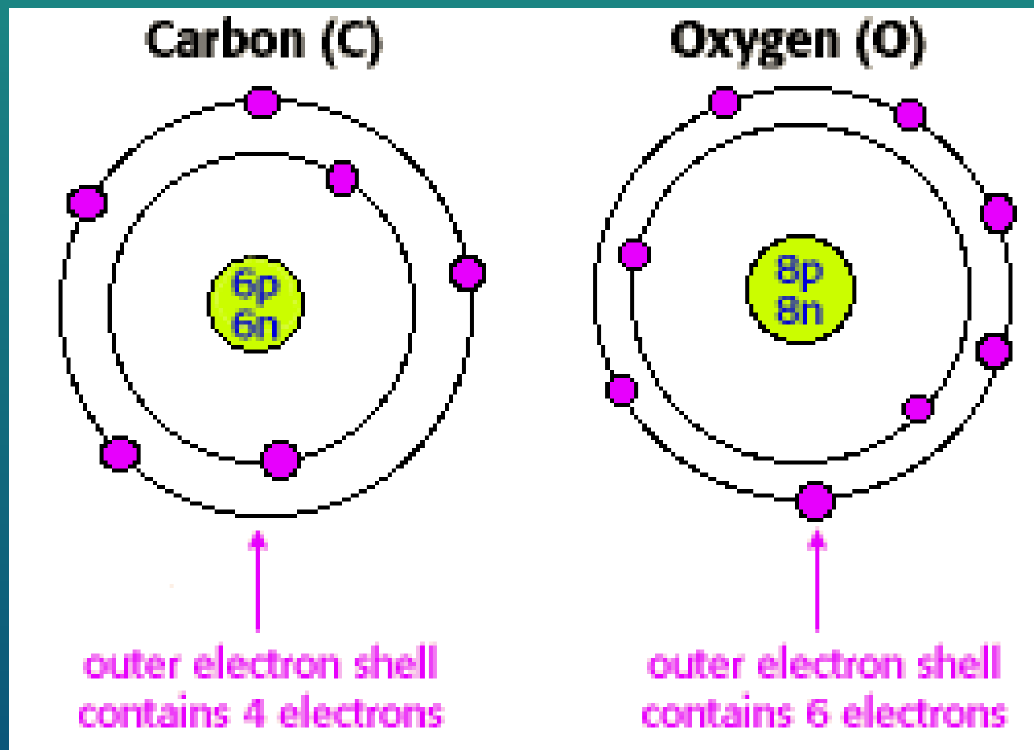
Small, dense, positive charge in the center of an atom that contains protons & neutrons.

Electrons

Surround the nucleus. Diffuse region of negative charge.

Nucleus is a very small part of an atom.

If it was the size of a marble, the atom would fill a football stadium.


Carbon (C)
Oxygen (O)
6p
6n
8p
8n
outer electron shell
contains 4 electrons
outer electron shell
contains 6 electrons

The mole

If we had one mole of water and one mole of hydrogen, we would have the name number of molecules of each.

1 mol H_2O = 6.022×10^{23} molecules

1 mol H_2 = 6.022×10^{23} molecules

We can't weigh out moles -- we use grams.

We would need to weigh out a different number of grams to have the same number of molecules

Moles and weights

Atoms come in different sizes and masses.

A mole of atoms of one type would have a different weight than a mole of another type.

H	-	1.008 AMU or grams/mol
O	-	16.00 AMU or grams/mol
Mo	-	95.94 AMU or grams/mol
Pb	-	207.2 AMU or grams/mol

We rely on a straight forward system to relate mass and moles.

Masses of atoms and molecules

H_2O - water

2 hydrogen	2 x	1.008 amu
1 oxygen	1 x	16.00 amu
mass of molecule		18.02 amu
		18.02 g/mol

Rounded off based on significant figures

Another example

CH_3CH_2OH - ethyl alcohol

2 carbon	2 x	12.01 amu
6 hydrogen	6 x	1.008 amu
1 oxygen	1 x	16.00 amu
mass of molecule		46.02 amu
		46.02 g/mol

Formula mass

Sum the atomic masses of all elements in a compound based on the chemical formula.

You must use the atomic masses of the elements listed in the periodic table.

CO_2 1 atom of C and 2 atoms of O

1 atom C	x 12.011 amu	=	12.011 amu
2 atoms O	x 15.9994 amu	=	31.9988 amu
	Formula Weight	=	44.010 amu or g/mol

Example - (NH4)2SO4

OK, this example is a little more complicated.

The formula is in a format to show you how the various atoms are hooked up.

$(NH_4)_2SO_4$

We have two (NH_4) units and one SO_4 unit.

Now we can determine the number of atoms.

Example - (NH4)2SO4

Ammonium sulfate contains - 2 nitrogen, 8 hydrogen, 1 sulfur and 4 oxygen.

2 N	x	14.01	=	28.02
8 H	x	1.008	=	8.064
1 S	x	32.06	=	32.06
4 O	x	16.00	=	64.00

Formula Weight = 132.14

Units are either AMU or grams / mol.

Organic Polymers

Macromolecules

Why all the interest ?

Numerous and Diverse

in

Structure - Property Relationship

Electrical
- Insulators
- Capacitors
- Microwave
- Conducting Polymers

Optical

Biochemical

Thermal

Mechanical - most important

Functional Role in Living Animals and Plants
- Hoof
- Skin
- Hair
- Tendons
- Proteins

Organic Polymers

Macromolecules

Why all the interest ?

Numerous and Diverse
in
Structure - Property Relationship

Electrical
- Insulators
- Capacitors
- Microwave
- Conducting Polymers

Optical

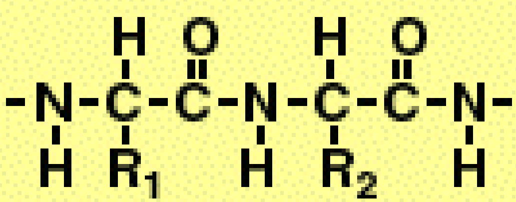
Biochemical

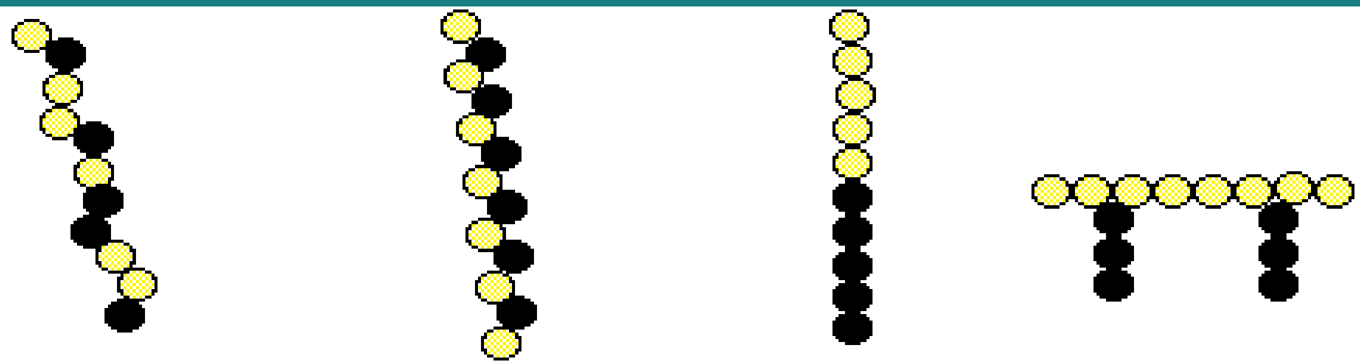
Thermal

Mechanical - most important

Functional Role in Living Animals and Plants
- Hoof
- Skin
- Hair
- Tendons
- Proteins

Poly-Peptides





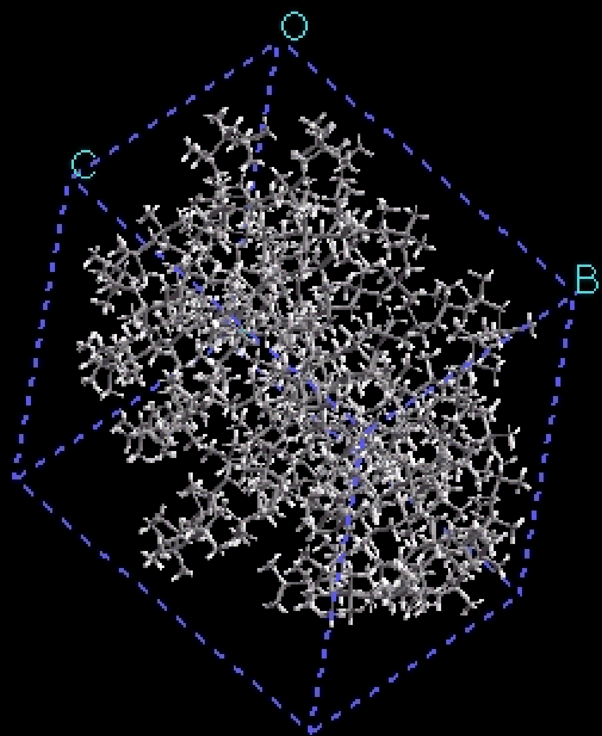
Random Copolymers: Different monomers are randomly arranged within the polymer chains.

Alternating Copolymers: Different monomers show a definite ordered alternation.

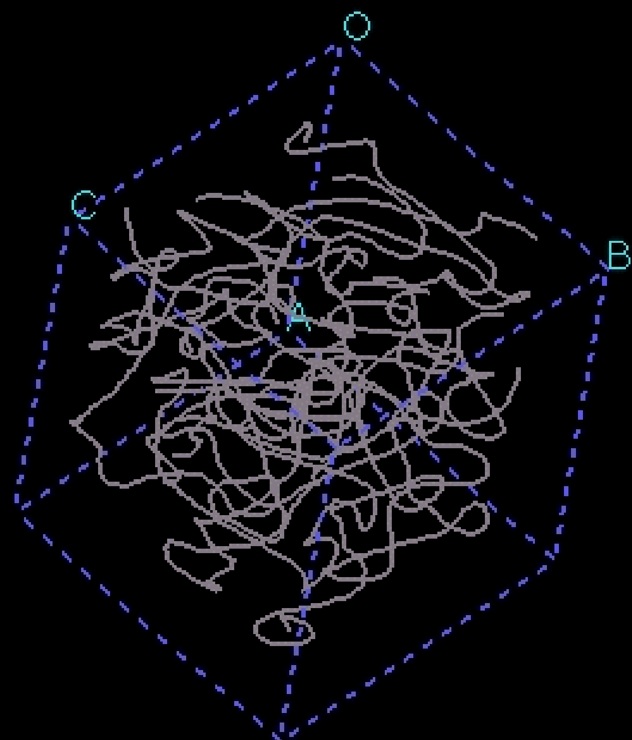
Block Copolymers: Different monomers are arranged in long blocks of each monomer.

Graft Copolymers: Appendages of one type of monomer are grafted to a long chain of the other.

Butyl rubber models



microscopic model
(atomistic, 2000
atoms)



mesoscopic model
(coarse-grained,
1500 monomers)

R_1, R_2 ....

- H
- CH
- CH_2OH

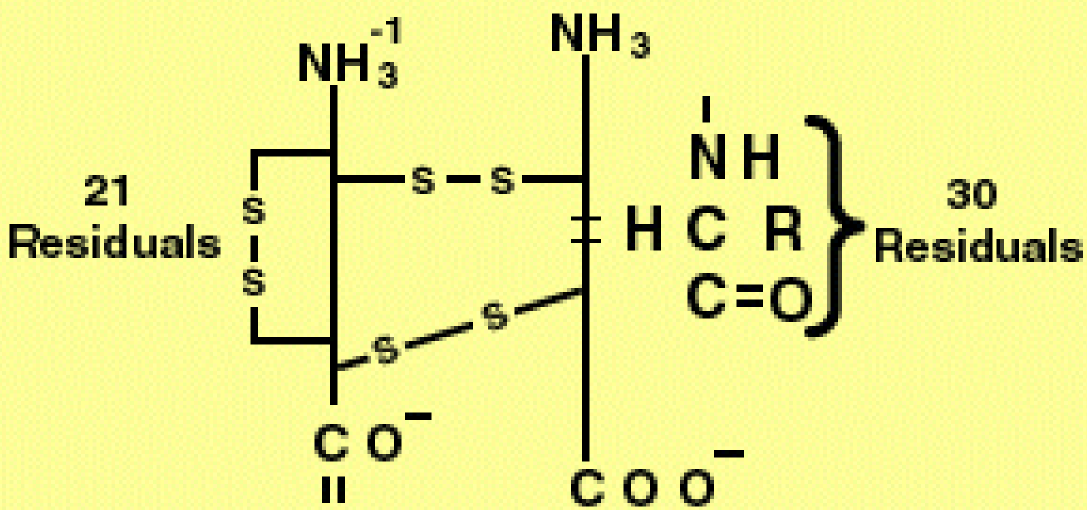
} unc

$CH_2\overset{\displaystyle O}{\overset{\|}{C}}O^-$ NEGATIVE charge

$CH_2-CH_2-CH_2\ CH\ NH_3^+$ POSITIVE

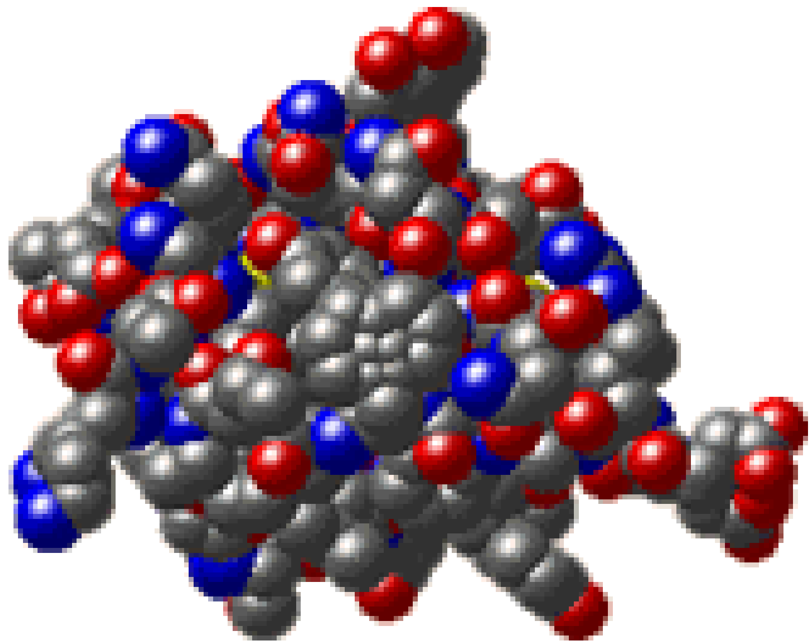
INSULIN - MACROMOLECULE

Mw = 57.33



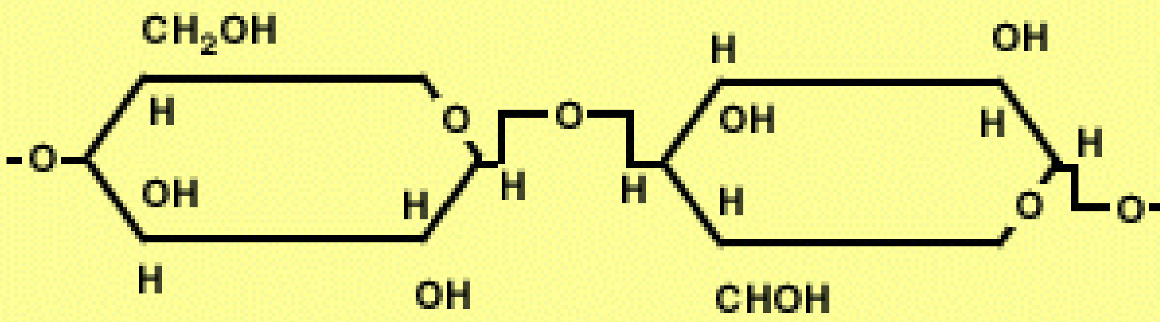
Insulin

$C_{254}H_{377}N_{65}O_{76}S_6$

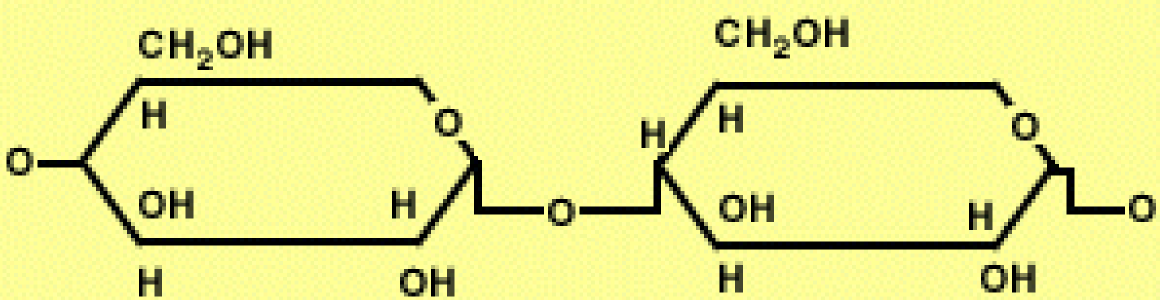


Polysaccharides

Cellulose mw >106



Starch - Amylose mw 10 - 40 k



Lignin

Glue that ties the cellulose together in the tree

The half we throw away

Vanilla

Krodt Process - rotten eggs

↓

Produces steam

Natural polymers

Used since the dawn of history and civilization

For:

- tools
- weapons
- clothing
- shelter
- sport

(tools, weapons, clothing, shelter } tanned hides, bone, horn)

sport → Mayans used a rubber ball of coagulated latex in their national sport

Today

wood, rubber, wool, silk, cotton leather, paper, oil base paint, casein (adhesives)

Problem ?

Utility and limitations of these materials

Related to their mechanical properties

under fabrication conditions

under use conditions

Our goal in this course:

Relate physical - organic chemistry

and

Process parameters

to

Part properties

What you see is what you get !

Mother Nature does not provide much diversity

Solution ?

