



UNIVERSITY OF ROME “LA SAPIENZA” NANOTECHNOLOGIES ENGINEERING

MICROPARTICLES CSD

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CRYSTAL SIZE DISTRIBUTION (CSD)

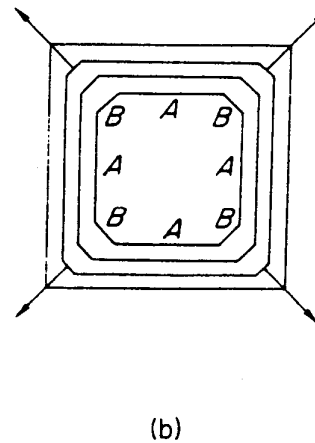
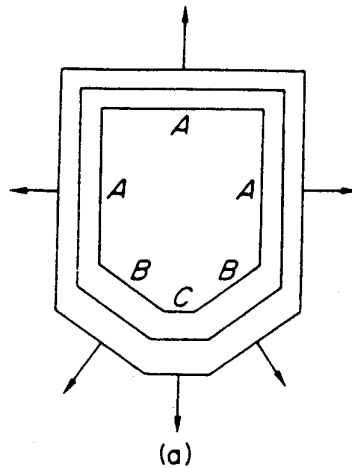
Essential for:

- performance of the process
- solid/liquid separation
- drying, storage, handling
- purity, caking, colour, etc.

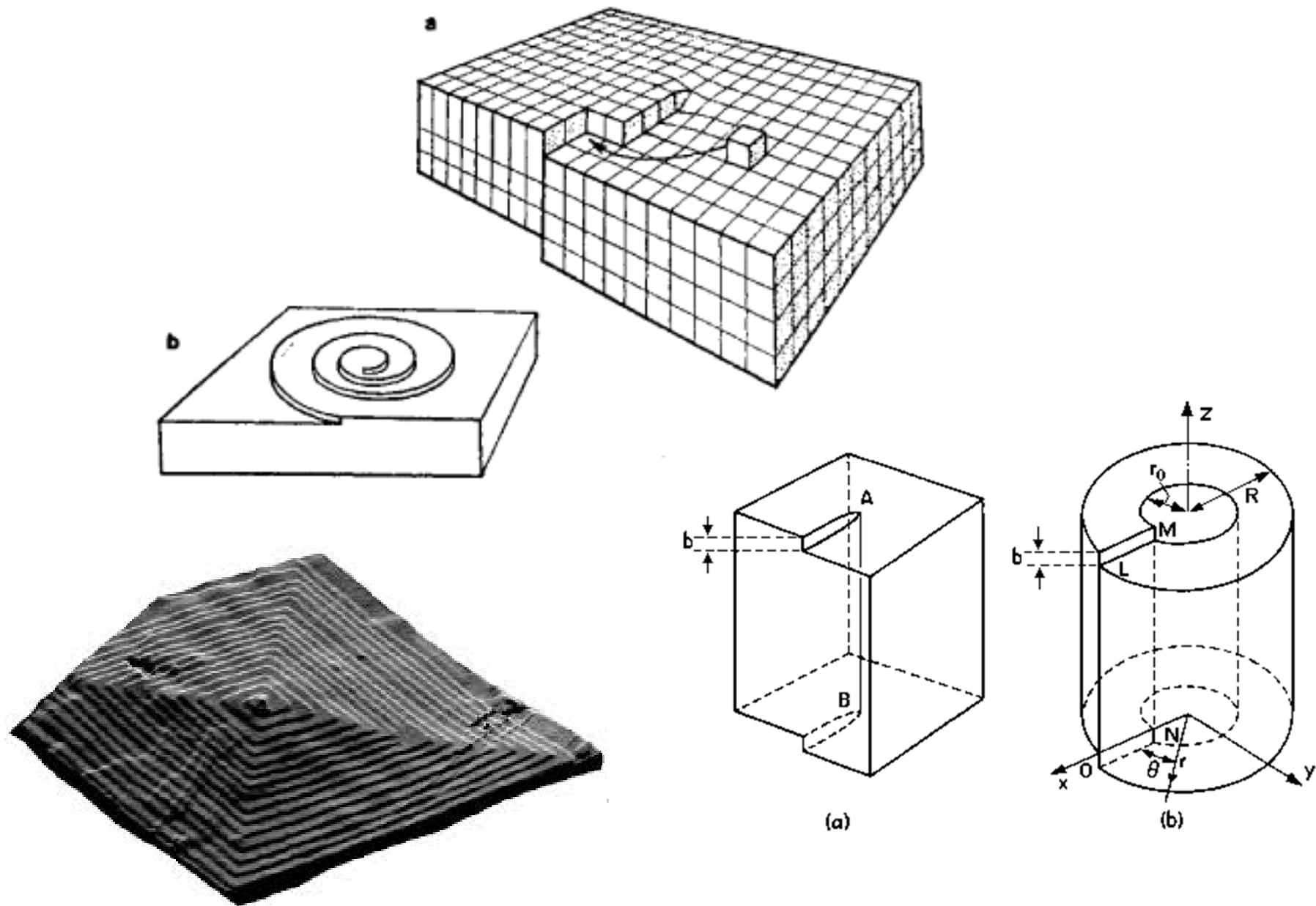
Dominant properties are average size L_{50}
and width of the CSD

