$$w_N = \frac{c_N}{c} \quad \left\{ \begin{array}{ll} c_N & \text{μάζα μορίων με βαθμό πολυμερισμού} \\ N & \text{στη μονάδα όγκου} \\ c & \text{συνολική συγκέντρωση μάζας} \end{array} \right.$$

k_{th} moment of number fraction distribution:

$$m_k \equiv \sum_N n_N M_N^k$$

$$k=0 \qquad m_0 = \sum_N n_N = 1$$

Αριθμητικό μέσο μοριακό βάρος (μάζα)

$$M_n \equiv \frac{m_1}{m_0} = \frac{\sum_N n_N M_N}{\sum_N n_N} = \sum_N n_N M_N$$

$$w_N = \frac{M_N}{M_n} n_N = \frac{N}{N_n} n_N$$

Αριθμητική πυκνότητα: $\frac{c N_{Av}}{M_n} \left(\frac{\#}{ml}\right) = \sum_N \frac{c_N N_{Av}}{M_N}$

$$M_n = \frac{c}{\sum_N c_N / M_N} = \frac{1}{\sum_N w_N / M_N}$$

Μέσο κατά βάρος: $M_w = \frac{m_2}{m_1} = \frac{\sum_N n_N M_N^2}{\sum_N n_N M_N}$

$$= \frac{\sum_N n_N M_N^2}{M_n} = \sum_N w_N M_N$$

$$= \sum_N \frac{c_N}{c} M_N$$

Πολυδιασπορά $\frac{M_w}{M_n}$

z-μέσον $$M_z = \frac{m_3}{m_2} = \frac{\sum_N n_N M_N^3}{\sum_N n_N M_N^2} = \frac{\sum_N w_N M_N^2}{\sum_N w_N M_N}$$

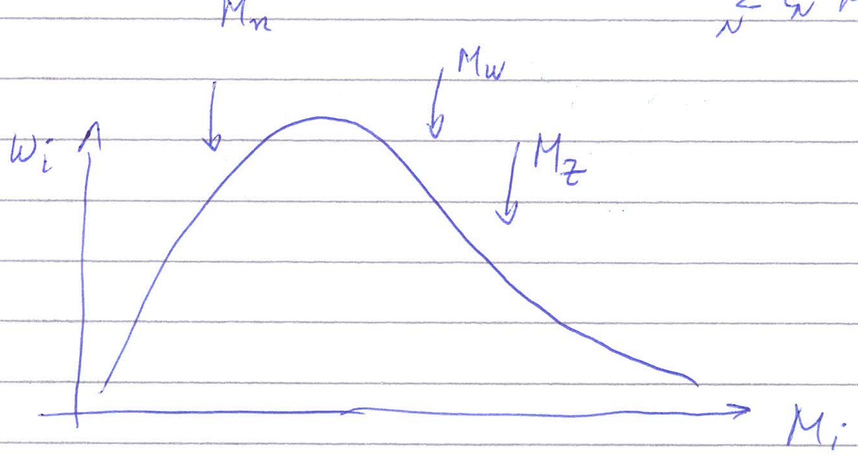
$$= \frac{\sum_N c_N M_N^2}{\sum_N c_N M_N}$$

(z+1) μέσον $$M_{z+1} = \frac{m_4}{m_3} = \frac{\sum_N n_N M_N^4}{\sum_N n_N M_N^3} = \frac{\sum_N w_N M_N^3}{\sum_N w_N M_N^2} = \frac{\sum_N c_N M_N^3}{\sum_N c_N M_N^2}$$

(z+k) μέσον $$M_{z+k} = \frac{m_{k+3}}{m_{k+2}} = \frac{\sum_N n_N M_N^{k+3}}{\sum_N n_N M_N^{k+2}} = \frac{\sum_N w_N M_N^{k+2}}{\sum_N w_N M_N^{k+1}}$$

$$= \frac{\sum_N c_N M_N^{k+2}}{\sum_N c_N M_N^{k+1}}$$

Κατανομή



Παράδειγμα 1   Μείγμα με κατά αριθμό κλάσμα $n_A = 1/2$ $M_A = 10^5$ g/mol
και $n_B = 1 - n_A = 1/2$ $M_B = 2\times 10^5$ g/mole. M_n? M_w?