Synthetic Polymers

Hard glassy resins
Soft sticky adhesives
Strong, tough textile fibers
Highly extensive elastomers
Durable surface coatings

Garbage bags
Bottles
Films
Egg cartons
Glasses
Seats
Tires

Rubber Industry

Developed along product lines

* Mayans made rubber ball

* MacIntosh and Hancock 1838
  - Goodyear -

Sulfur + natural rubber + heat
(vulcanized)
Non - tacky, stable material
raincoats
boots
tires

Between WWI and WWII
Synthetic rubber

WWII

GR - S-SBR 1940 - 0

1945 - 700,000 Tons

Resulted in

Styrene production

Butadiene production

Independence from imports

Latex available for other uses

Most important result of GR - S program

People trained

Insights into polymers

Production and characterization

Plastics

* Hyatt - cellulose nitrate camphor

Hard plastic for billiard balls - 1868

* Bakerland

phenol-formaldehyde - 1907

WWII

Styrene

Polyethylene - Radar

Polyvinylchloride

Fibers

Rayon - regenerated cellulose

Rayon acetate

Nylon

Coatings

Shellac, linseed, tung oil

Alkyd resins (1930)

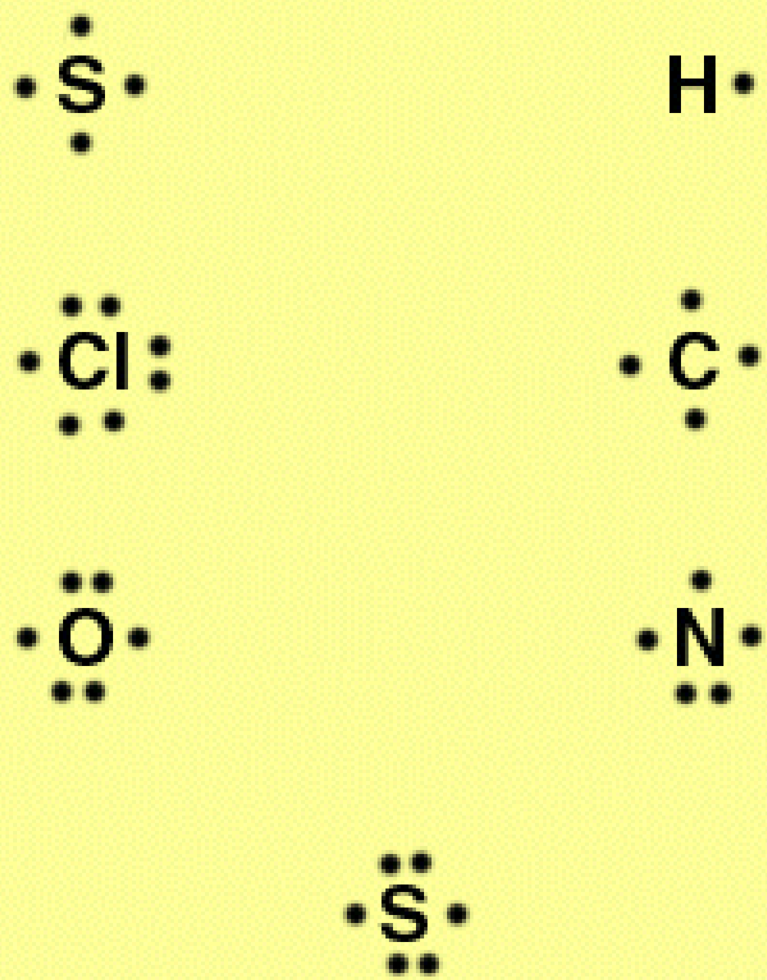
Latex paint (1940)

Recent Trend

Oil companies - commodities

Chemical companies - specialties

Molecular Aspects of Polymers



Two Types of Bonds

Ionic $\longrightarrow$ Electron Transfer

$Na_{2,8,1} + Cl_{2,8,7} \longrightarrow Na^{+}Cl^{-}$

$Mg_{2,8,2} + 2(Cl_{2,8,7}) \longrightarrow Mg^{++}(Cl^{-})_2$

Covalent Bonds

Equal protons and electrons on each atom

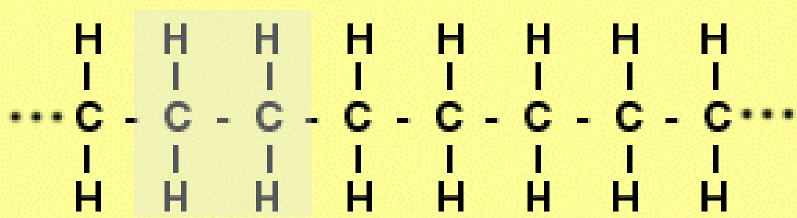
more or less

Single	C : C	Ethane
Double	C :: C	Ethylene
Triple	C ⋮⋮ C	Acetylene

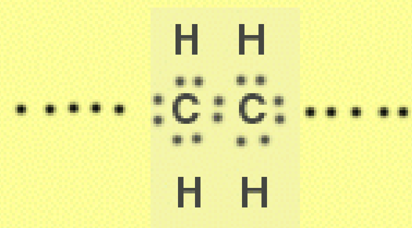
Polymer Molecules

Made up of covalently bonded atoms

Polyethylene



Carbon is ***Always*** tetravalent



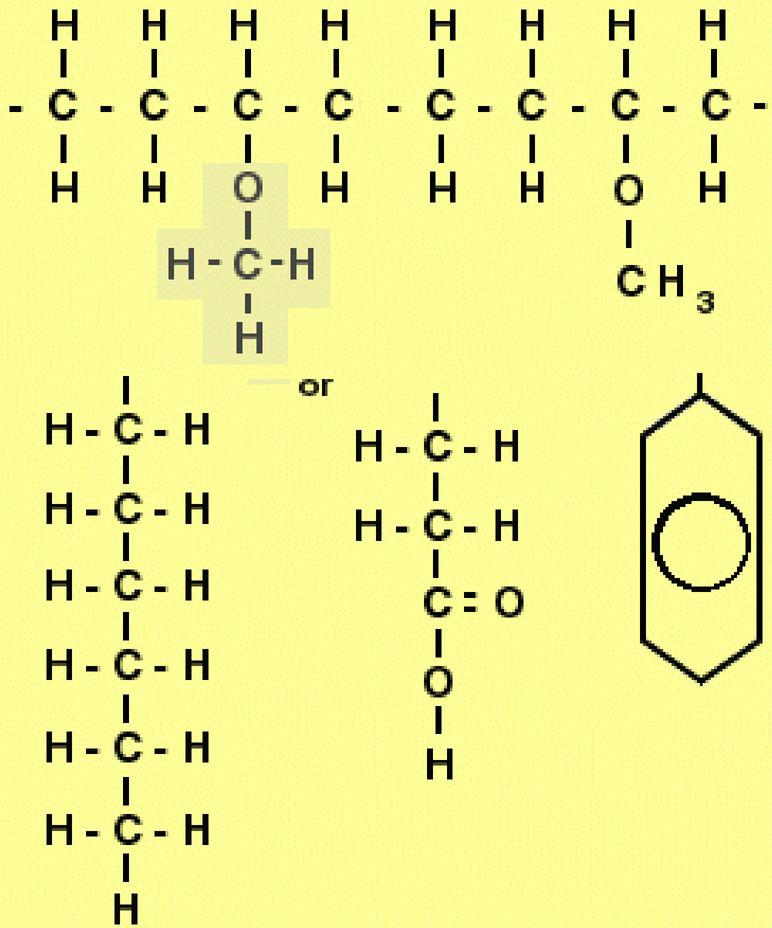
Carbon Bonds with

H·	Hydrogen
·S· (with two dot pairs)	Sulfur
Cl·	Clorine
·N· (one dot above, a dot pair below)	Nitrogen
·Si· (one dot above and one below)	Silicone

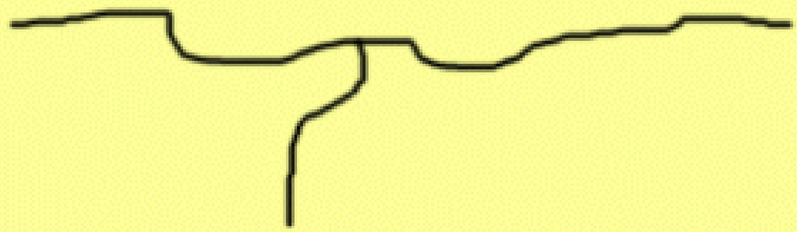
N, O } Incorporated

S, Si } Chain formers

Pendent Groups



Long polymer chains lead to branches



Can lead to a 3 - dimensional network
i.e. vulcanized rubber

Stylized structural formulars

Obscure certain important features of these molecules

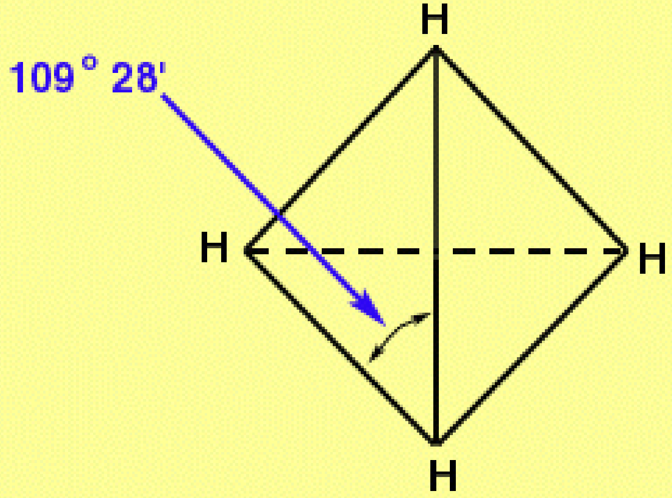
We *MUST* examine

Tetrahedral geometry of the saturated carbon atom

Rotation about the C - C bond

Controls many properties of polymer chains

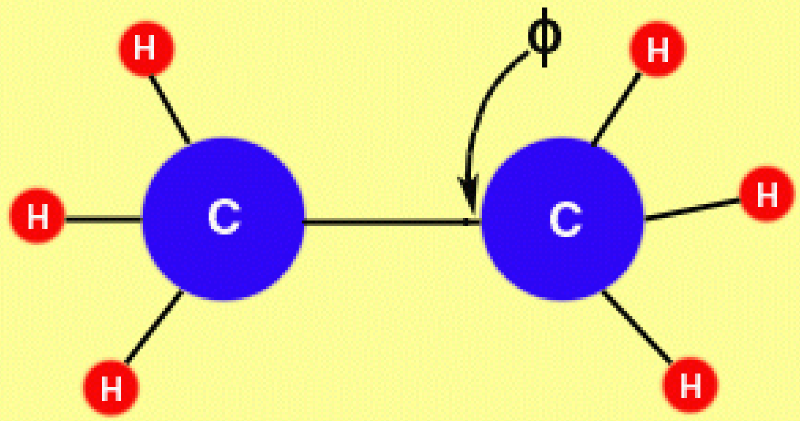
Methane CH_4



Every pair of **C - H** bonds form an angle of 109°28'

Ethane $CH_3 - CH_3$

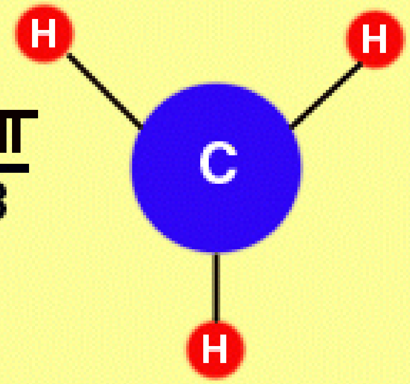
Rotation about Carbon - Carbon bonds



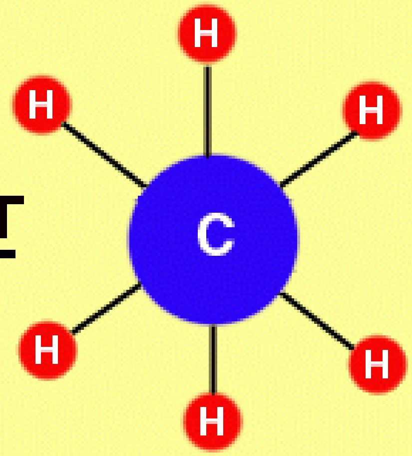
Side View

Ethane CH_3- CH_3 End View

$$\phi = \frac{\pi}{3},\ \pi,\ \frac{5\pi}{3}$$

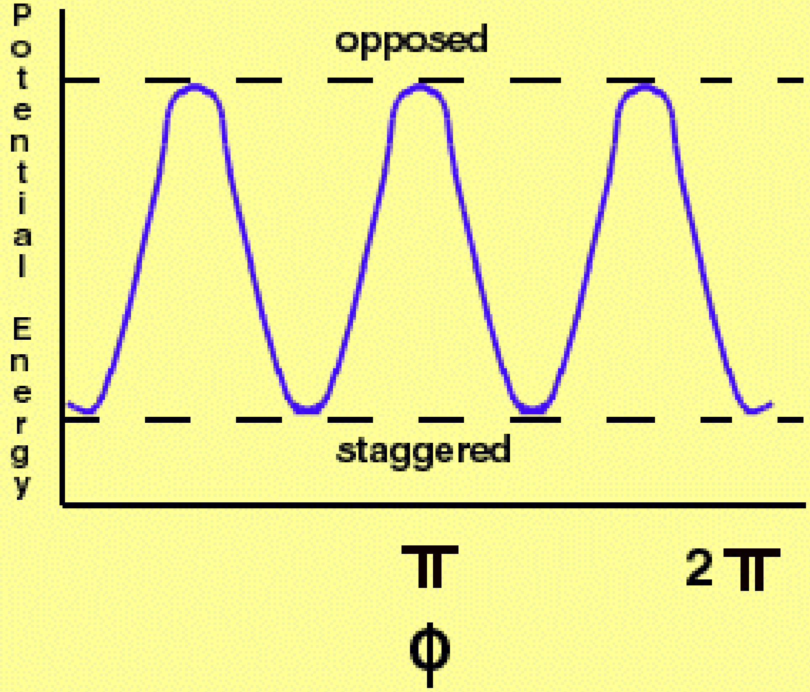


$$\phi = 0,\ \frac{2\pi}{3},\ \frac{4\pi}{3}$$



Rotation is not completely free

Potential energy has two "values"



Larger Substituent Groups

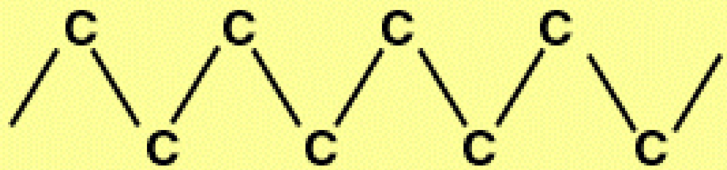
$Cl_3C - CCl_3$

More restrictions on rotation because potential energy of opposed state is much higher

Even so we have many jumps from one staggered position to another

Not much time spent in opposed

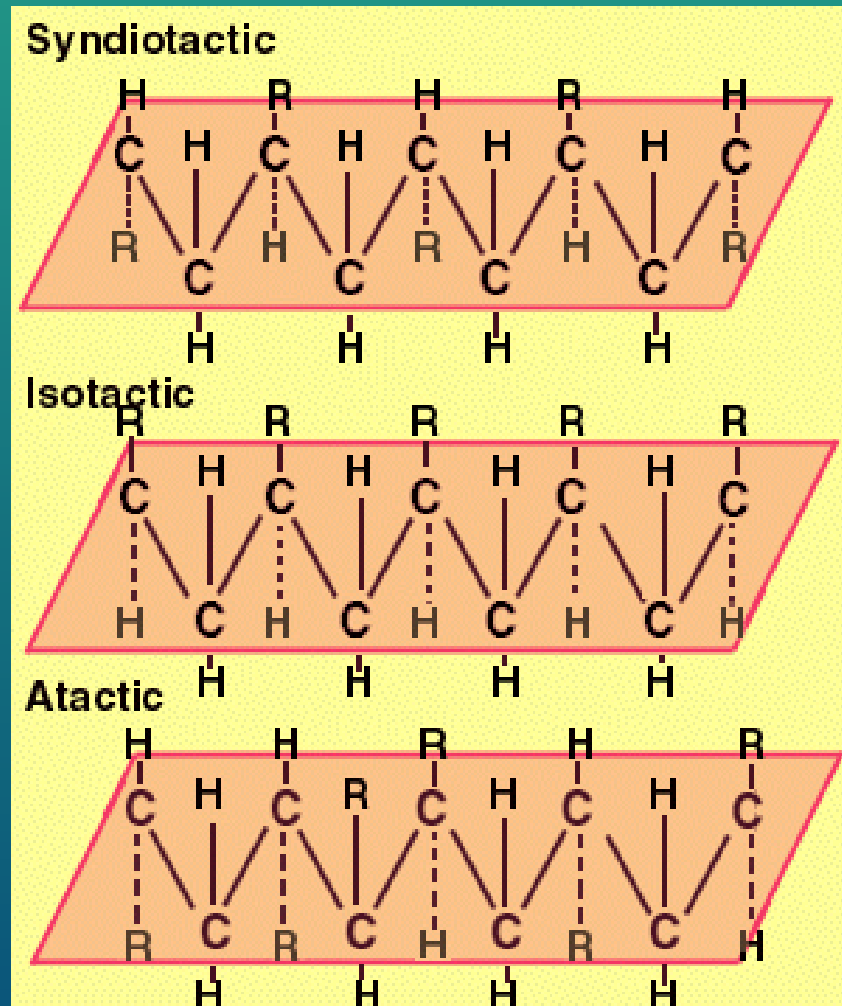
Tetrahedral Geometry

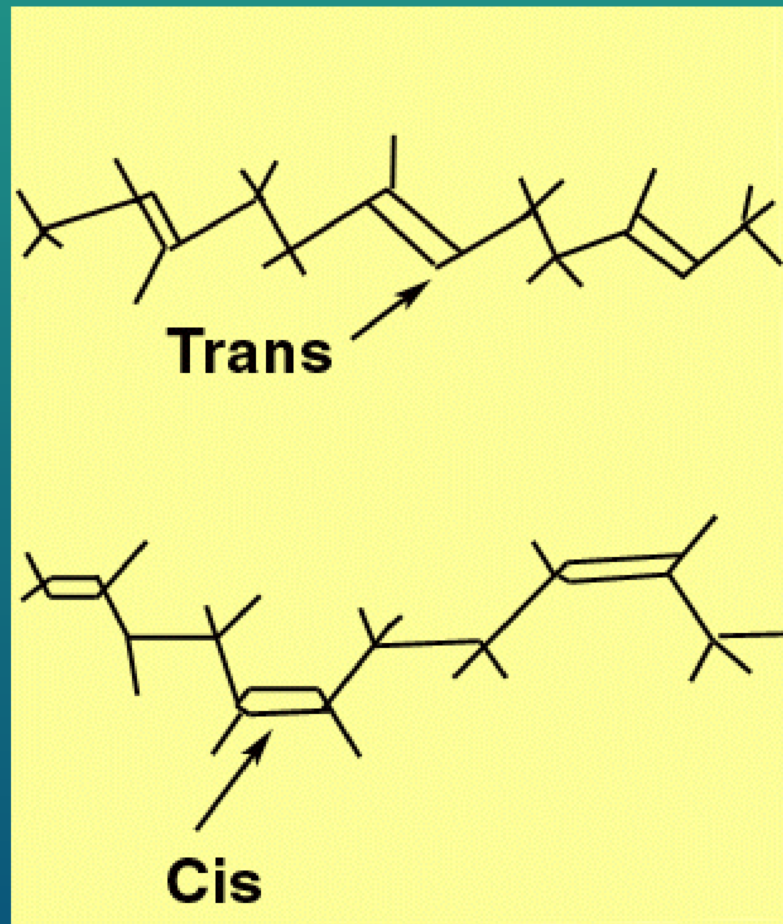


Polyethylene

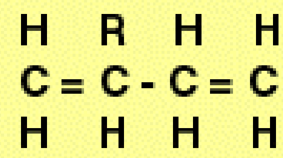
Hydrogen atoms are located above and below plane of carbon atoms and are not shown