HOW CRYSTALS GROWTH

- Crystals grow by the advance of the individual faces that are present in the crystal.
- A crystal does not always maintain geometric similarity during growth, faster growing faces are often eliminated.



HOW CRYSTALS GROW – SPIRAL GROWTH ON LINEAR DISLOCATION



CRYSTAL GROWTH RATE DEFINITIONS

There are three main ways of expressing the growth rate of a crystal or population of crystals:

- Faces growth rate, this is the velocity of advance of the crystallographic face (hkl), v expressed in m per second and measured perpendicular to the face:

$$v = \frac{ds}{dt}$$

- Linear growth rate, G which is defined as the time rate of change of a characteristic dimension, L , of the crystal. Usually the second dimension of the crystal is assumed as the characteristic one. Thus

$$G = \frac{dL}{dt}$$

CRYSTAL GROWTH RATE DEFINITIONS

- Overall mass growth rate, best expressed as the total mass flux to the crystal surface, R_G . Typical units of R_G would be $\text{kg m}^{-2} \text{ s}^{-1}$. This is the growth rate averaged over the whole crystal. For a crystal, mass M_C and surface area A_C it is given by:

$$R_G = \frac{1}{A_G} \frac{dM_C}{dt}$$

- The overall mass is useful for yield calculations and design purposes. G and R_G can be related as follows:

$$R_G = \frac{3\alpha\rho_C}{\beta} G$$

CRYSTAL GROWTH RATE KINETIC EXPRESSIONS

- Crystal growth rate expression is the relationship between the crystals growth rate and the solute supersaturation. Because of the many different ways of the expressing both of these variables there is a multiplicity of growth rate expressions.
- The simplest expression is an empirical relation between overall growth rate, expressed in terms of R_G and the overall concentration driving force. Thus

$$R_G = k_G (c - c^*)^m$$

where m is overall “order” of the growth process and R_G is the growth rate constant which will in general be a function of temperature, relative crystal/solution velocity and impurities within the system.

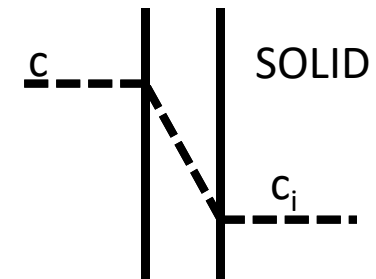
EFFECT OF MASS TRANSFER RESISTANCE ON CRYSTAL GROWTH RATE

- The mechanism of crystal growth from solution requires that solute be transported to the crystal surface and then oriented into the crystal lattice. Two successive steps are required, a diffusional step followed by a surface reaction step.
- The growth rate of the diffusion step can be represented by the simple mass transfer equation

- The rate of the integration step is in general expressed as

$$R_G = k_d A(c - c_i)$$

$$R_G = k_r (c_i - c^*)^\nu$$



- Both the diffusion and integration steps are temperature dependent according to the Arrhenius law

$$k_d = k_{d0} e^{-E_d/R_g T}$$

$$k_r = k_{r0} e^{-E_r/R_g T}$$

EFFECT OF TEMPERATURE ON CRYSTAL GROWTH

- In order to evaluate the activation energy of the overall growth rate the use of properly defined supersaturation is of great importance. In fact the absolute difference of concentration ($c - c^*$), usually assumed as the driving force, strongly depends on the temperature, as shown by the relationship:

$$c - c^* = \sigma \cdot c^*(T)$$

where $\sigma = c/c^*$ is the relative supersaturation.

