Molecular weight and molecular weight distribution.

In a polymer sample the chains hardly ever have the same length. They have an average length.

Exceptions are for example proteins.
Number average molecular weight.

Mole fraction \( n_i = \frac{\text{Number of chains with length } i}{\text{Total number of chains}} = \frac{N_i}{\sum N_i} \)

\( \sum n_i = 1 \)

\[
\overline{M_n} = \frac{\sum N_i \cdot M_i}{\sum N_i} = \sum \left( \frac{N_i}{\sum N_i} \right) \cdot M_i = \sum n_i \cdot M_i
\]
Weight average molecular weight.

Weight fraction \( w_i \) = \( \frac{\text{Weight of chains with length } i}{\text{Total weight of all chains}} \) = \( \frac{n_i \cdot M_i}{\sum n_i \cdot M_i} \) = \( \frac{n_i \cdot M_i}{M_n} \)

\[ \sum w_i = 1 \]

\[ \overline{M}_w = \sum w_i \cdot M_i = \frac{\sum n_i \cdot M_i^2}{\sum n_i \cdot M_i} \]

Compare: \( \sum n_i \cdot M_i = \frac{\sum N_i \cdot M_i}{\sum N_i} \)
An example:

<table>
<thead>
<tr>
<th>City</th>
<th>Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amsterdam</td>
<td>1,000,000</td>
</tr>
<tr>
<td>Groningen</td>
<td>200,000</td>
</tr>
<tr>
<td>Schiermonnikoog</td>
<td>1,000</td>
</tr>
</tbody>
</table>

Average population:

\[
\frac{1}{3} \times 1,000,000 \quad \frac{1}{3} \times 200,000 \\
\frac{1}{3} = 400,333
\]

We can say that the average person lives in a city of about 400,000.
An example:

*Weighted average:* This is an average that would account for the fact that a large city like Amsterdam holds a larger percentage of the total population of the three cities than Schiermonnikoog.

<table>
<thead>
<tr>
<th>City</th>
<th>Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amsterdam</td>
<td>1,000,000</td>
</tr>
<tr>
<td>Groningen</td>
<td>200,000</td>
</tr>
</tbody>
</table>

\[
\left(\frac{1,000,000}{1,201,000}\right) \times 1,000,000 = 1,000,000 \times 0.8326 = 832,600
\]
\[
\left(\frac{200,000}{1,201,000}\right) \times 200,000 = 200,000 \times 0.1665 = \underline{33,300}
\]
\[
\left(\frac{1,000}{1,201,000}\right) \times 1,000 = 1,000 \times 0.0008 = \underline{0.8}
\]

\[
M_w = \sum w_i \cdot M_i
\]

We can say that the average person lives in a city of about 866,000.
Calculating $M_n$ & $M_w$.

\[
M_1 = 100 \\
M_2 = 10
\]

\[
n_1 = \frac{1}{2} \\
n_2 = \frac{1}{2}
\]

\[
\bar{M}_n = \sum n_i \cdot M_i = \frac{1}{2} \cdot 100 + \frac{1}{2} \cdot 10 = 50 + 5 = 55
\]

\[
w_1 = \frac{n_1 \cdot M_1}{\bar{M}_n} = \frac{\frac{1}{2} \cdot 100}{55} = \frac{10}{11}
\]

\[
w_2 = \frac{n_2 \cdot M_2}{\bar{M}_n} = \frac{\frac{1}{2} \cdot 10}{55} = \frac{1}{11}
\]

\[
\bar{M}_w = \sum w_i \cdot M_i = \frac{10}{11} \cdot 100 + \frac{1}{11} \cdot 10 = 90.9 + 0.9 = 91.8
\]
Calculating $M_n$ & $M_w$.

$n_1 = 1/11$
$n_2 = 10/11$

$$
\bar{M}_n = \sum n_i \cdot M_i = \frac{1}{11} \cdot 100 + \frac{10}{11} \cdot 10 = 18.2
$$

$$
w_1 = \frac{n_1 \cdot M_1}{\bar{M}_n} = \frac{1/11 \cdot 100}{18.2} = \frac{1}{2}
$$

$$
w_2 = \frac{n_2 \cdot M_2}{\bar{M}_n} = \frac{10/11 \cdot 10}{18.2} = \frac{1}{2}
$$

$$
\bar{M}_w = \sum w_i \cdot M_i = \frac{1}{2} \cdot 100 + \frac{1}{2} \cdot 10 = 50 + 5 = 55
$$
\[ \bar{M}_n = \sum n_i \cdot M_i = \frac{\sum N_i \cdot M_i}{\sum N_i} \]

\[ w_i = \frac{n_i \cdot M_i}{\sum n_i \cdot M_i} = \frac{n_i \cdot M_i}{\bar{M}_n} \]

\[ \bar{M}_w = \sum w_i \cdot M_i = \frac{\sum n_i \cdot M_i^2}{\sum n_i \cdot M_i} \]

\[ z_i = \frac{w_i \cdot M_i}{\sum w_i \cdot M_i} = \frac{w_i \cdot M_i}{\bar{M}_w} \]

\[ \bar{M}_z = \sum z_i \cdot M_i = \frac{\sum n_i \cdot M_i^3}{\sum n_i \cdot M_i^2} \]

\[ M_1 = 100 \]
\[ M_2 = 10 \]

\[ n_1 = 1/11 \quad n_2 = 10/11 \]

\[ \bar{M}_n = \sum n_i \cdot M_i = 1/11 \cdot 100 + 10/11 \cdot 10 = 18.2 \]

\[ w_1 = \frac{n_1 \cdot M_1}{M_n} = 1/11 \cdot 100 / 18.2 = \frac{1}{2} \]

\[ w_2 = \frac{n_2 \cdot M_2}{M_n} = 10/11 \cdot 10 / 18.2 = \frac{1}{2} \]

\[ \bar{M}_w = \sum w_i \cdot M_i = \frac{1}{2} \cdot 100 + \frac{1}{2} \cdot 10 = 50 + 5 = 55 \]

\[ z_1 = \frac{w_1 \cdot M_1}{M_w} = \frac{1}{2} \cdot 100 / 55 = \frac{10}{11} \]

\[ z_2 = \frac{w_2 \cdot M_2}{M_w} = \frac{1}{2} \cdot 10 / 55 = \frac{1}{11} \]

\[ \bar{M}_z = \sum z_i \cdot M_i = 10/11 \cdot 100 + 1/11 \cdot 10 = 91.8 \]
Schulz-Flory distribution:

• Chain growth and chain transfer independent of chain length

\[
\frac{[C_{(n+1)}]}{[C_{(n)}]} = \text{const} = \frac{\nu_{\text{prop}}}{(\nu_{\text{prop}} + \nu_{\text{CT}})}
\]
Weight fractions

Probability for chain transfer:

0.3 0.1 0.01 0.001

number of monomers in polymer chain
Consequences of the Schultz Flory Distribution:

Dispersity (D): $M_w / M_w = 2$

$M_w = \text{weight average} = \Sigma w_i M_i$, $\Sigma w_i = 1$

$M_n = \text{number average} = \Sigma n_i M_i$, $\Sigma n_i = 1$