Not really representative 3 dimensional structure due to bond rotation


Syndiotactic
Isotactic
Atactic


Trans
Cis

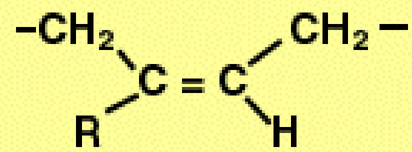
1 - 3 Butadiene



mono substituted

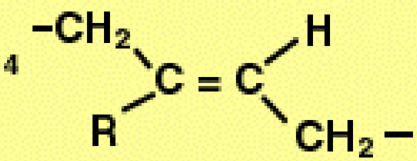
Poly isoprene

$Cis_{1,4}$



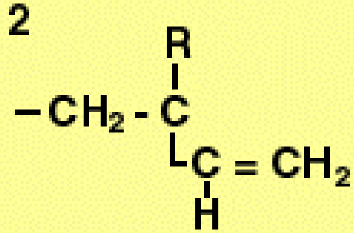
Tg -73° C
Tm +28° C

$Trans_{1,4}$

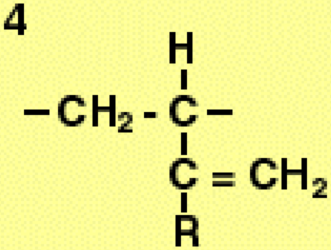


Tg -73° C
Tm +80° C

1, 2



3, 4



Speed of wriggling motion varies dramatically with temperature and polymer type.

	many	few
natural rubber	25°C	- 100°C
polystyrene	150°C	25°C

This inrtamolecular mobility, based on $(C - C)_x$ bond rotation, is one of the most important characteristics of polymer chains

Basis of rubber elasticity
and
visco elastic behavior

Cohesive Energy Density

Polymer segments are held together by covalent bonds in *"one direction"*

"secondary bonds" in two directions

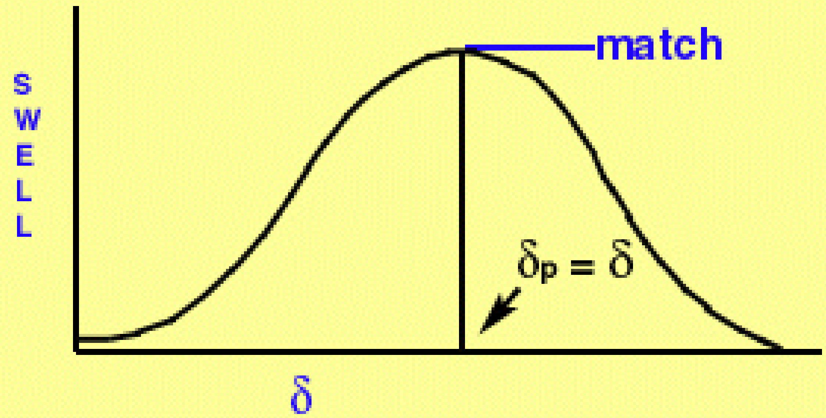
C.E.D. measures the strength of *secondary bonds*

$$\text{C.E.D.} = \frac{\Delta E_v \ \text{(molar energy of evaporation)}}{V_1 \ \text{(molar volume)}}$$

$\delta = \sqrt{\text{C.E.D.}}$ solubility parameter

Dissolving polymer in dilute solution causes it to swell - max swell when solvent $\delta = \delta_p$ - highest viscosity, therefore it can find C.E.D or δ from experiments

Cross - Linked Polymer Reach maximum swell (m or l)



Solubility

A) Chemical and structural similarity *favors* solubility

- solute-solvent attraction is greater than those between pairs of solvent or solute molecules
- solvent -solute attractions are greatest when the molecules have a similar polarity

B) Solubility decreases as molecular weight of the solute increases

C) Solubility decreases as the melting point of the solute increases

Solubility Occurs in Two Stages

1) solvent is imbibed into polymer to produce a swollen gel

2) gell gradually disintegrates into a true solution

Thermodynamic Review

$\Delta v = Q - w$ for a closed system

Q [=] heat

w [=] work

$dV = \delta Q - \delta W$

δ – not exact differential

Q and W - not system properties

δQ and δW represent energy exchange between system and surroundings

$$ds = \frac{\delta Q_{rev}}{T}$$

s is entropy

$$\delta W_{rev} = PdV$$

P = pressure

V = volume

For multicomponent systems

$$n = n_1 + n_2 + n_3 + \ldots\ldots = \Sigma n_i$$

Thermodynamic Review

For one component

$$dV = Ts - PdV$$

For multiple components

$$nV = u\,(ns, nv)$$

$$d(nv) = \left[\frac{\delta\,(nv)}{\delta\,(ns)}\right]_{nv,\,n} d(ns) + \left[\frac{\delta(nv)}{\delta(nv)}\right]_{ns,\,n} d(nv)$$

Thus

$$\left[\frac{\delta\,(nv)}{\delta\,(ns)}\right]_{nv,\,n} = T$$

$$\left[\frac{\delta(nv)}{\delta(nv)}\right]_{ns,\,n} = -P$$

Thermodynamic Review

For an open system, n_i may change, so:

$$d(nv) = \left[\frac{\delta\,(nv)}{\delta\,(ns)}\right]_{nv,\,n} d(ns) + \left[\frac{\delta(nv)}{\delta(nv)}\right]_{ns,\,n} d(nv) \; + \sum \left[\frac{\delta(nv)}{\delta(ni)}\right]_{ns,\,nv,\,ni} dn_i$$

$$\mu_i = \left[\frac{\delta(nv)}{\delta(ni)}\right]_{ns,\,nv,\,ni} = \underline{\underline{\text{Chemical Potential}}}$$

Thus:

$$d(nv) = Td(ns) - Pd(nv) + \Sigma(\mu_i\, dn_i)$$

Let $ni = nx_i$ $\quad x_i$ = mole fraction of (i)

Then

$$dv = Tds - Pdv + \Sigma\mu_i\, dx_i$$

$$v = Ts - P\,v + \Sigma\mu_i x_i = \underline{\underline{\text{Internal Energy}}}$$

Thermodynamic Review

$$\mu_i = \hat{g} + RT \ln x_i$$

$$\mu_i = \mu_o + RT \ln x_i$$

Thermodynamic Review

For an open system:

Gibbs function $G = U\ PV - TS$

$$dG = dU + PdV + VdP - TdS - SdT$$

substitute dV

$$dG = TdS - PdV + \Sigma\mu_i dx_i + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT + \Sigma\mu_i dx_i$$

$$\mu_i = \left[\frac{\delta(n6)}{\delta(n_i)}\right]_{P,\ T,\ n_1 \ldots\ldots n_n}$$

$$S(T, P_i) = S(T, P) - R \ln \frac{P_i}{P}$$

$$\hat{\mu}_i = \hat{h}(T) - T\hat{s}(T, P_i)$$

Thus

$$\mu_i = h(T) - T\hat{s}(T, P) + RT \ln x_i$$

Solution Thermodynamics

Chemical potential

$$\mu_i = \left(\frac{\delta 6}{\delta \eta_i}\right)_{P,\,T,\,n_j + i}$$

In an open system moles may increase or decrease, therefore:

$$dG = \left(\frac{\delta 6}{\delta T}\right)_{P_n} dT + \left(\frac{\delta 6}{\delta P}\right)_{T_n} dP + \Sigma \left(\frac{\delta 6}{\delta n_i}\right)_{PTn_j} dn_i$$

$$\left(\frac{\delta 6}{\delta T}\right)_{P_n} = -s \qquad \left(\frac{\delta 6}{\delta P}\right)_{T_n} = V$$

$dG = -sdT + VdP + \Sigma\mu_i d\eta_i$

For constant T and P:

$dG = \Sigma\mu_i d\eta_i$

For two phases α and ϱ

$dG = dG_\alpha + dG_\beta = 0$ at Equilibrium

$\mu_{i\alpha} dn_{i\alpha} + \mu_{i\beta} dn_{i\beta} = 0$

in a closed system

$dn_{i\alpha} = -dn_{i\beta}$

$\mu_{i\alpha} = \mu_{i\beta}$

now, how to define in <u>one phase</u>

Activity a_i

$$\mu_i = \mu_i^\circ + RT\ln a_i$$

$a_i \approx$ mole fraction

$\mu_i \longrightarrow \mu_i^\circ$ at $a = 1$

$$\left(\frac{\delta U_i}{\delta P}\right)_{Tn} = \bar{V}_i$$ Particle molar volume

at Eq: $U_{iL} = U_{iV}$

$$\left(\frac{\delta U_{iL}}{\delta P}\right)_{Tn} = \left(\frac{\delta U_{iV}}{\delta P}\right)_{Tn} = \bar{V}_i = \frac{RT}{P_i}$$

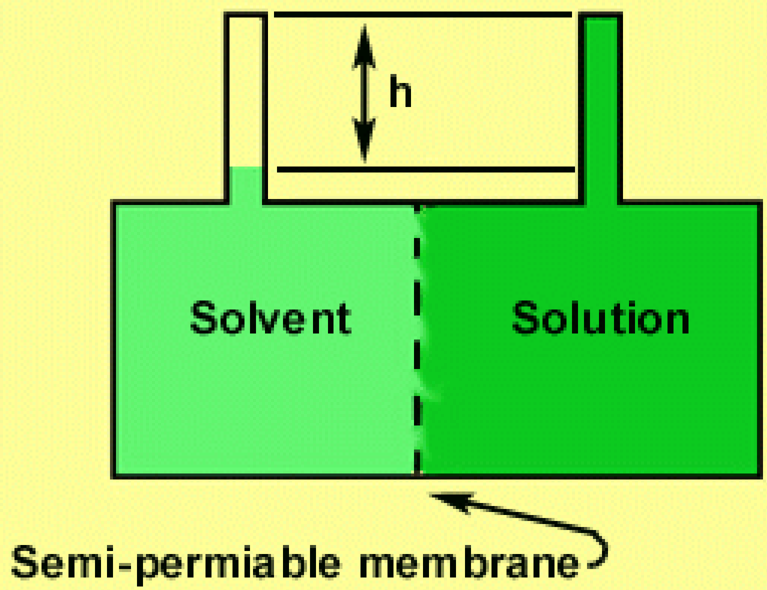
$$\longrightarrow RT\,\delta \ln a = RT\,\frac{\delta P_i}{P_i}$$

$$a_i = \frac{P_i}{P_o} = \text{Raoult's } \underline{\text{Law}}$$

IF IDEAL and $a_i = x_i$

This leads to the

Thermodynamics of Osmotic Pressure



Recall $\mu_i = \mu_i^o + RT\ln a_i$

$u_i < \mu_i^o \cdot F \quad a_i < 1$

$$a_i = \frac{P_i}{P_i^o}$$

$$u_i = u_i^o + RT\ln\frac{P_i}{P_i^o}$$

$P_i > P_i^o \qquad u_i > \mu_i^o$

$$\mu_i = \mu_i^o + RT\ln a_i \int_{P_i^o}^{P_i^o + P_i} \overline{V}_1 \, dP$$

1 = solvent

assume $\overline{V}_1$ constant

Condense (phase)

Integration gives

$$\ln a_i = - \frac{P\bar{V}_1}{RT}$$

Substitution back gives

$$u_i = u_i^o - P\bar{V}_1$$

now

$$\ln x1 = - \frac{P\bar{V}_1}{RT} = \ln(1-x_2) \approx - x_2 - \frac{x^2}{2}$$

For an *IDEAL* solution

$$x_2 = \frac{P\bar{V}_1}{RT} \qquad x_2 \approx \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$

$$n_2 = \frac{n_1 P\bar{V}_1}{RT} = \frac{PV_1}{RT}$$

Van Hoff equation
number of solute molecules

Ideal gas can be represented by

$$\frac{PV}{nRT} = 1 + BP + CP^2$$

$$\frac{PV}{nRT} = 1 + B\left(\frac{n}{v}\right) + c\left(\frac{n}{v}\right)^2$$

Verial Equation
For Van der Waals a & b

$$B = b - \frac{a}{RT} \quad \text{-interaction}$$

By analogy

$$\frac{P\bar{V}_1}{RT} = A' x^2 + \frac{1}{2} B' x_2^2$$

A' must be 1 to reduce to Von Hoff

$$\frac{P\bar{V}_1}{RT} = x_2 + \frac{1}{2} B' x_2^2$$

If m_2 is mass of solute in solution

$$C = \frac{m_2}{n_1\bar{V}_1 + m_2\bar{V}_2} \approx \frac{m_2}{n_1\bar{V}_1} \quad \text{Dilute}$$

$$C = \frac{n_2 m_2}{n_1\bar{V}_1} = x_2 \frac{m_2}{\bar{V}_1}$$

Substitution yields

$$\frac{P}{RT_c} = \frac{1}{m_2} + \frac{1}{2}\,\frac{B'\,\bar{V}_1}{m_2^{\,2}}\,c$$

$$= \frac{1}{m_2} + Bc$$

Plot $\left(\frac{P}{RT_c}\right)$ vs c

Intercept = $\left(\frac{P}{RT_c}\right)_o = \frac{1}{m_2}$

Slope = B = $\frac{1}{2}\,\frac{B'\,\bar{V}_1}{m_2^{\,2}}$

Polymer "Solubility"

Up to now we have assumed that the polymer will disolve in the solvent

This is not always the case

Solubility occurs when the free energy of mixing

$$F_m = \Delta H_m \; T \Delta S_m$$

is negative

$$\Delta S_m > 0$$

ΔF is ALWAYS determined by the sign and magnitude of ΔH_m

$S = K \ln \Omega$

Ω = thermodynamic probability

from this we see

ΔS is always > 0

If there is a positive interaction between polymer & solvent (polar)

ΔH is negative and

$\Delta F < 0$

solution occurs

If dispersion forces only

solution may not occur

ΔF depends on magnitude of ΔH

For endothermic mixing

ΔH is positive

$$\Delta H = \upsilon_1 \upsilon_2 (\delta_1 - \delta_2)^2$$

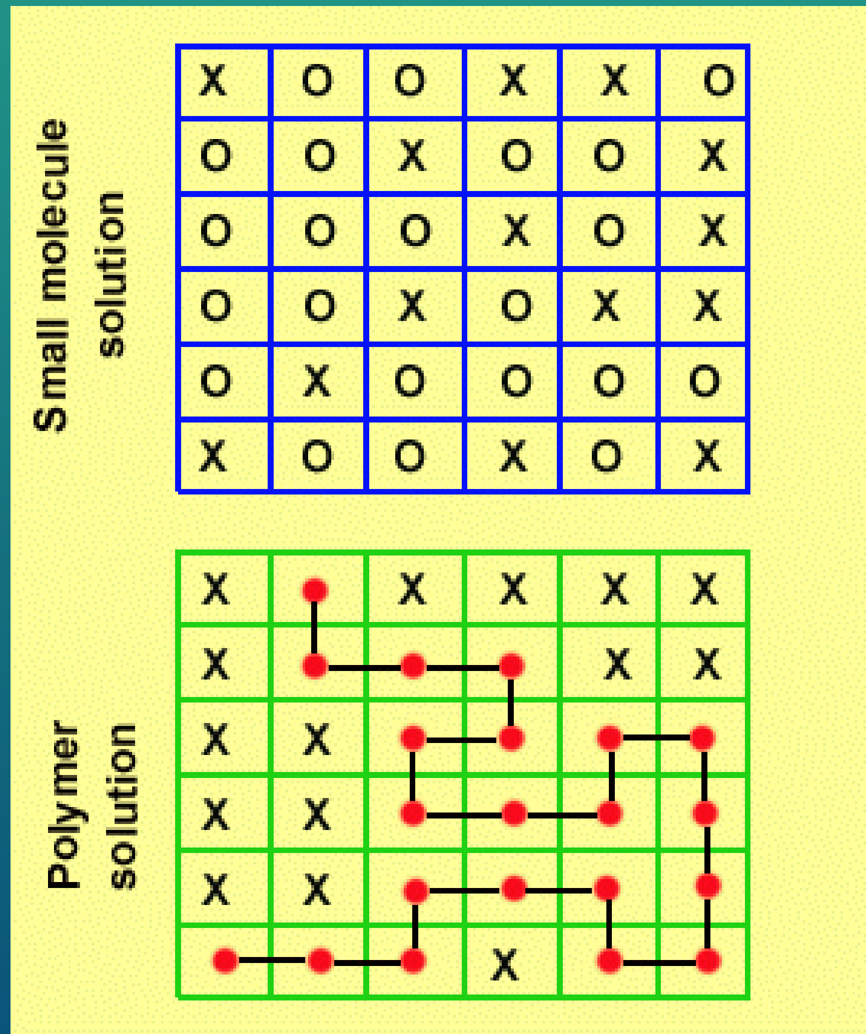
1 solvent

2 solute

$(\delta_1 - \delta_2)$ ← must be small

Why does ΔH have to be small?