- When the influence of temperature on the overall growth rate is investigated, the fundamental dimensionless driving force $\sigma_a = \ln(\sigma + 1)$ has to be concerned and the following rate expression for the overall growth rate is assumed

$$R_G = k_G \sigma_a^{g'}$$

Size dependent growth and growth rate dispersion

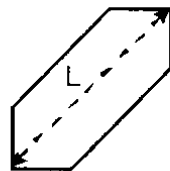
- A growth rate dispersion occurs for crystals also of the same size. The potential causes of this phenomenon are: the variation of dislocation density in the growth sectors and the variation of lattice strain within the crystal body.
- Crystals with a greater number of dislocations per unit area should grow faster, whereas submitted by a plastic deformation they grow very slowly. In particular, the fragments generated by collision of large crystals have a very low growth rate due to internal strain.
- In the light of the crystal growth dispersion it is also possible to explain the size growth dependency: the crystals exhibiting a higher growth rate become large because they have an inherent higher growth rate, thus a high growth rate is measured for larger crystals.
- The crystal growth dependency can be approximated by different growth rate expressions. One of the most popular expression is that one proposed by Abegg, Stevens and Larson (b and τ are fitting parameters):

$$G(L) = G_0 \left(1 + \frac{L}{G_0 \tau} \right)^b$$

DEFINITIONS OF CRYSTAL SIZE

<i>name</i>	<i>definition</i>
length	maximal visible length
sieve diameter	width of the minimum square aperture through which the particle will pass
volume diameter	diameter of a sphere having the same volume as the crystal
surface diameter	diameter of a sphere having the same surface area as the crystal
projected area diameter	diameter of a sphere having the same projected area as the crystal viewed from a fixed direction

Shape factors k_a and k_v



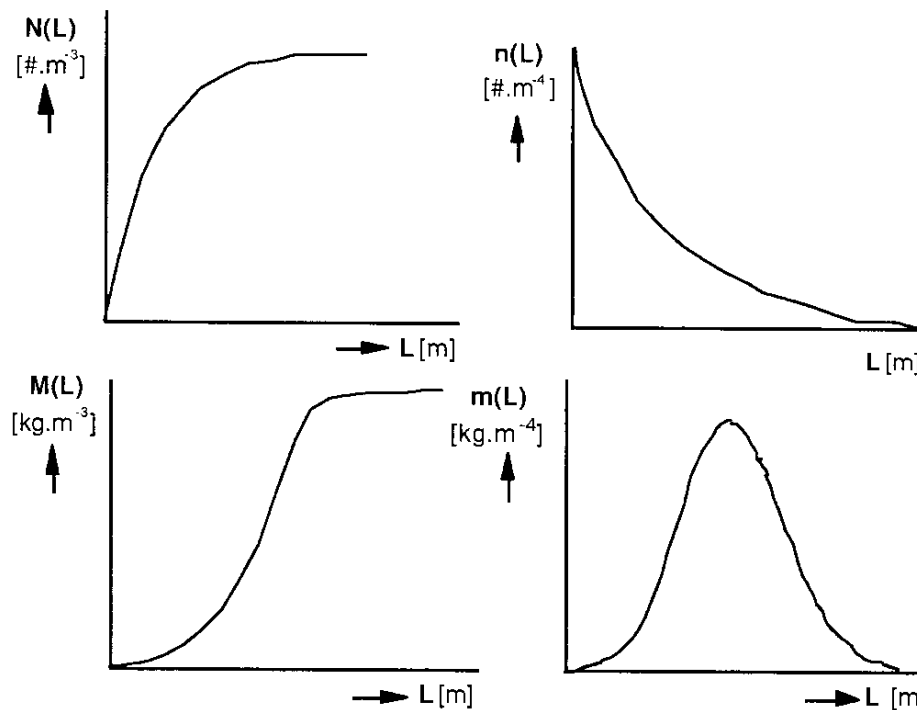
$$\text{crystal surface} = k_a L^2$$

$$\text{crystal volume} = k_v L^3$$

EXAMPLES OF SHAPE FACTORS

Geometric Shape	k_v	k_s
Sphere	0.524	3.142
Tetrahedron	0.118	1.732
Octahedron	0.471	3.464
Hexagonal prism	0.867	5.384
Cube	1.000	6.000
Needle 5 x 1 x 1	0.040	0.880
Plate 10 x 10 x 1	0.010	2.400

