

There is a simple relationship between the polydispersity index and the relative standard deviation. That is:

s = standard deviation

m = quantity being averaged (*e.g.*, molecular weight of polymer molecules)

m_i = quantity of m for item i in the set

n_i = number of items in set with quantity m_i

N = total number of items in set = Σ(n_i)

M = total amount of quantity “m” for the entire data set = (N)x(M_N) = Σ(n_im_i)

M_N = number average

M_W = weight average

$$\left(\frac{s}{M_N}\right)^2 = \frac{M_W}{M_N} - 1$$

Note that while the polydispersity index is most commonly used to describe the distribution of molecular weights in a polymer, the concept is equally applicable to any set of data. Consider the following data for the height of eleven individuals working at a local fire department:

Individual	Height (mm)	(Height)/(Total Height)
1	2001	0.0974339
2	1851	0.090130009
3	1722	0.083848663
4	1903	0.092662025
5	1931	0.094025418
6	1897	0.092369869
7	1754	0.085406827
8	2017	0.098212981
9	1771	0.086234601
10	1907	0.092856795
11	1783	0.086818912
Totals →	20537	1
Number Average (M _N) →	1867	
Weight Average (M _W) →	1871.804499	
Variance	8970	
Standard Deviation	94.71008394	

So, the variance divided by the number average squared equals the value of “ $M_N/M_w - 1$ ” (*i.e.*, 0.002573379).

The weight average has some intuitive value. If one has five bowling balls that weigh 10 kg and five bowling balls that weigh 12 kg, then the number average of the weight is simply the sum of the weights divided by the total number of balls (*i.e.*, $110/10 = 11$ kg). That is, dividing the total amount by the number of items in the set gives the number average. Stated differently, the number average equals the number fraction of the lighter balls times the lighter weight plus the number fraction of the heavier balls times the heavier weight. However, one might alternatively consider that there are 60 kg of 12 kg bowling balls and only 50 kg of 10 kg bowling balls. Thus, the average of the weight fraction of heavy balls times the weight of the heavy balls plus the weight fraction of the lighter balls times the weight of the lighter balls is the weight average. While the number average has a very tangible intuitive meaning, the weight average is a bit tougher to abstract until one realizes that the ratio of M_w/M_N is related to the relative standard deviation of the data.

Derivation of the relationship between the polydispersity (*i.e.*, M_w/M_N) and the relative standard deviation is straightforward. Referring to the letter designations given previously:

$$s = \sqrt{\sum_i \frac{n_i(m_i - M_N)^2}{N}}$$

$$M_N = \sum_i \frac{n_i m_i}{N}$$

$$M_w = \sum_i \frac{n_i m_i^2}{M}$$

$$\frac{M_W}{M_N} - 1 = \frac{\sum \frac{n_i m_i^2}{M}}{\sum \frac{n_i m_i}{N}} - 1 = \frac{\sum \frac{n_i m_i^2}{NM_N}}{M_N} - 1$$

$$\frac{M_W}{M_N} - 1 = \frac{\sum n_i m_i^2}{NM_N^2} - \frac{NM_N^2}{NM_N^2} = \frac{\sum n_i m_i^2 - NM_N^2}{NM_N^2}$$

$$\left(\frac{s}{M_N}\right)^2 = \frac{\sum \frac{n_i (m_i - M_N)^2}{N}}{M_N^2} = \frac{\sum n_i (m_i^2 - 2m_i M_N + M_N^2)}{NM_N^2}$$

$$\left(\frac{s}{M_N}\right)^2 = \frac{\sum (n_i m_i^2)}{NM_N^2} - \frac{2 \sum n_i m_i M_N}{NM_N^2} + \frac{\sum n_i M_N^2}{NM_N^2}$$

$$\left(\frac{s}{M_N}\right)^2 = \frac{\sum (n_i m_i^2)}{NM_N^2} - \frac{2M_N \sum n_i m_i}{NM_N^2} + \frac{M_N^2 \sum n_i}{NM_N^2}$$

$$\left(\frac{s}{M_N}\right)^2 = \frac{\sum (n_i m_i^2)}{NM_N^2} - \frac{2NM_N^2}{NM_N^2} + \frac{NM_N^2}{NM_N^2}$$

$$\left(\frac{s}{M_N}\right)^2 = \frac{\sum (n_i m_i^2)}{NM_N^2} - \frac{NM_N^2}{NM_N^2}$$

$$\left(\frac{s}{M_N}\right)^2 = \frac{\sum n_i m_i^2}{NM_N^2} - \frac{NM_N^2}{NM_N^2} = \frac{\sum n_i m_i^2 - NM_N^2}{NM_N^2}$$

$$\frac{M_W}{M_N} - 1 = \frac{\sum n_i m_i^2 - NM_N^2}{NM_N^2}$$

$$\sum n_i m_i^2 - NM_N^2 = \sum n_i m_i^2 - NM_N^2$$

Thus:

$$\left(\frac{s}{M_N}\right)^2 = \frac{M_W}{M_N} - 1$$