Look at ***ENTROPY*** for solution of small molecules and for polymer solution


Small molecule solution
Polymer solution

$S = K \ln \Omega$

Ω = thermodynamic probability

from this we see

ΔS is always > 0

If there is a positive interaction between polymer & solvent (polar)

ΔH is negative and

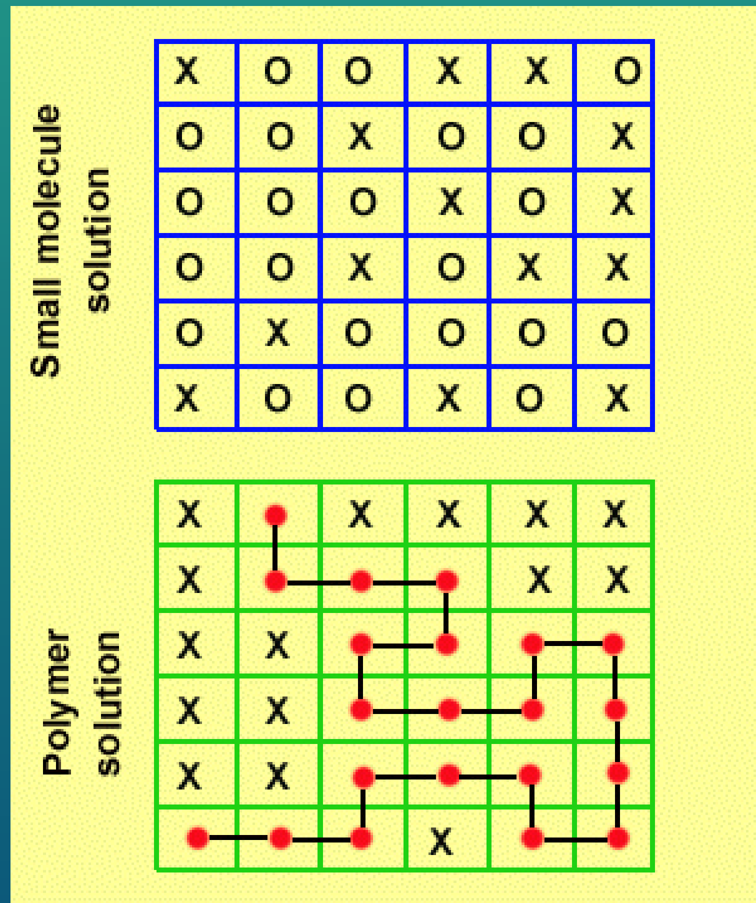
$\Delta F < 0$

solution occurs

If dispersion forces only

solution may not occur

ΔF depends on magnitude of ΔH


Small molecule solution
Polymer solution

Pure Component

$$\Delta S = k \ln(1)$$
$$= 0$$

For solution

$$\Delta S = k \ln \Omega$$

Given the linear lattice

N_1 = solvent molecule
N_2 = solute (polymer with η segments)

$$N = N_1 + \eta N_2$$

We can show . . .

$$\Delta S = -\kappa \left(N_1 \ln \nu_1 + N_2 \ln \nu_2\right)$$

1 = solvent   2 = solute

ν_1 & ν_2 are Volume Fractions

$$\nu_1 = \left(\frac{N_1}{N_1 + \eta N_2}\right)$$

$$\nu_2 = \left(\frac{\eta N}{N_1 + \eta N_2}\right)$$

It can be shown that

$$\Delta H = \chi_1 \kappa T N_1 \nu_2$$

$$\Delta F = \Delta H - T\Delta S$$

$$\Delta F = \kappa T[\, N_1 \ln \nu_1 + N_2 \ln \nu_2 + \chi_1 N_1 \nu_2 \,]$$

Eliminating N_i

$$\Delta F = \kappa T[\, \ln(1 - N_1) + \left(1 - \frac{1}{n}\right)\nu_2 + \chi_1 \nu_2^2 \,]$$

$$\Pi = -\frac{\kappa T}{V_1}[\, \ln(1 - N_1) + \left(1 - \frac{1}{n}\right)\nu_2 + \chi_1 \nu_2^2 \,]$$

$$-\frac{\Pi \bar{V}_1}{RT} = [\ln v_1 + \left(1 - \frac{1}{n}\right) v_2 + \chi_1 v_2^2]$$

now $v_1 = (1 - v_2)$

$v_1 = \phi_1$

$v_2 = \phi_2$

using the same expansion

$$-\frac{\Pi \bar{V}_1}{RT} = \phi_2 + \frac{1}{2}\phi_2^2 - \left(1 - \frac{1}{n}\right)\phi_2 - \chi_1 \phi_2^2$$

$$\phi_2 \approx C_2 \frac{\bar{V}_2}{M_2}$$

Recall the last derivation

$$-\frac{\Pi \bar{V}_1}{RTc} = \frac{\bar{V}_2}{M_2 n \bar{V}_1} + \left(\frac{\frac{1}{2} - \chi_1}{v_1}\right) + \left(\frac{\bar{V}_2}{M_2}\right)^2 c$$

$$\Delta F = \Delta H - T\Delta S$$

$$\Delta F = \kappa T[\ N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2\ ]$$

Eliminating N_i

$$\Delta F = \kappa T[\ \ln (1 - N_1) + \left(1 - \frac{1}{n}\right) v_2 + \chi_1 v_2^2\ ]$$

$$\Pi = -\frac{\kappa T}{V_1}[\ \ln (1 - N_1) + \left(1 - \frac{1}{n}\right) v_2 + \chi_1 v_2^2\ ]$$

$$-\frac{\Pi \bar{V}_1}{RT} = [\ln v_1 + \left(1 - \frac{1}{n}\right) v_2 + \chi_1 v_2^2]$$

now $v_1 = (1 - v_2)$

$v_1 = \phi_1$

$v_2 = \phi_2$

using the same expansion

$$-\frac{\Pi \bar{V}_1}{RT} = \phi_2 + \frac{1}{2}\phi_2^2 - \left(1 - \frac{1}{n}\right)\phi_2 - \chi_1 \phi_2^2$$

$$\phi_2 \approx C_2 \frac{\bar{V}_2}{M_2}$$

Recall the last derivation

$$-\frac{\Pi \bar{V}_1}{RTc} = \frac{\bar{V}_2}{M_2 n \bar{V}_1} + \left(\frac{\frac{1}{2} - \chi_1}{V_1}\right) + \left(\frac{\bar{V}_2}{M_2}\right)^2 c$$

$$\frac{\Pi}{RT_c} = \frac{1}{M_2} + \left(\frac{\frac{1}{2} - \chi_1}{\bar{V}_1}\right) + \left(\frac{\bar{V}_2}{M_2}\right)^2 c$$

$$\beta = \frac{\frac{1}{2} - \chi_1}{\bar{V}_1}\left(\frac{\bar{V}_2}{M}\right)^2$$

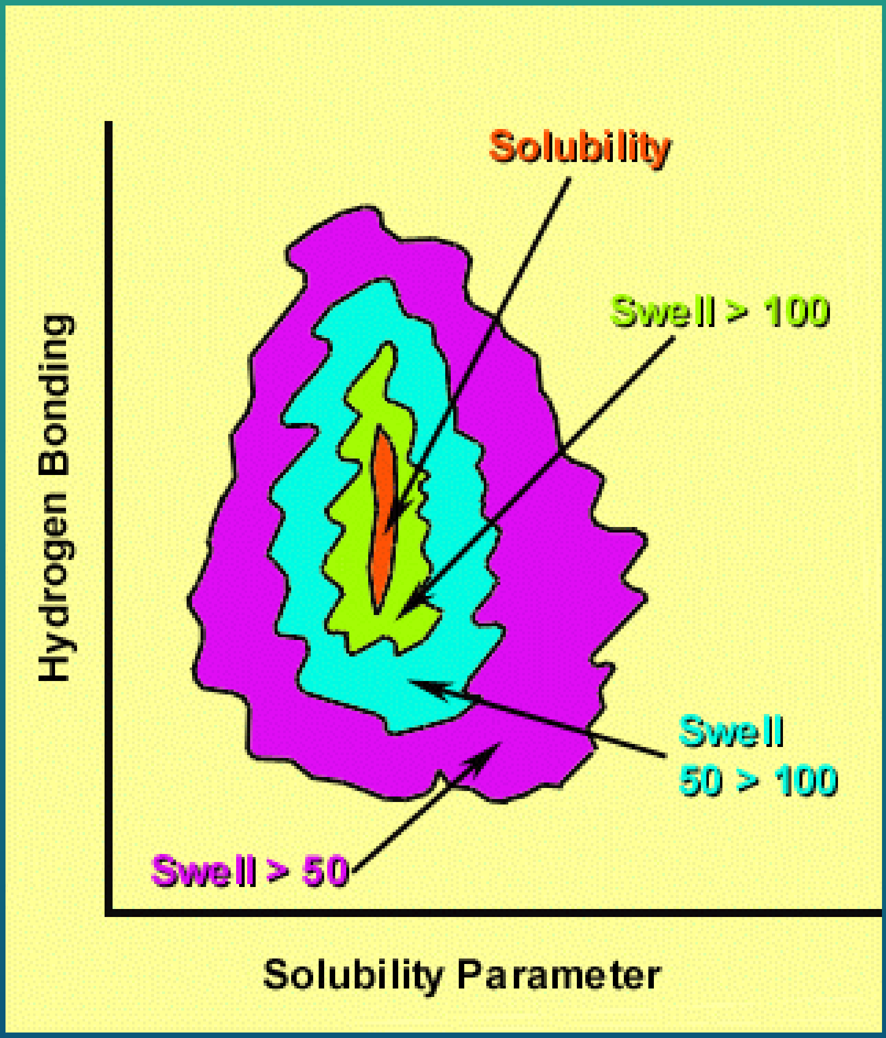
$$\chi_1 = \frac{1}{2} \qquad \beta = 0$$

and solutions behave *IDEALLY*

Temperature effects this ????????

$$\left(\frac{1}{2} - \chi\right) = \psi\left(1 - \frac{\Theta}{T}\right)$$

when $\beta = 0$ theta condition


Solubility
Swell > 100
Swell
50 > 100
Swell > 50
Hydrogen Bonding
Solubility Parameter

Swelling

$\Delta F = \Delta F_m + \Delta F_{el}$

No internal energy change

$\Delta F_m = - T \Delta S$

$= \kappa T \left(\eta_1 \ln \upsilon_1 + \chi_1 \eta_1 \upsilon_2\right)$

$\Delta F_{el} = - T \Delta S_{el}$

$$= \left(\kappa T \frac{\upsilon_e}{2}\right)\left(3\alpha_s^2 - 3 - \ln \alpha_s^3\right)$$

υ_e = effective chains

α_s = linear deformation factor

Swelling

$$\Delta F = \Delta F_m + \Delta F_{el}$$

No internal energy change

$$\Delta F_m = - TDS$$

$$= \kappa T \left(\eta_1 \ln \upsilon_1 + \chi_1 \eta_1 \upsilon_2\right)$$

$$\Delta F_{el} = - T\,\Delta S_{el}$$

$$= \left(\kappa T\,\frac{\upsilon_e}{2}\right)\left(3\alpha_s^2 - 3 - \ln \alpha_s^3\right)$$

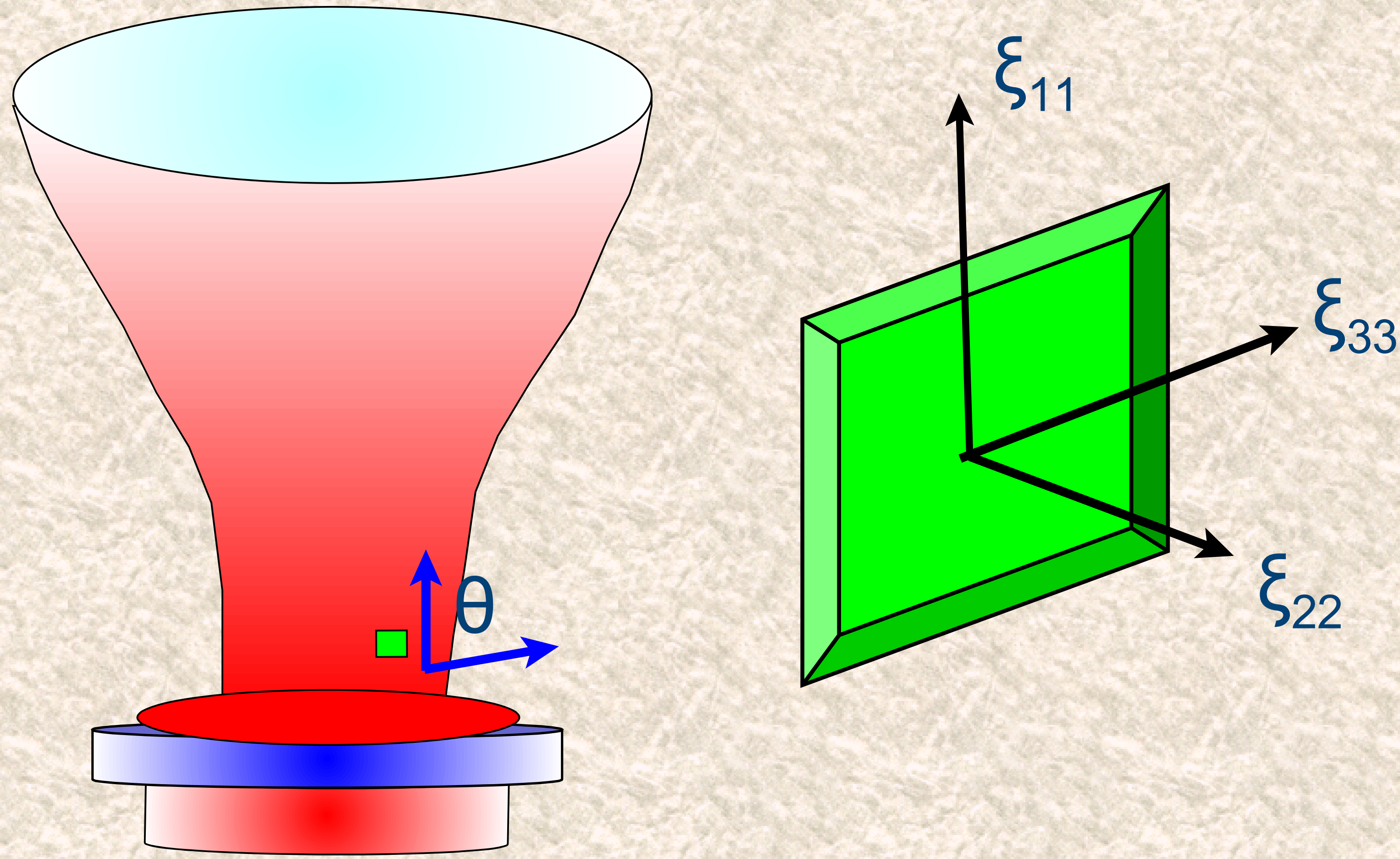
υ_e = effective chains

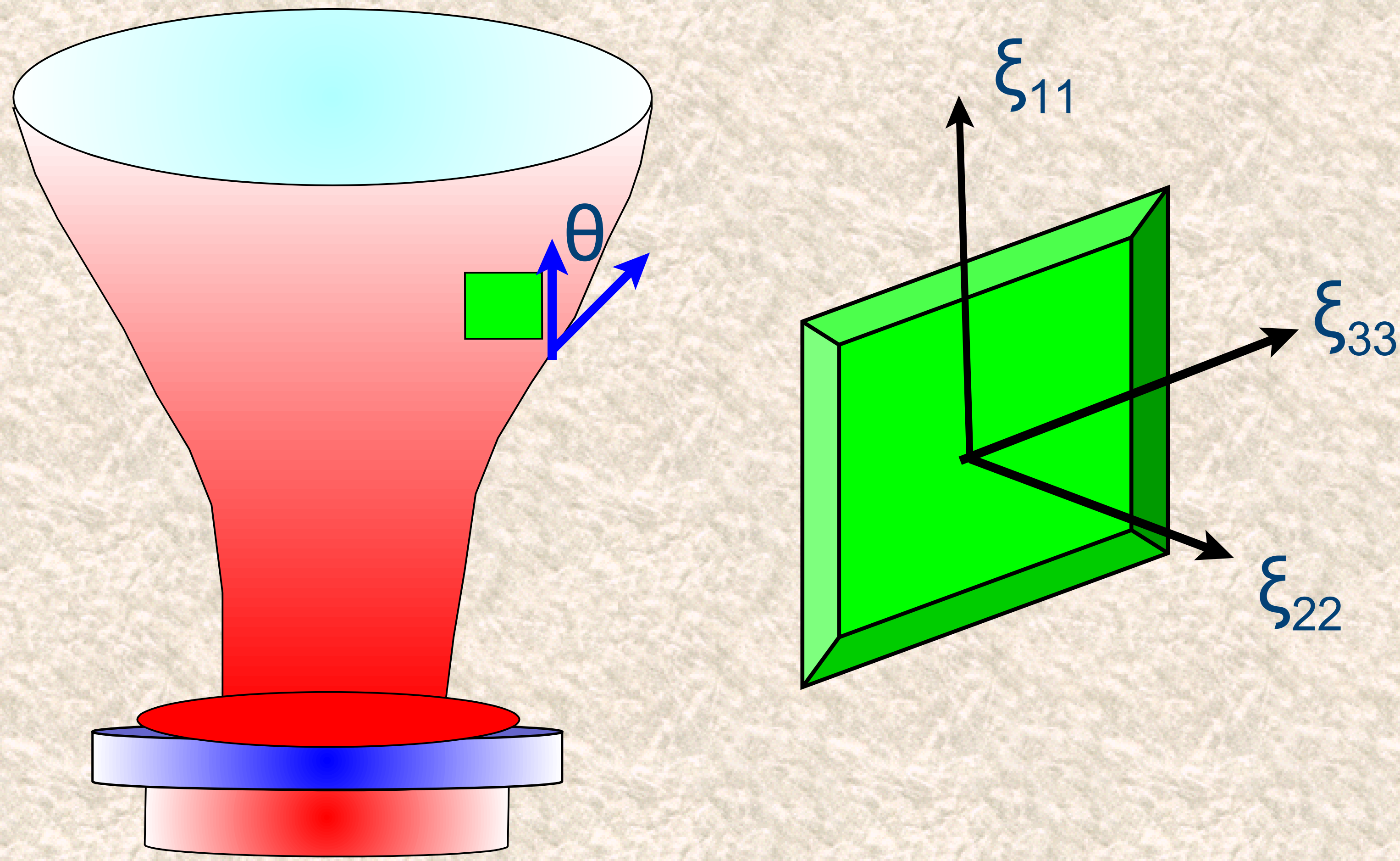
α_s = linear deformation factor

Chemical potential of solvent in swollen gel is:

$$\mu_i - \mu_i^o = N\left[\left(\frac{\delta \Delta F_m}{\delta n_1}\right)_{TP} + \left(\frac{\delta \Delta F_{el}}{\delta \alpha_s}\right)\left(\frac{\delta \alpha_s}{\delta n_1}\right)_{TP}\right]$$

$$\ln(1 - \upsilon_2) + \upsilon_2 + \chi_1 \upsilon_2^2 = -NV_1\left(\upsilon_2^{1/3} - \frac{\upsilon_2}{2}\right)$$