REPRESENTATIONS OF CSD



- the cumulative
oversize number
 $N(L)$ and mass
 $M(L)$ distribution
- the number
density $n(L)$ and
mass density
 $m(L)$ distribution

REPRESENTATIONS OF CSD

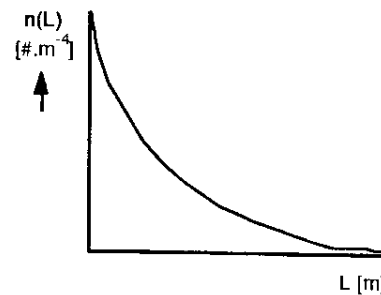
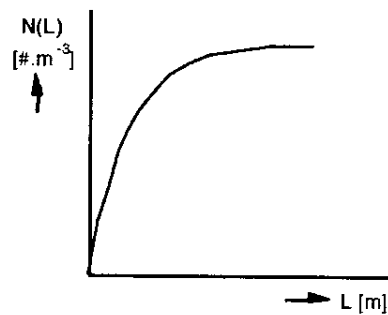
Cumulative oversize number distribution, $N(L)$

$$N(L) = \int_0^L n(L) dL \quad [\# / m^3]$$

$$N_T = \int_0^{\infty} n(L) dL$$

number (or population density distribution, $n(L)$

$$n(L) = \frac{dN(L)}{dL} \Big|_L \quad [\# / m \cdot m^3]$$



REPRESENTATIONS OF CSD

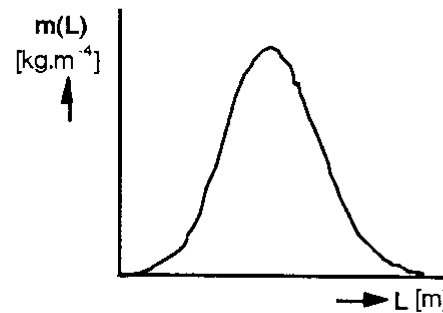
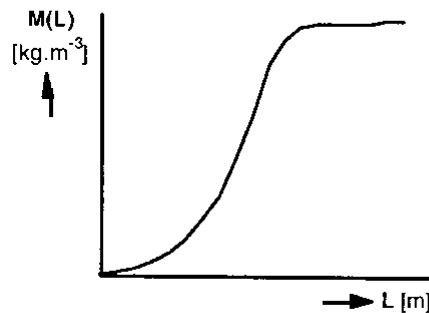
Cumulative oversize mass distribution $M(L)$

$$M(L) = \int_0^L m(L) dL = \rho k_v \int_0^L L^3 n(L) dL \quad [\text{kg} / \text{m}^3]$$

$$M_T = \int_0^{\infty} m(L) dL = \rho k_v \int_0^{\infty} L^3 n(L) dL$$

mass density distribution, $m(L)$

$$m(L) = \left. \frac{dM(L)}{dL} \right|_L \quad [\text{kg} / \text{m} \cdot \text{m}^3]$$