$$M_n = m_1 = \sum_N n_N M_N = n_A M_A + n_B M_B = 1.5\times 10^5 \text{ g/mole}$$

$$m_2 = \sum_N n_N M_N^2 = n_A M_A^2 + n_B M_B^2$$

$$M_w = \frac{m_2}{m_1} = 1.67\times 10^5 \text{ g/mole}$$

$$\frac{M_w}{M_n} = \frac{10}{9} = 1.11$$

Παράδειγμα 2   Μείγμα με κατά βάρος κλάσμα $w_A = 1/2$ $M_A = 10^5$
και $w_B = 1/2$ $M_B = 2\times 10^5$.

$$M_n = \frac{1}{\sum_N w_N / M_N} = \frac{1}{\frac{w_A}{M_A} + \frac{w_B}{M_B}} = 1.33\times 10^5$$

$$M_w = \sum_N w_N M_N = w_A M_A + w_B M_B = 1.5\times 10^5$$

$$\frac{M_w}{M_n} = \frac{9}{8} > \frac{10}{9}$$

Μείγματα $\quad M_n = \frac{W}{N} = \frac{\sum_i w_i}{\sum_i N_i}$

i πολυδιάσπαρτο συστατικό ενός μείγματος

$$N_i = \frac{w_i}{\langle M_{n_i} \rangle}$$

$$\langle M_{n_i} \rangle_\mu = \frac{\sum_i w_i}{\sum_i \frac{w_i}{\langle M_{n_i} \rangle}}$$

$$\langle M_w \rangle = \frac{\sum w_x M_x}{W} = \frac{\sum_i \left(\sum_x w_x M_x \right)_i}{\sum_i w_i}$$

$$\langle M_{w_i} \rangle = \frac{\left(\sum_x w_x M_x \right)_i}{w_i}$$

$$\langle M_w \rangle_\mu = \frac{\sum_i \left(\langle M_w \rangle_i w_i \right)}{\sum_i w_i} = \sum_i \underbrace{\left(\frac{w_i}{\sum_i w_i} \right)}_{\text{κλάσμα βάρους}} \langle M_{w_i} \rangle$$

Μείγμα A, B $\quad \langle M_{n_A} \rangle = 10^5 \quad \langle M_{n_B} \rangle = 2 \times 10^5$

$\langle M_{w_A} \rangle = 2 \times 10^5 \quad \langle M_{w_B} \rangle = 4 \times 10^5$

$\langle M_n \rangle_\mu = 133600 \quad w_A = w_B = 1\,g$

$\langle M_w \rangle_\mu = 300000$

<u>Κατανομές</u>

$$n_N(p) = \frac{N}{N_n}\, n_N(p) = N p^{N-1}(1-p)^2$$

most probable $\quad w_N(p) = N p^{N-1}(1-p)^2 \simeq$

$w_N = \frac{N}{N_n} n_N \leftarrow$ $\quad n_N = \frac{(N_n-1)^{N-1}}{(N-1)!}\exp(1-N_n) \simeq \frac{N}{N_n^2}\exp(-N/N_n)$

Poisson $\quad \frac{N_w}{N_n} = 1 + \frac{1}{N_n} - \frac{1}{N_n^2} \qquad N_n \geq 10^3 \longrightarrow 1$

Schultz
Addition polymerization
w termination

$$w_N = \frac{1}{N_n \Gamma(s)}\left(\frac{sN}{N_n}\right)^s \exp\left(-\frac{sN}{N_n}\right)$$

$$\frac{N_w}{N_n} = \frac{s+1}{s}$$

$s=1 \longrightarrow$ most probable distribution $\frac{N_w}{N_n} = 2$

$s<1 \Rightarrow \frac{N_w}{N_n} > 2$

$s<1 \Rightarrow 1 < \frac{N_w}{N_n} < 2$

<u>Measure</u>

$\Pi V = nRT \qquad \lim \frac{\Pi}{c} = \frac{kT\, N_{Av}}{M} \qquad (R = kN_A)$

$$\Pi = RT\left(\frac{c}{M_n} + \sum\sum A_{ij} c_i c_j \cdots\right)$$

$$= RT\left(\frac{c}{M_n} + A_{2,w} c^2 + \cdots\right)$$

$$A_{2,w} = \frac{1}{c^2}\sum_i\sum_j A_{ij} c_i c_j$$

$$\frac{\Pi}{cRT} = \frac{1}{M_n} + A_{2,w} c + \cdots$$

Σκέδαση $\quad I = \frac{4\pi^2 n^2}{\lambda^4 r^2} \left(\frac{dn}{dc}\right)^2 \frac{cM}{N_A} I_i$