θ
ξ11
ξ33
ξ22


θ
ξ11
ξ33
ξ22

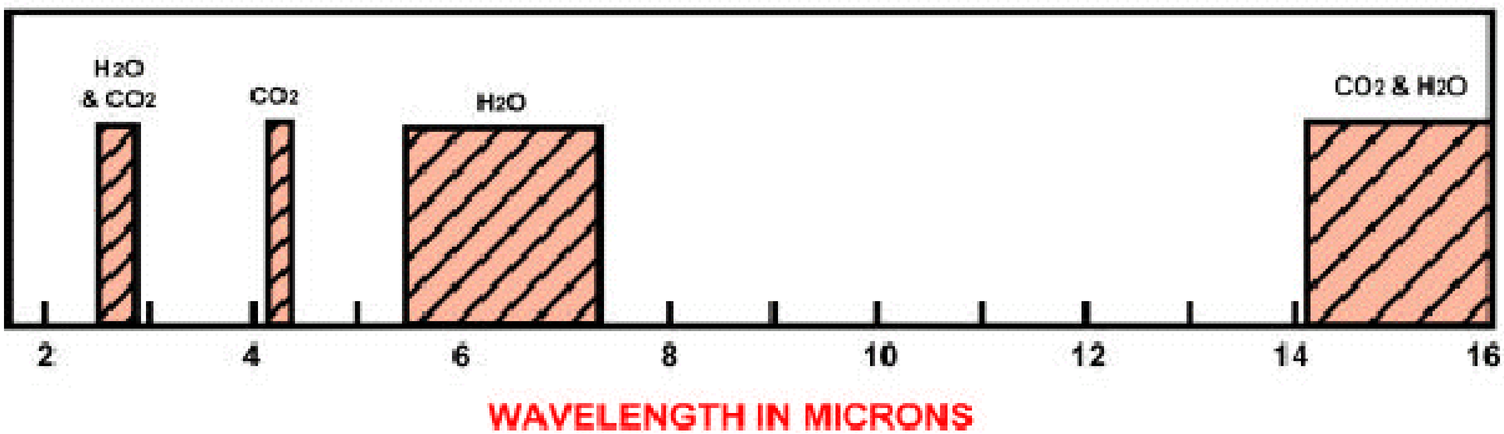


Fig. 1: Areas of significant atmospheric absorption over a path length of 10 feet

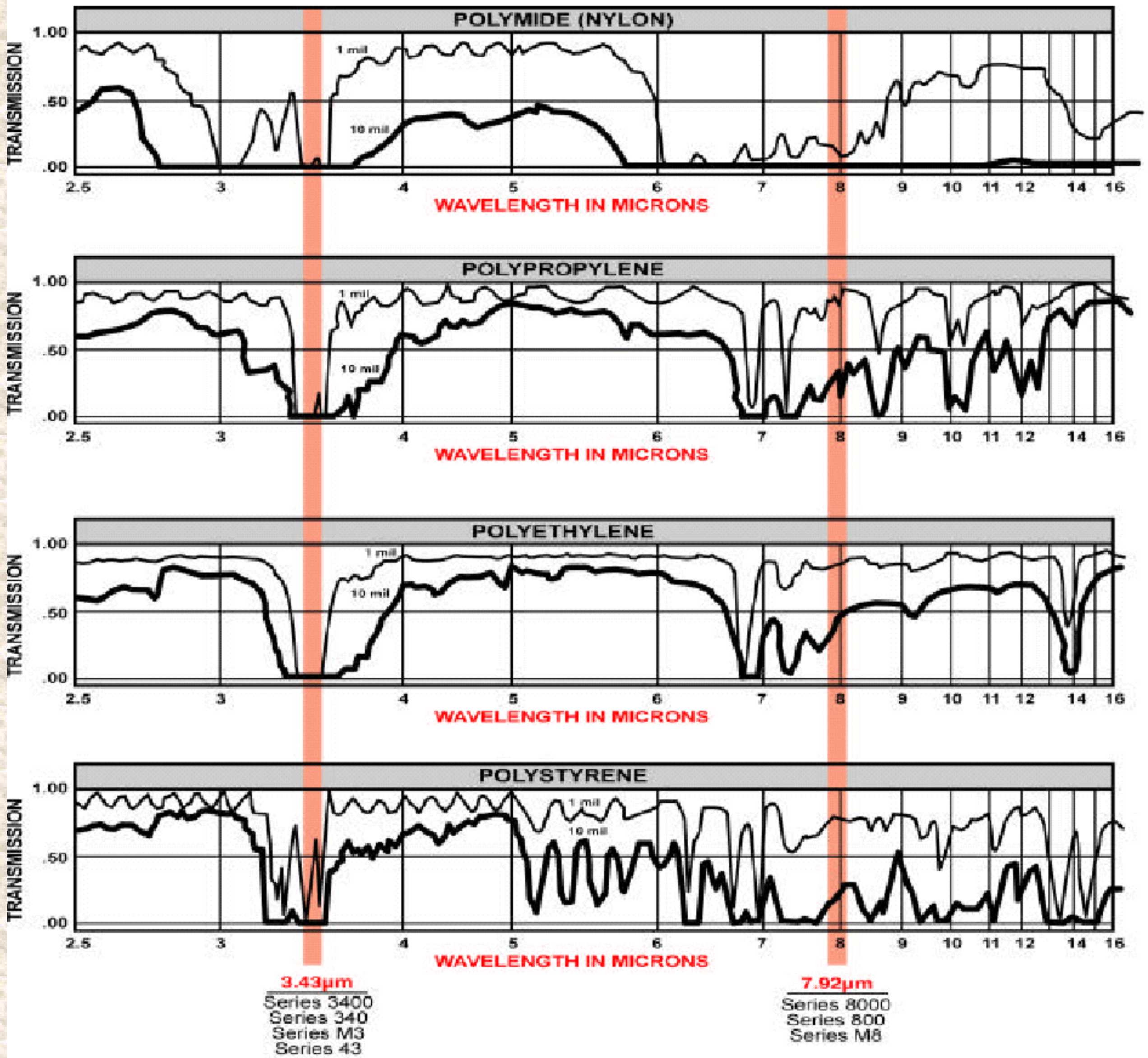


Fig 5 – Transmission spectra of several commercial plastics
(1 mil = 0.001 inches = 0.025 millimeters)

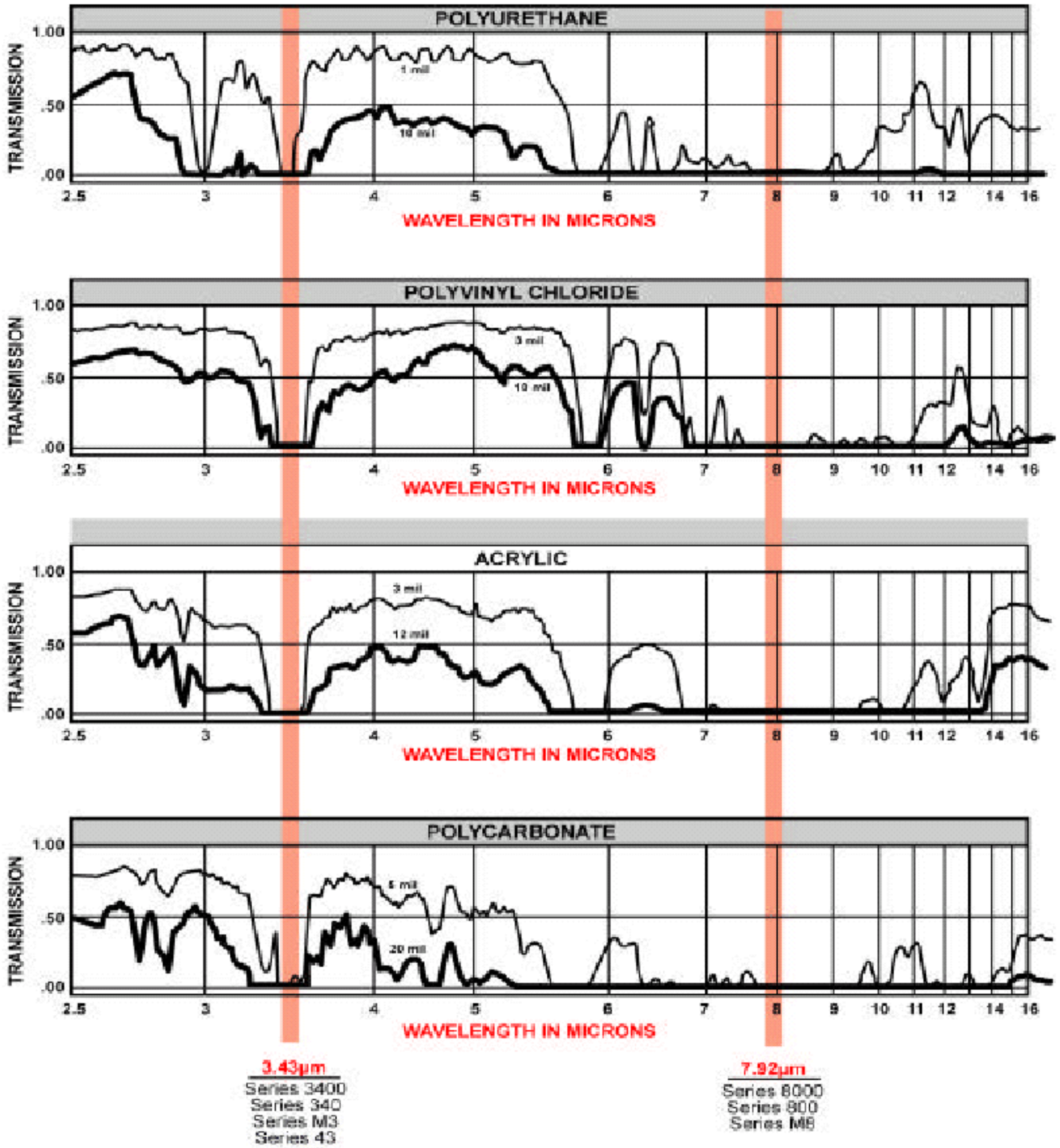
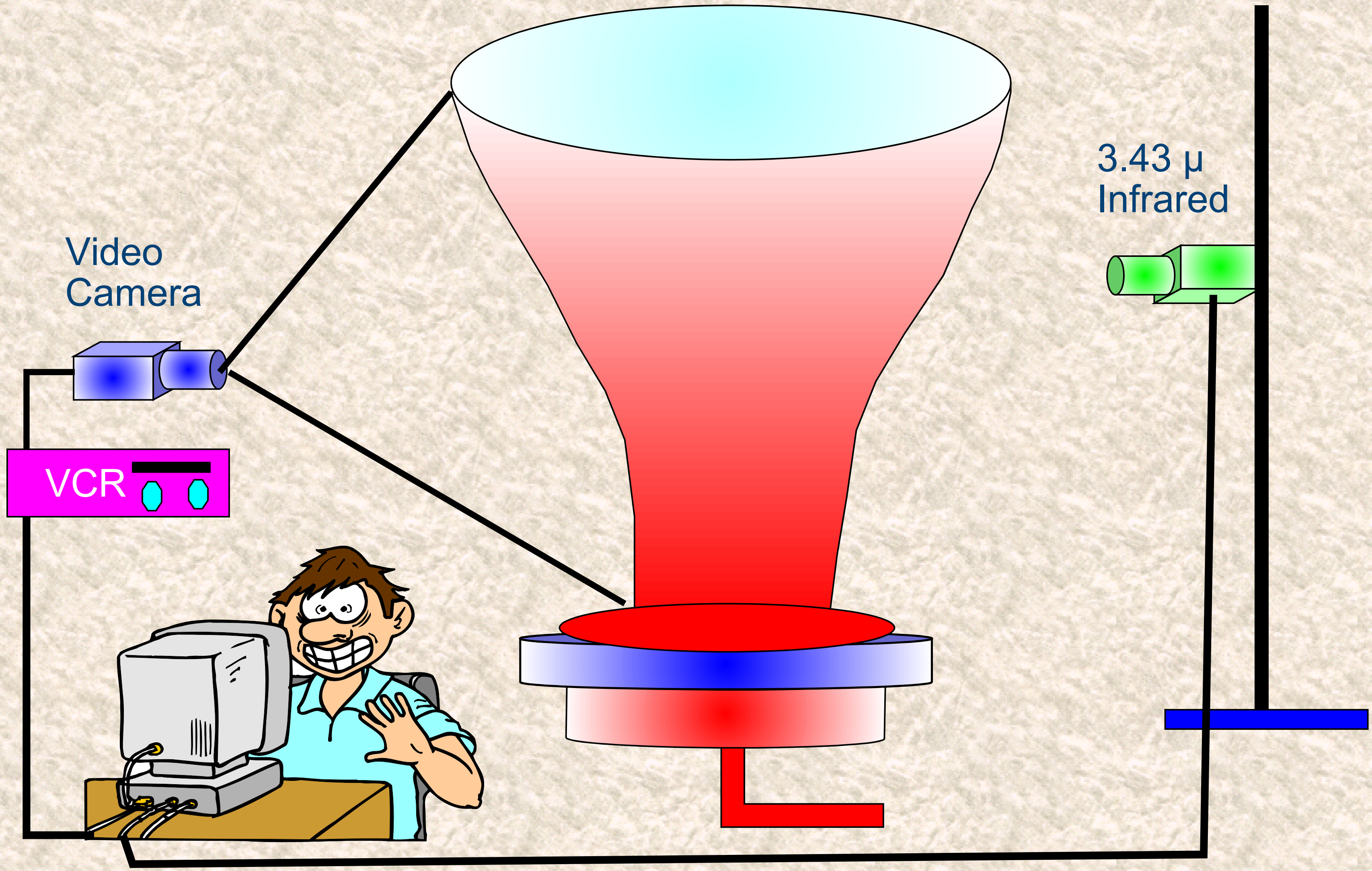
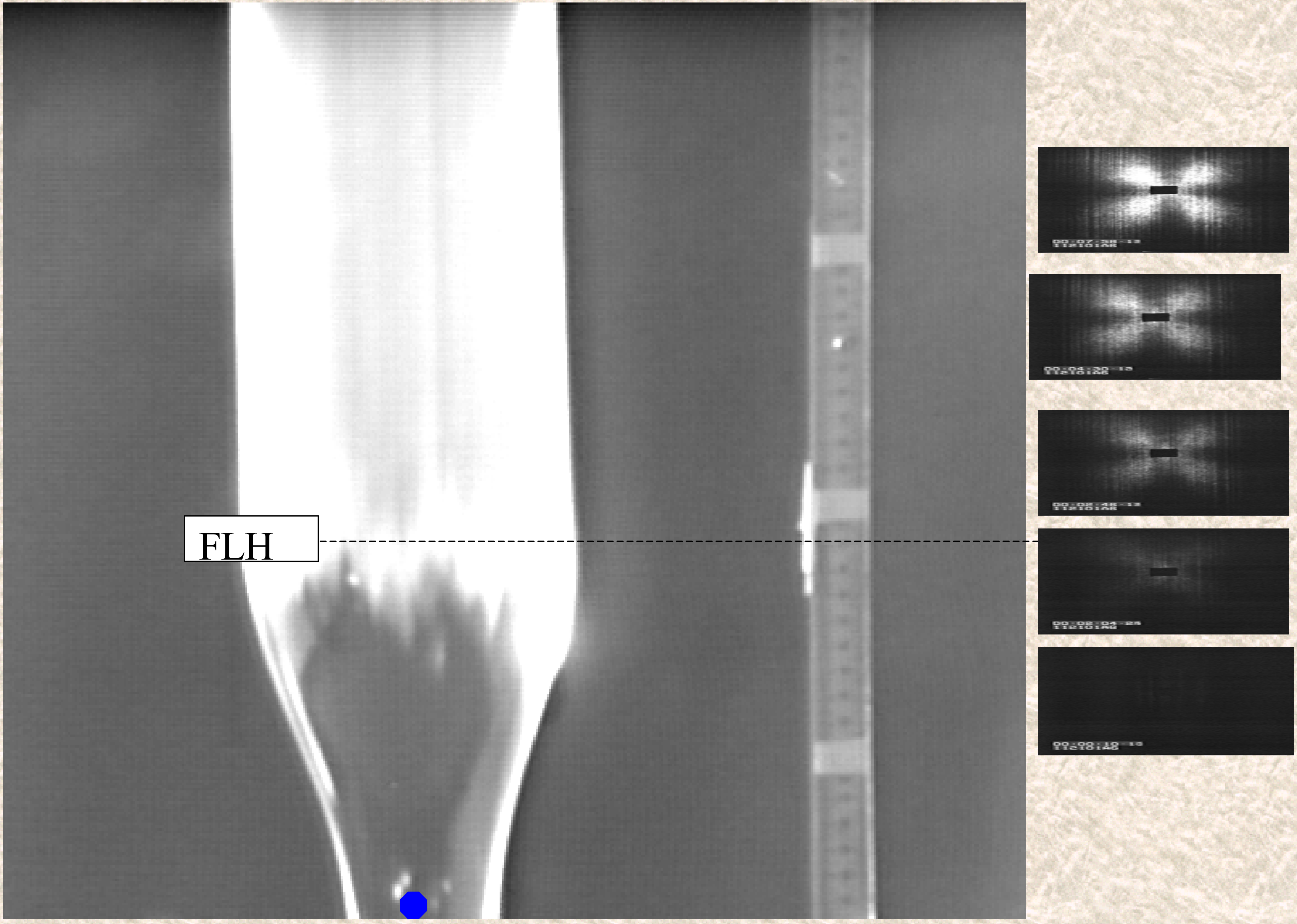
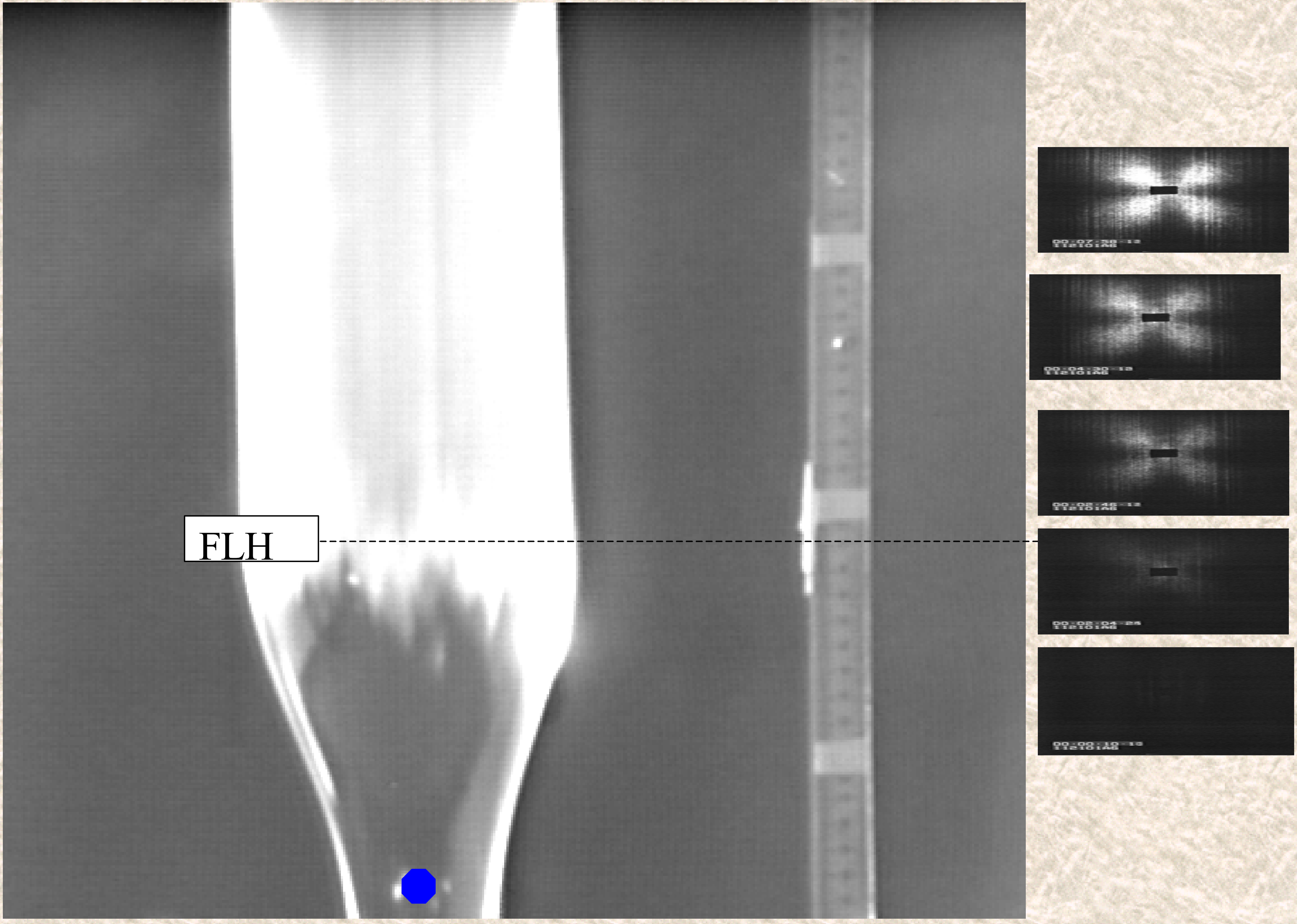