REPRESENTATIONS OF CSD

Moments of the CSD

$$m_j = \int_0^{\infty} L^j n(L) dL \quad [m^j / m^3]$$

total number	$N_T = m_0$
total length	$L_T = m_1$
total surface area	$A_T = k_a m_2$
total volume	$V_T = k_v m_3$
total mass	$M_T = \rho k_v m_3$

$$M_T = \rho_c k_v \int_0^{\infty} n(L) \cdot L^3 dL = \rho_c k_v \cdot m_3$$

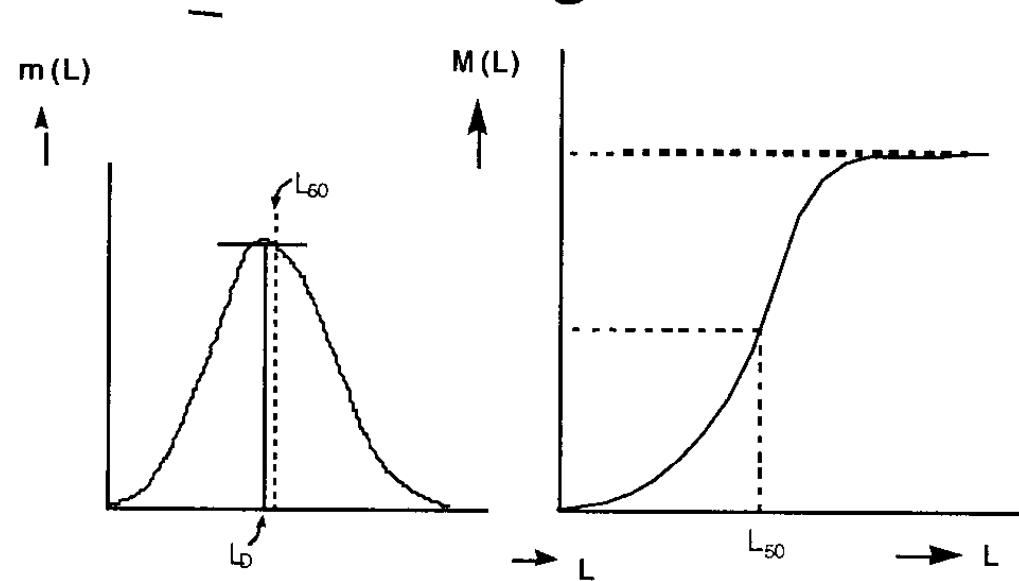
If $n = n_0 \cdot e^{-\frac{L}{\tau \cdot G}}$

$$M_T = 6 \cdot \rho_c k_v \cdot n_0 \cdot (G \cdot \tau)^4$$

**PARTICULAR CASE OF
THE POPULATION
BALANCE**
(see LESSON 02 PART 4)

REPRESENTATIONS OF CSD

Average size of the CSD



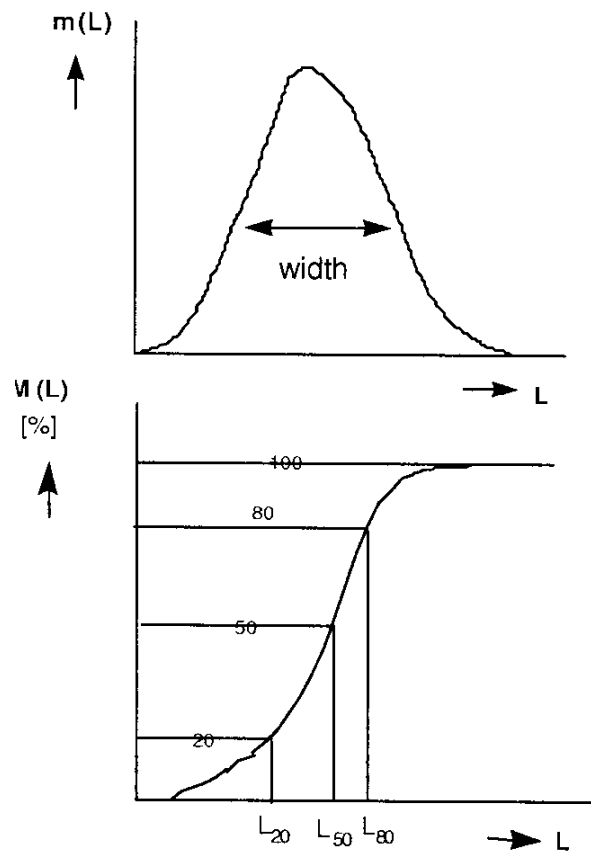
mode $L_D =$ maximum size of the $m(L)$ distribution