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} + 2A_{2,2}\,c + \dots$$

$$\eta = \eta_s \left(1 + [\eta]c + k_H [\eta]^2 c^2 + \dots\right)$$

$$[\eta] = \frac{1}{c^*} \sim \frac{V}{M} \simeq \frac{R^3}{M}$$

Fox-Flory $\quad [\eta]M \sim M \sim R^3$

Mark-Houwink $\quad [\eta] = kM^a \quad a = \frac{3}{D} - 1$

Huggins $\quad \frac{\eta - \eta_s}{\eta_s c} = [\eta] + k_H [\eta]^2 c + \dots$

Κατανομές $M_N = mN$

x-μερές $M_x = mx$

$M_{n_x} = m x_n$ μέσο κατά αριθμό

$M_{w_x} = m x_w$ —″— βάρος

$$x_n = \frac{\sum n_x x}{\sum n_x} = \sum\left(\frac{n_x}{N}\right)x$$

βαθμός πολυμερισμού

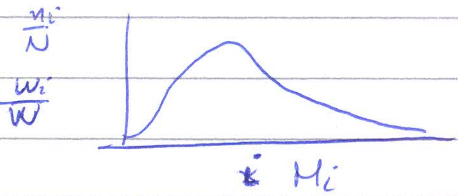
αριθμός moles, ~~βαθμός πολυμερισμού~~ του x-μερούς

$\left\{ \frac{n_x}{N} \right.$ κλάσμα moles ~~x~~-μερούς $\left. \right\}$

$$x_w = \frac{\sum n_x x^2}{\sum n_x x} = \sum\left(\frac{w_x}{W}\right)x \qquad \left(M_n = \frac{W}{N}\right)$$

Κατανομή: $$\boxed{x_n = \int_0^\infty \left(\frac{n}{N}\right) x\,dx}$$ Συνεχής γραμμή

$$\int_0^\infty \left(\frac{n}{N}\right) dx = 1$$



$$M_w = \frac{\int_0^\infty n M^2 dM}{\int_0^\infty n M dM} = \frac{\int_0^\infty \left(\frac{n}{N}\right) M^2 dM}{\int_0^\infty \left(\frac{n}{N}\right) M dM}$$

$$M_w = m x_w \quad \text{και} \quad x_w = \frac{\int_0^\infty \left(\frac{n}{N}\right) x^2 dx}{\int_0^\infty \left(\frac{n}{N}\right) x\,dx} = \frac{1}{x_n}\int_0^\infty \left(\frac{n}{N}\right) x^2 dx$$

$$M_n = \frac{\int_0^\infty n M dM}{\int_0^\infty n\,dM} = \frac{\int_0^\infty w\,dM}{\int_0^\infty \left(\frac{w}{M}\right) dM} = \frac{\int_0^\infty \left(\frac{w}{W}\right) dM}{\int_0^\infty \left(\frac{1}{M}\right)\left(\frac{w}{W}\right) dM}$$

$$x_n = \frac{\int_0^\infty \left(\frac{w}{W}\right) dx}{\int_0^\infty \left(\frac{1}{x}\right)\left(\frac{w}{W}\right) dx}$$

$$M_w = \frac{\int_0^\infty n M^2 dM}{\int_0^\infty n M dM} = \frac{\int_0^\infty (nM) M dM}{\int_0^\infty (nM) dM} = \frac{\int_0^\infty w M dM}{\int_0^\infty w\,dM} = \frac{\int_0^\infty \left(\frac{w}{W}\right) M dM}{\int_0^\infty \left(\frac{w}{W}\right) dM}$$

$$\boxed{x_w = \int_0^\infty \left(\frac{w}{W}\right) x\,dx} \qquad \int_0^\infty \left(\frac{w}{W}\right) dx = 1 \qquad \left(\frac{w}{W}\right) = \frac{M}{M_n}\frac{n}{N} = \frac{x}{x_n}\frac{n}{N}$$