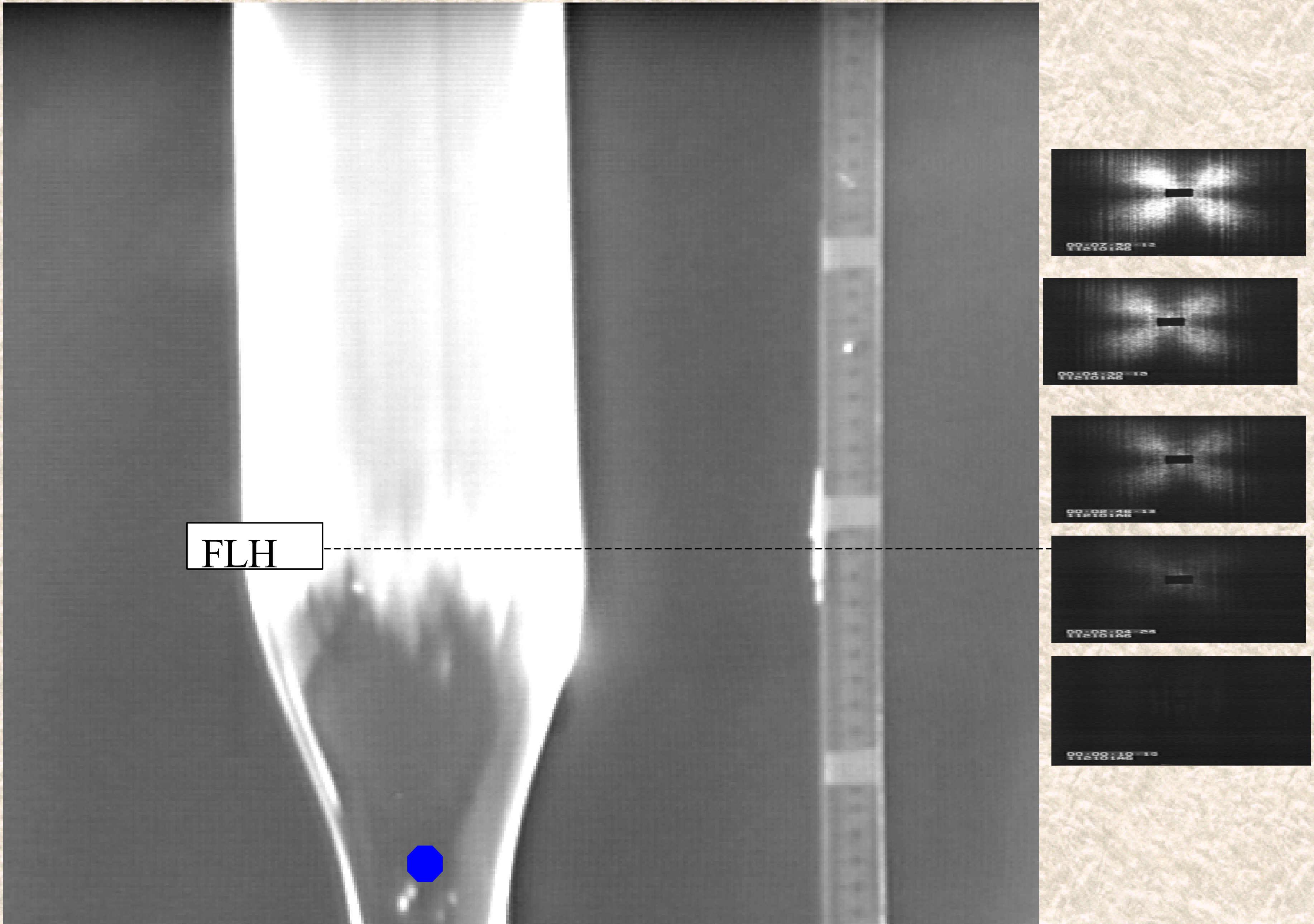
Fig. 4: Transmission spectra of several commercial plastics
(1 mil = 0.001 inches = 0.025 millimeters)