median size $L_m = L_{50}$ $\int_0^{L_{50}} \frac{n(L) L^3 dL}{m_3} = 0.5$

mean size $= \frac{m_4}{m_3}$

REPRESENTATIONS OF CSD

Width of the CSD



$$CV = \left[\frac{m_3 m_5}{m_4^2} - 1 \right]^{0.5}$$

$$CV = \frac{L_{80} - L_{20}}{2L_{50}}$$

or

$$CV = \ln \frac{L_{75}}{L_{25}}$$

quartile ratio

POPULATION DENSITY NUMBER

- In case of size measurement by sieving, it is possible to convert the sieving data to crystal population density by means of the equation:

$$n(L) = \frac{M(L)}{k_v \rho L^3 \Delta L}$$

where L is the average size with respect to the size of the two sieves, ΔL is the deviation between the size of the two sieves, $M(L)$ is the mass of crystals over the lower sieve, k_v is the volume shape factor and ρ is the crystal mass density.

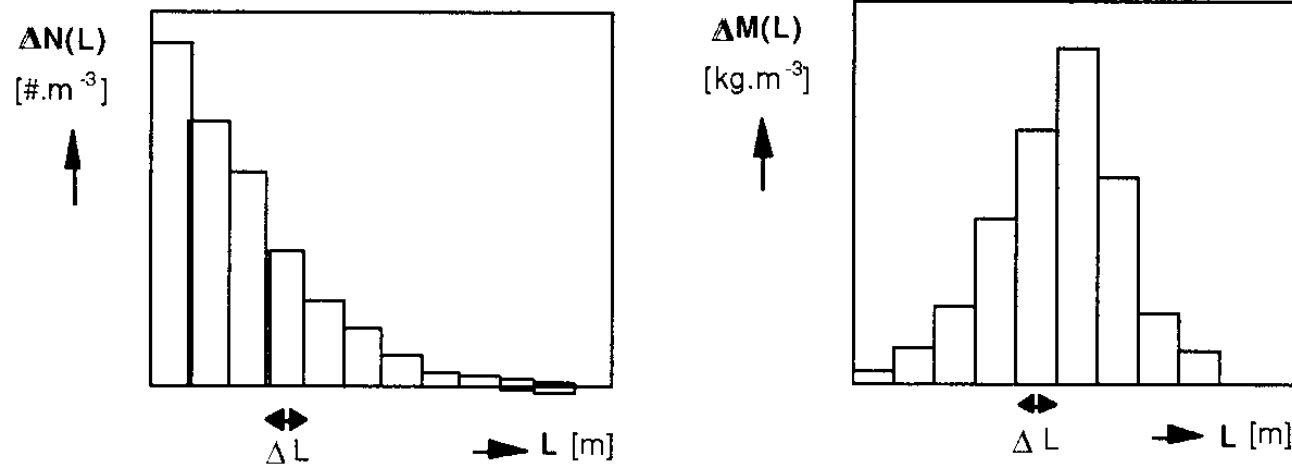
- $n(L)$ is expressed as $\# / l^4$ (with l in m, cm, mm, μm)

CUMULATIVE AND DENSITY VARIABLES

Cumulative Distribution			Density Distribution		
<i>Name</i>	<i>Symbol</i>	<i>Unit</i>	<i>Name</i>	<i>Symbol</i>	<i>Unit</i>
Number	N(L)	#/m ³ slurry	Population density	n(L)	#/m ³ slurry m
Volume	V(L)	m ³ crystal/m ³ slurry	Volume density	v(L)	m ³ /m ³ slurry m
Mass	M(L)	kg/m ³ slurry	Mass density	m(L)	kg/m ³ slurry m

REPRESENTATIONS OF CSD

Histograms



- Note: we measure $\Delta N(L)$ and use $n(L)$ in the population balance equation

DIRECT CHARACTERIZATION OF CSD

- The most easy way to characterize CSD is to use directly the mass fraction of crystals measured by sieving. The mass fraction of crystals of an average size equal to L can be calculated as:

$$x(L) = \frac{M(L)}{M_T}$$

- The size distribution may be characterized by two parameters: the mass mean size, L_{wm} and the coefficient of variation, that is:

$$L_{wm} = \sum_i x_i(L)L$$

and

$$CV = \frac{1}{L_{wm}} \sqrt{\frac{\sum_i (L_i - L_{wm})^2}{N-1}}$$