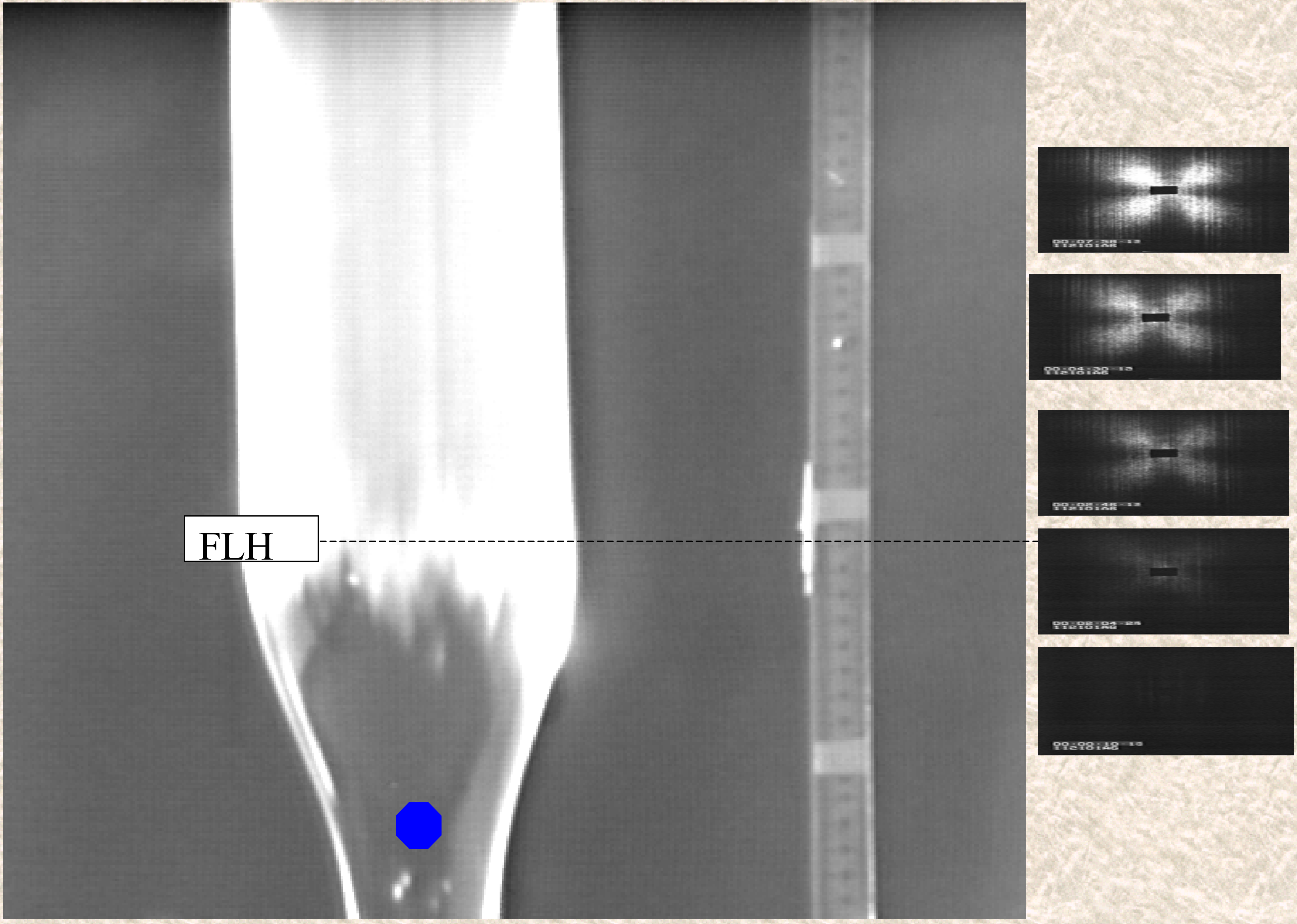


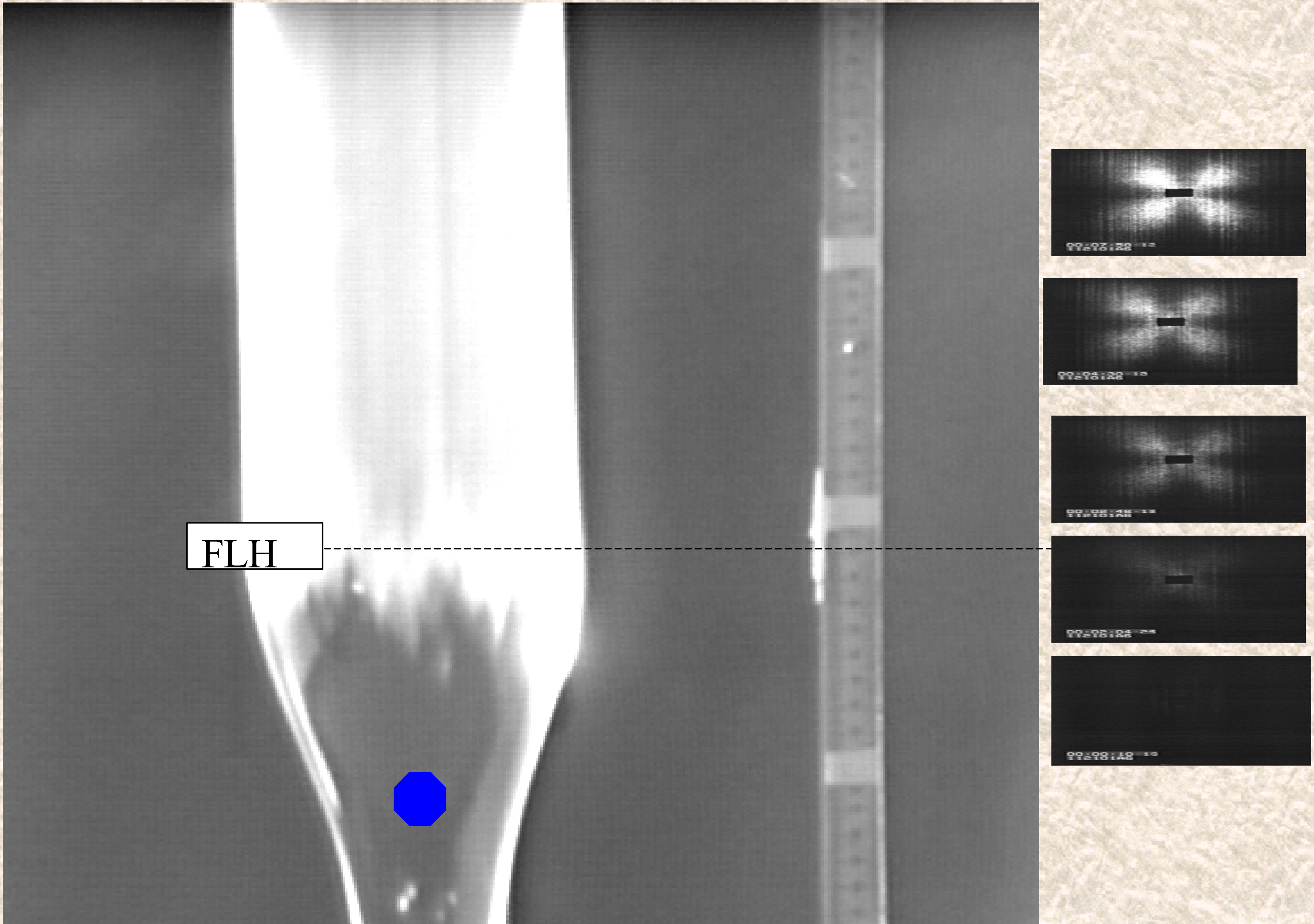
G. A. Campbell and T. A. Huang 1982

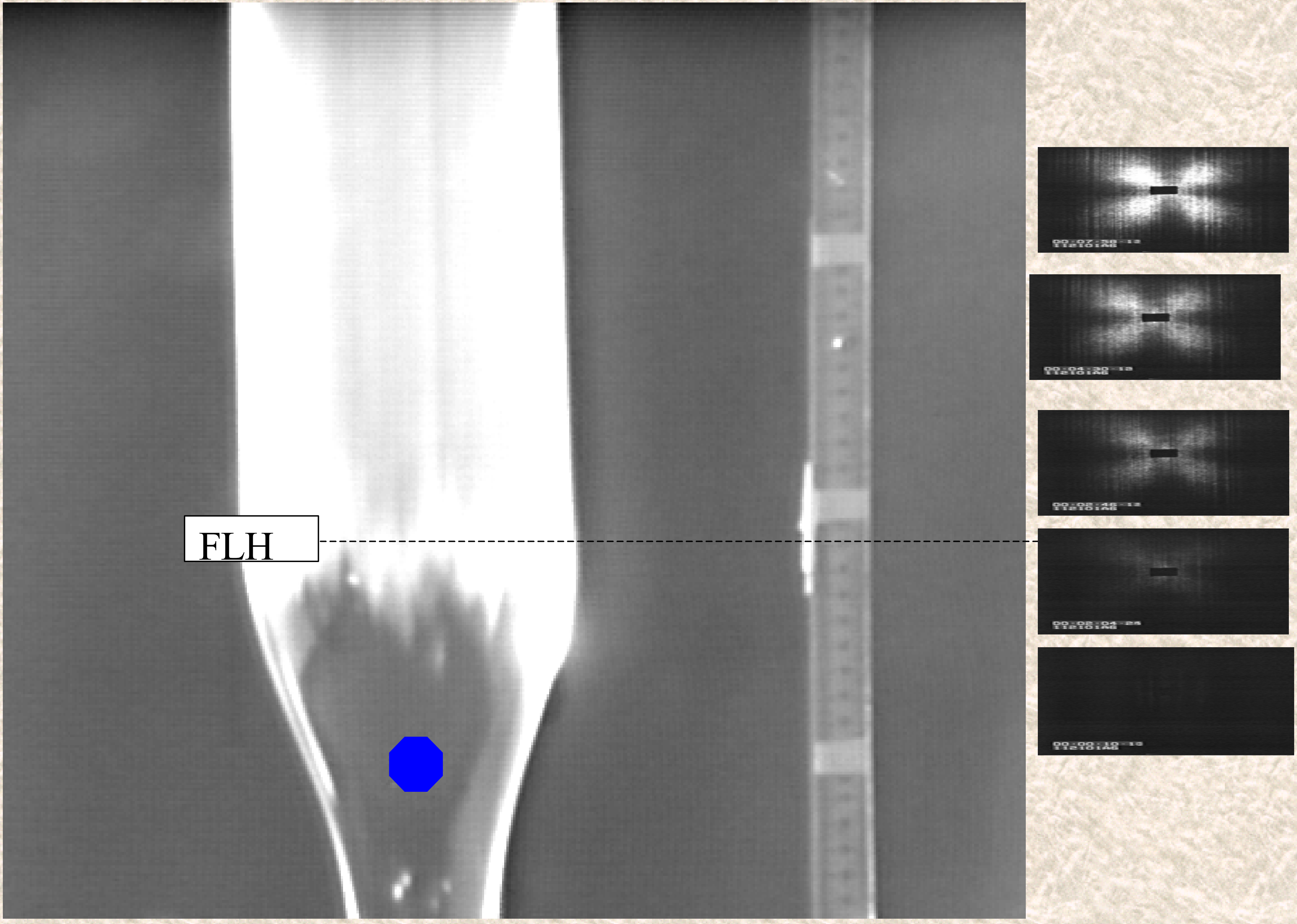

FLH

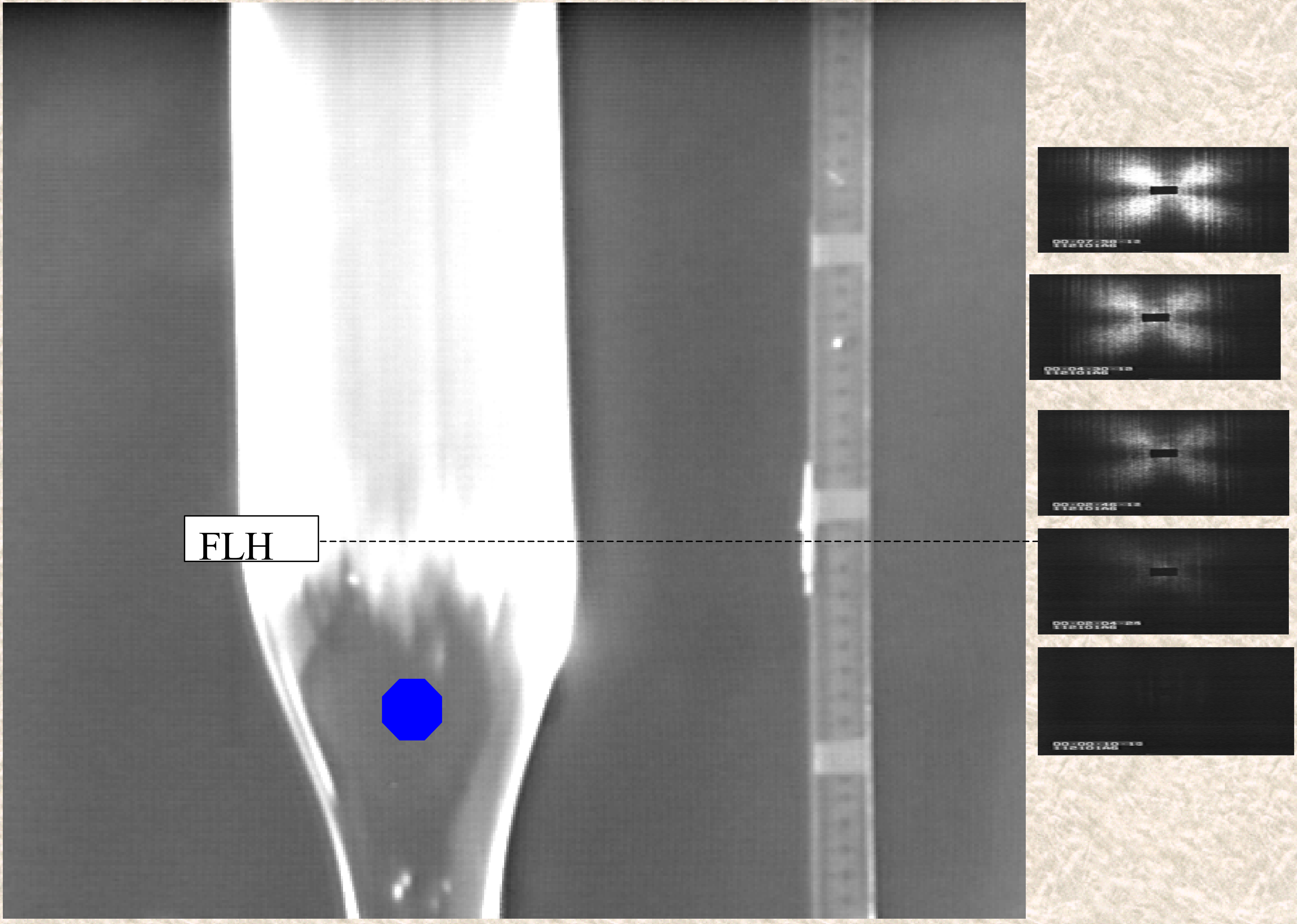

FLH

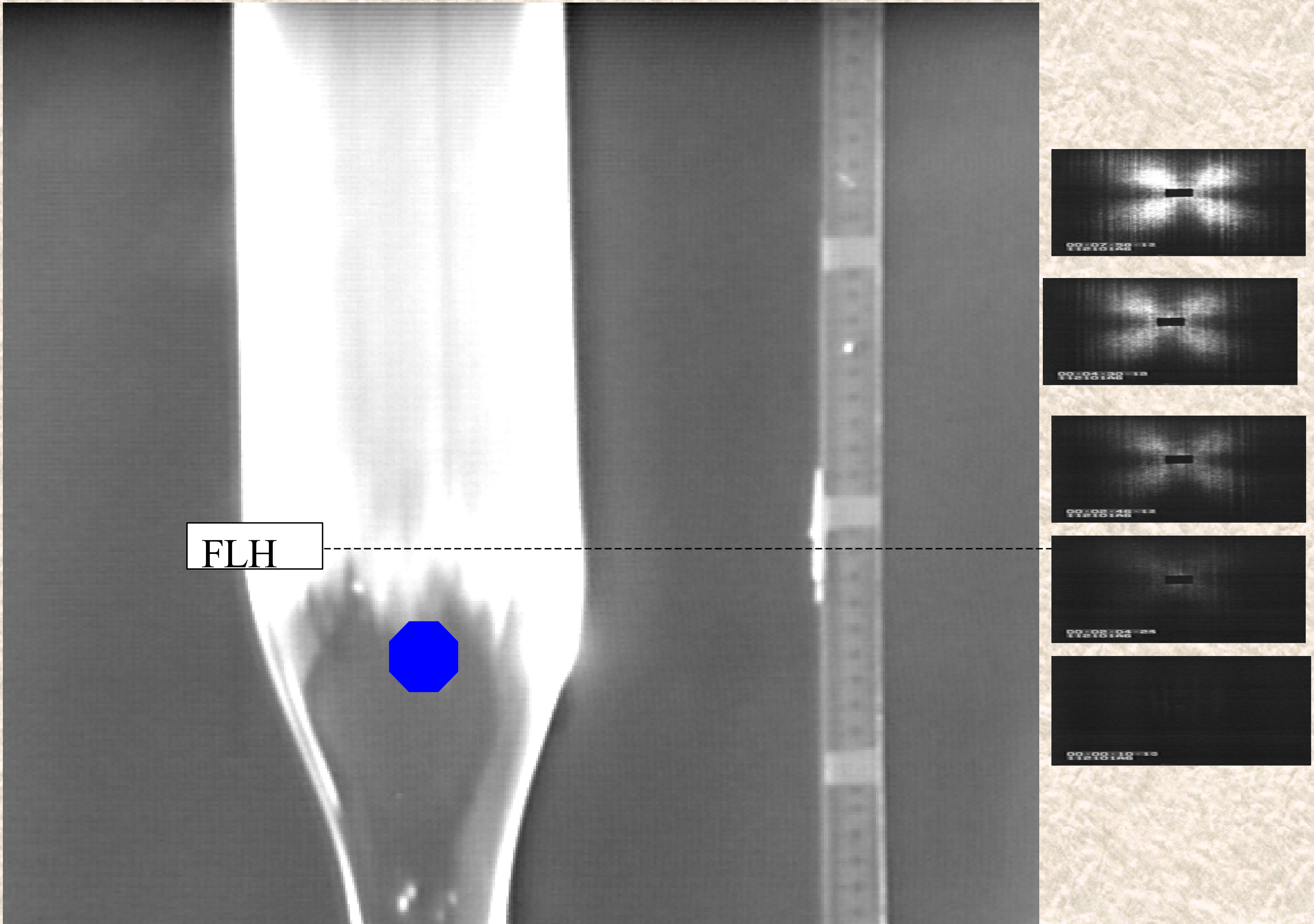

FLH

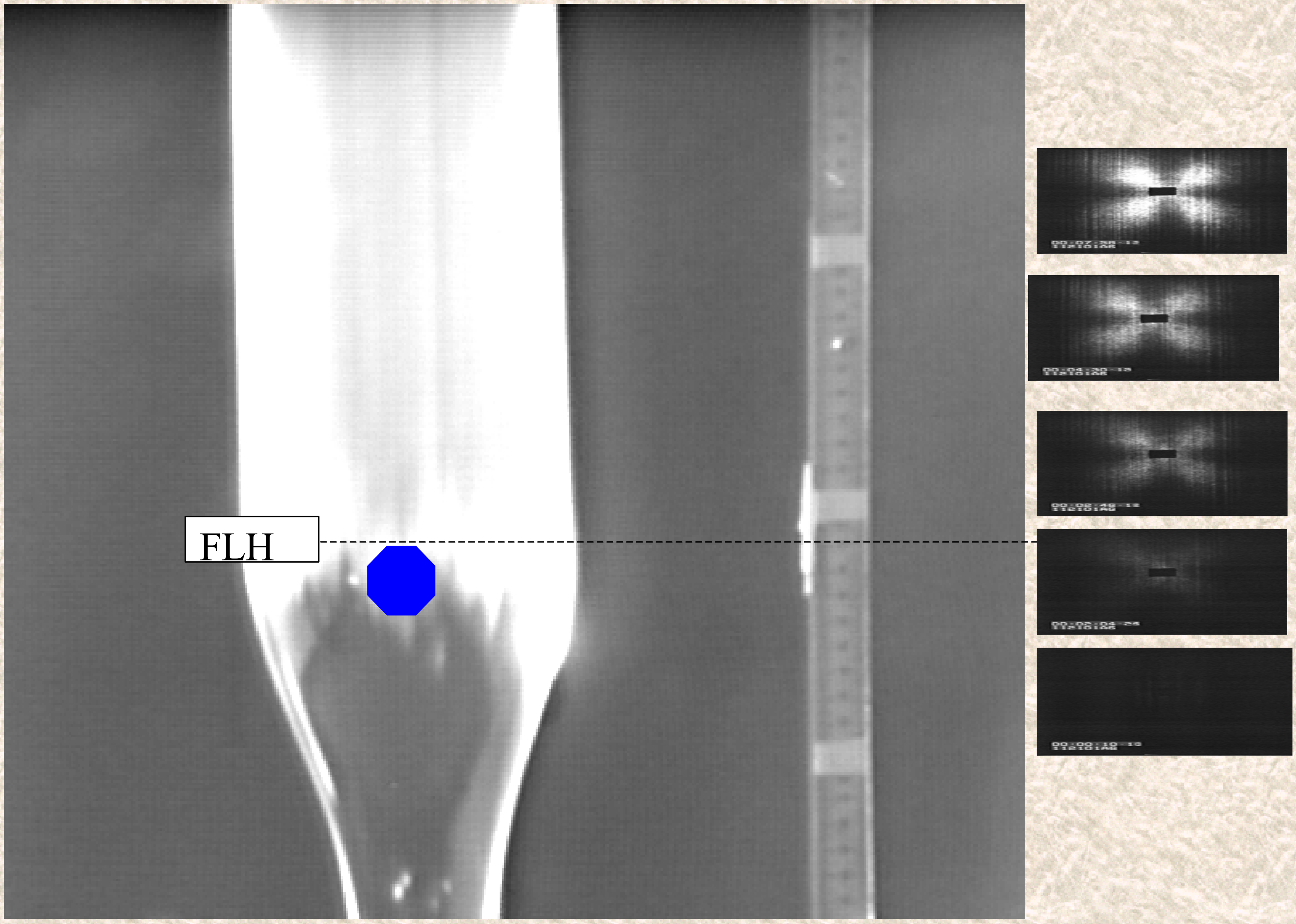

FLH

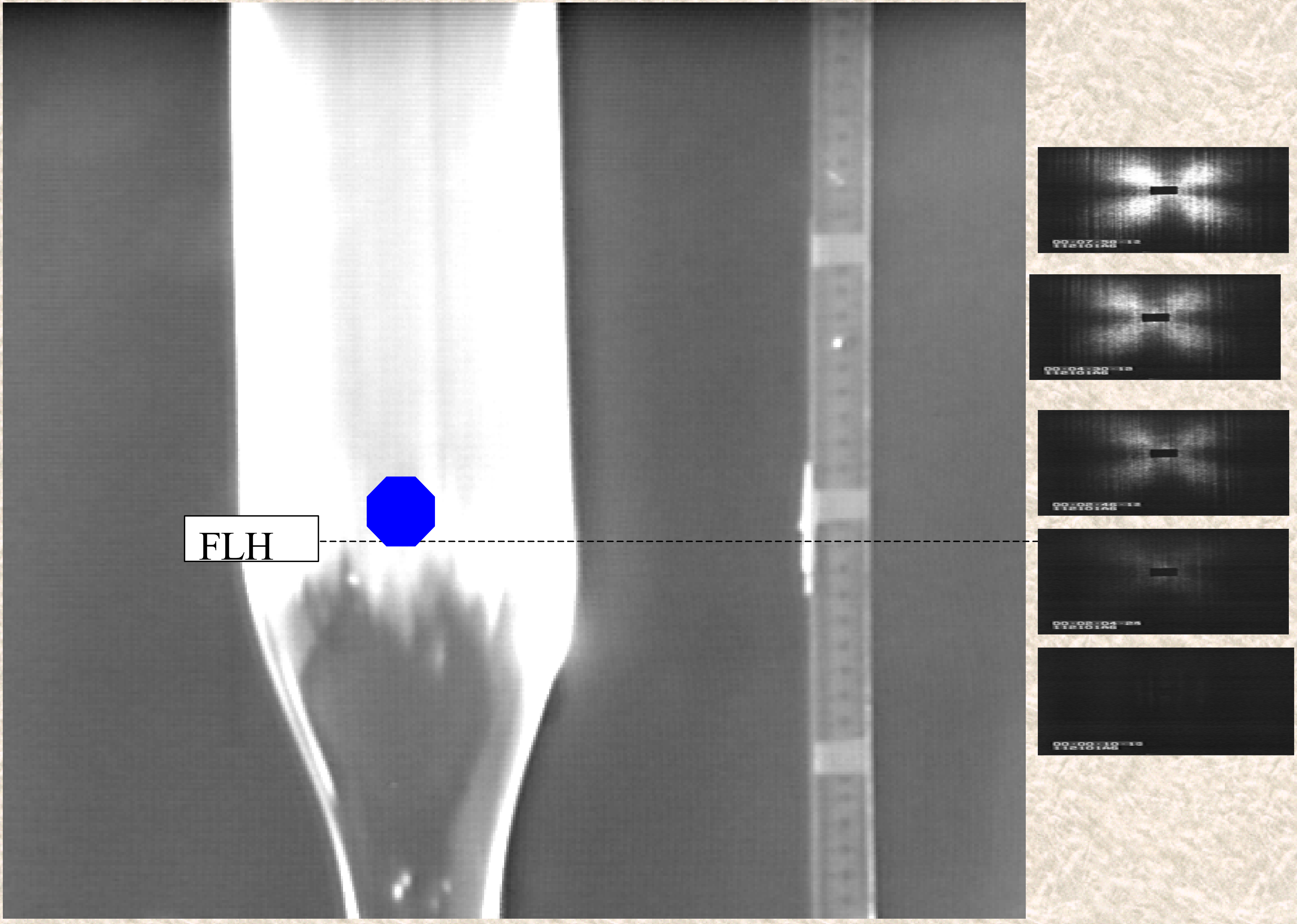

FLH

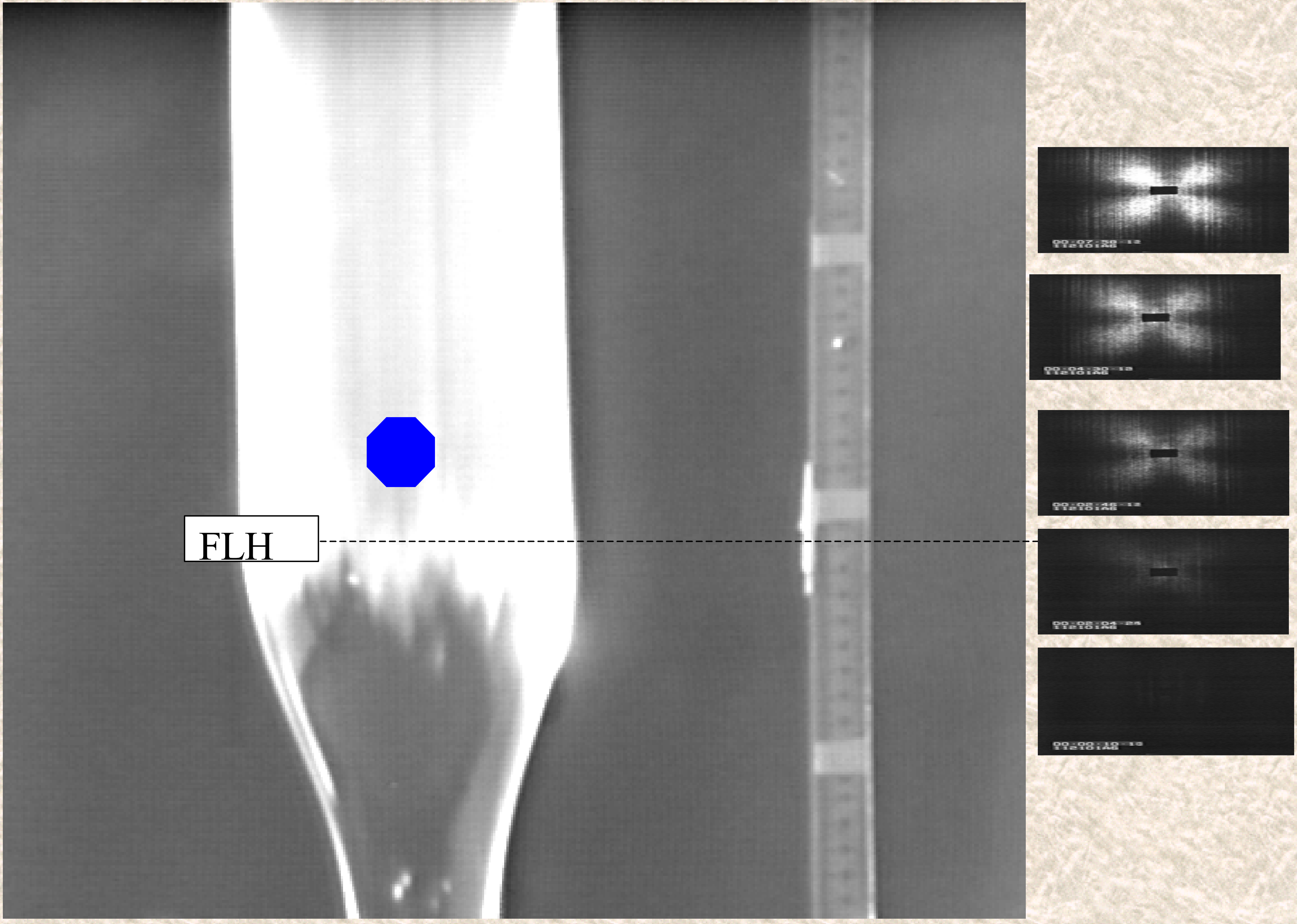

FLH

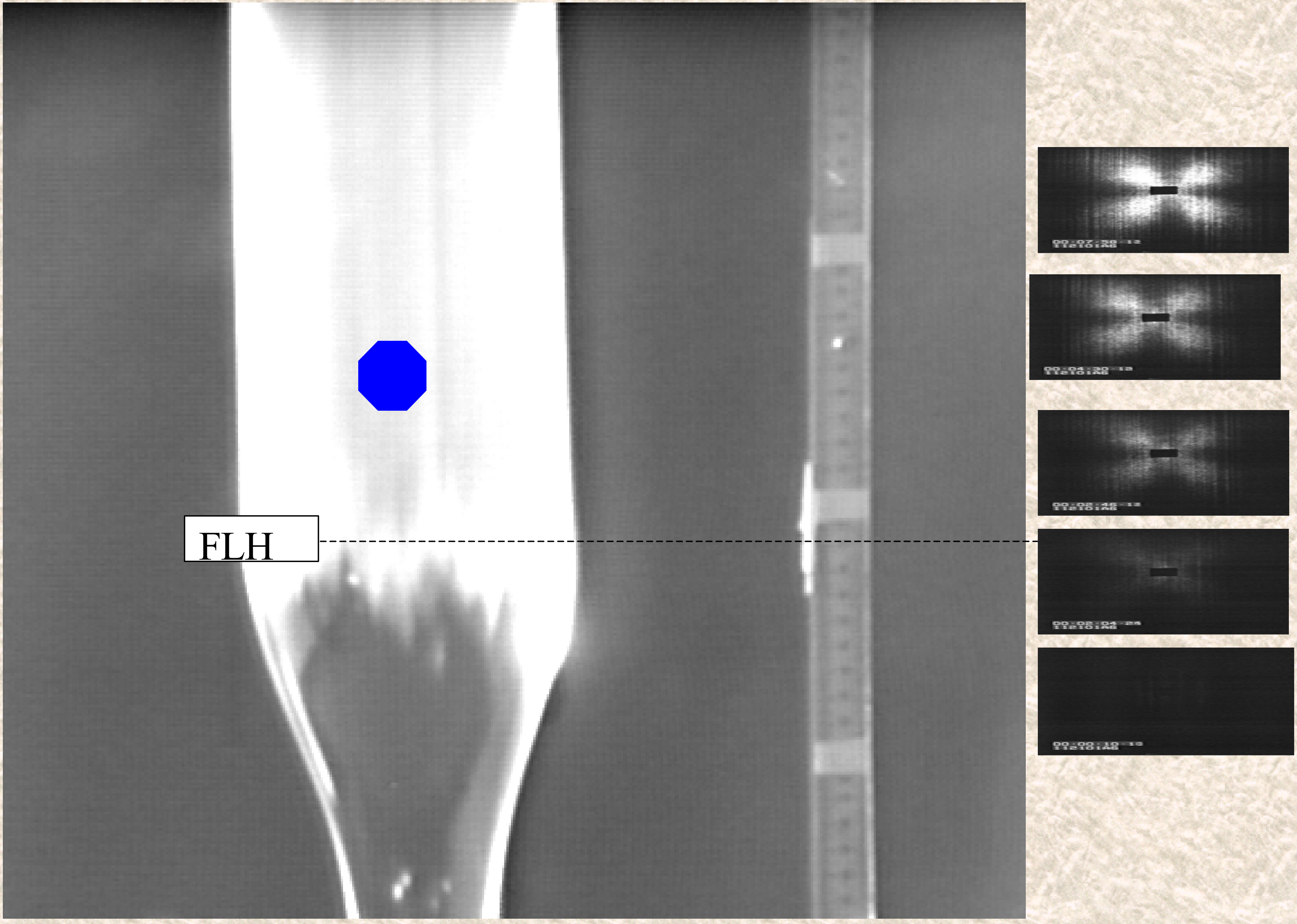

FLH

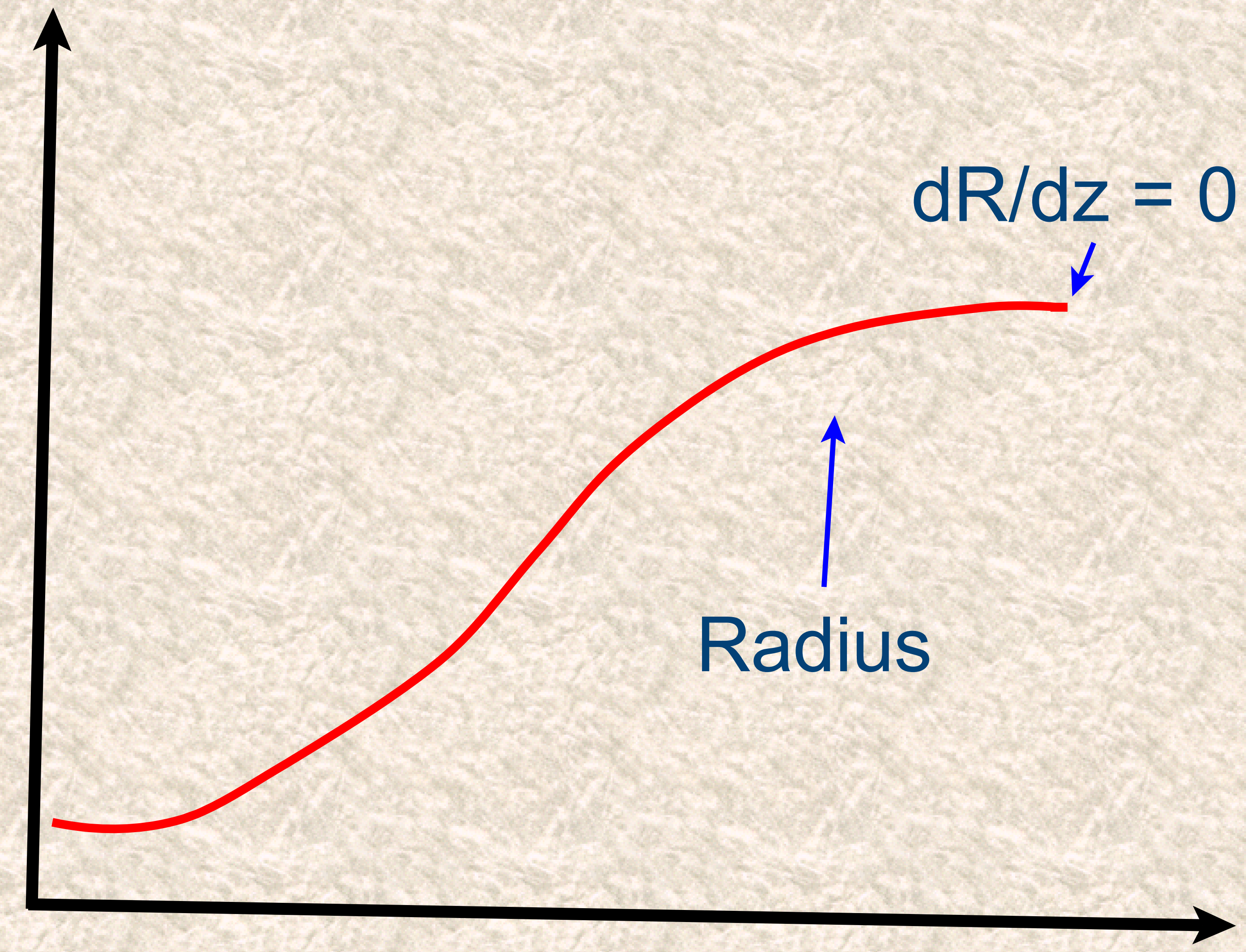

FLH

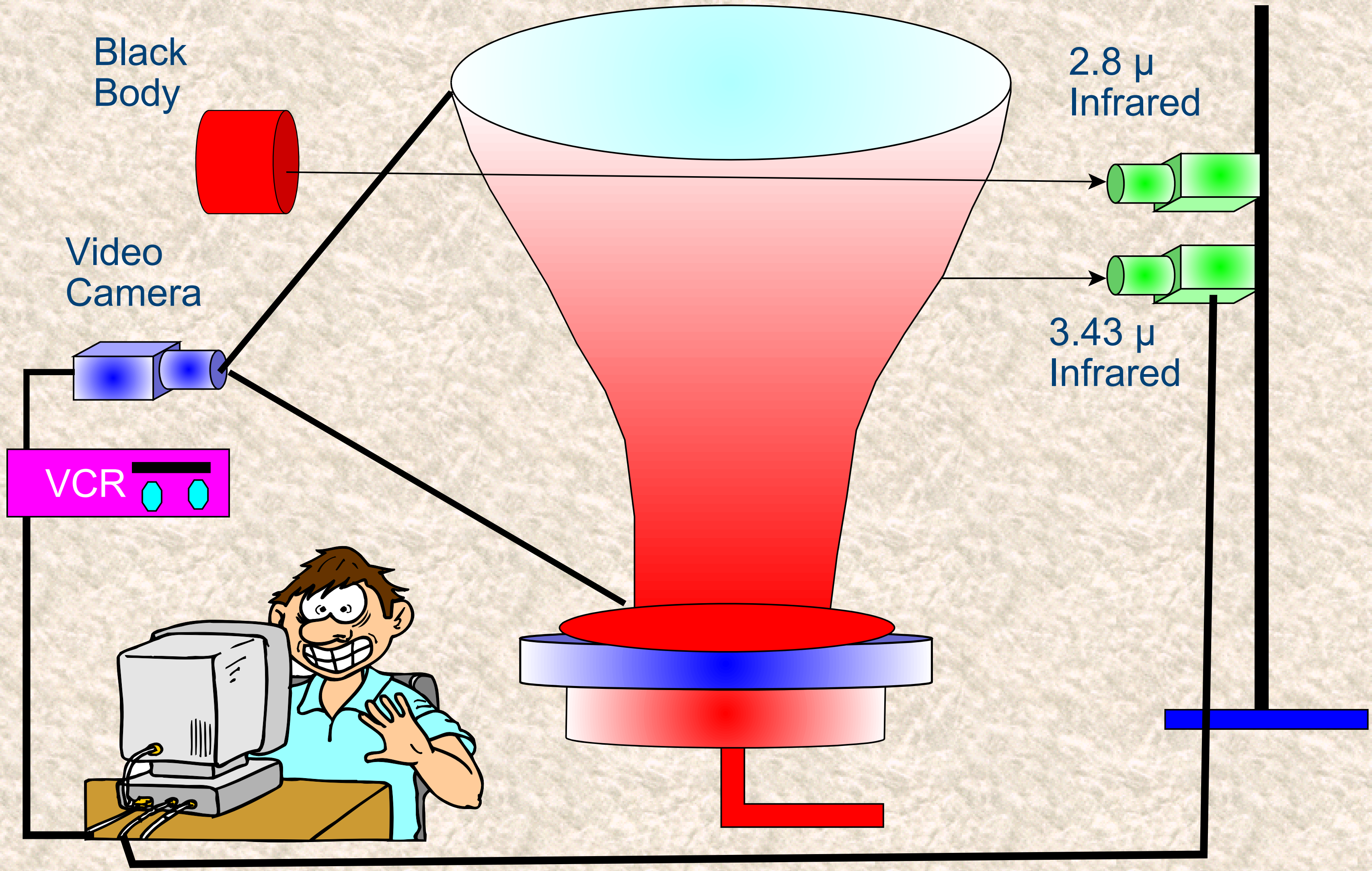

FLH


FLH

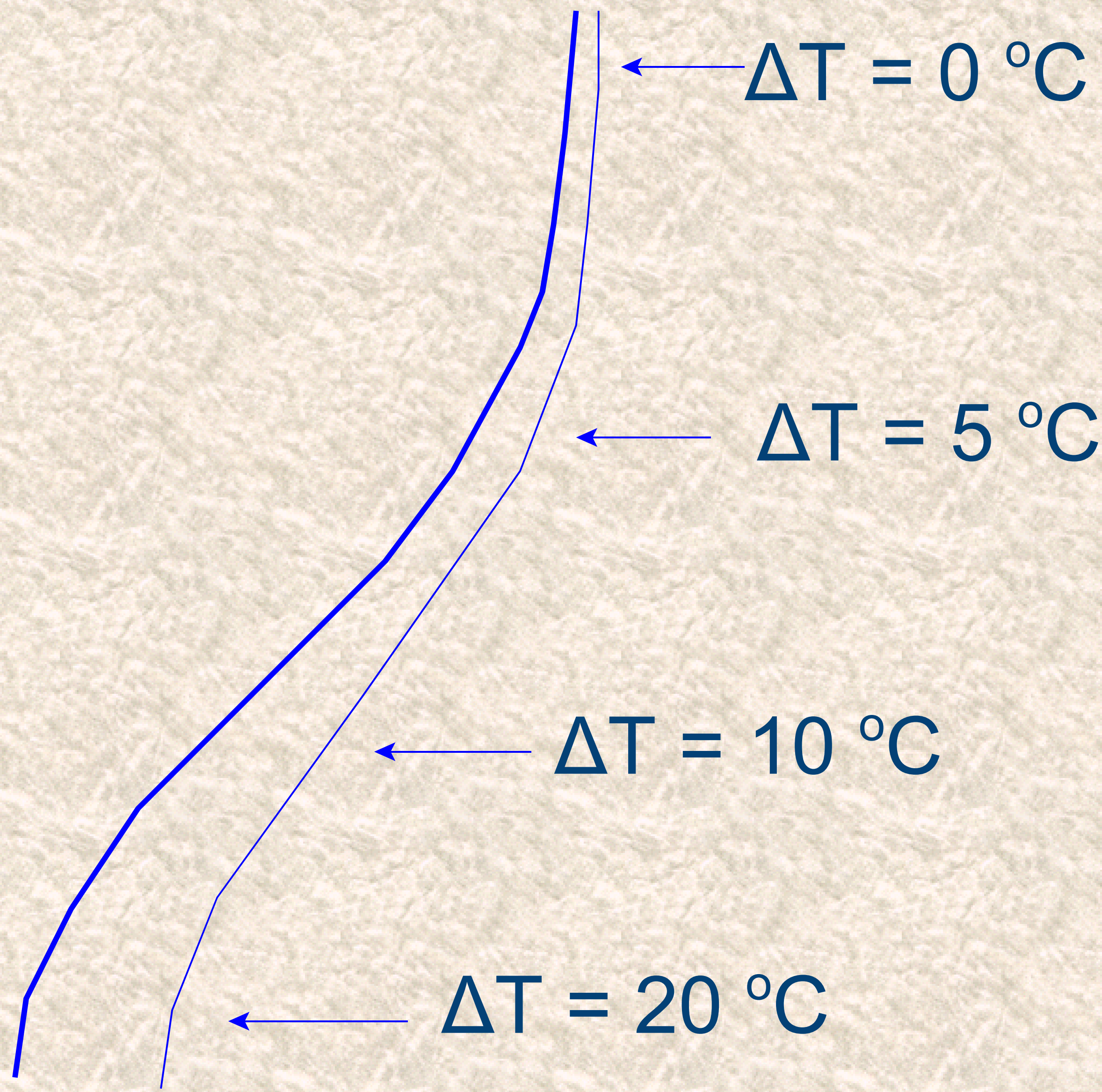

FLH


FLH


dR/dz = 0
Radius



G. A. Campbell and Banshu Cao 1990


ΔT = 0 °C
ΔT = 5 °C
ΔT = 10 °C
ΔT = 20 °C

$$\dot{Q} = k\,(T_1 - T_2)$$