

Polymers: Molecular Weight and its Distribution

1. Introduction

Synthetic polymers are polydisperse to varying degrees in a variety of ways. The chains in a sample may differ in, for example, molecular weight, degree of long or short-chain branching, stereostructure or composition (either grossly, as with copolymers, or slightly, as with end group or foreign moieties incorporated in the chain during polymerization). This article deals with the distribution of molecular weight.

2. General Features of a Molecular Weight Distribution

The molecular weight distribution (MWD) is conveniently characterized by either the number $N(n)$ or weight $W(n)$ of chains with n repeating units (e.g., a chain with molecular weight $M = nm_0$ with m_0 the molar weight of a repeating unit). The normalized functions

$$\overline{N}(n) = N(n)/\Sigma N(n) \quad (1)$$

$$\overline{W}(n) = W(n)/\Sigma W(n) \quad (2)$$

respectively, are the number and weight fraction of chains with n repeating units $\Sigma \overline{N}(n) = \Sigma \overline{W}(n) = 1$; here, and in the following, unless noted otherwise, sums are over the range 1 to ∞).

Both $\overline{N}(n)$ and $\overline{W}(n)$ obey the well-studied mathematical properties of probability functions (Cramer 1946, Zelen and Severs 1964), a few of which find frequent application in their use. For example, the s th moment $\mu_F^{(s)}$ of a normalized distribution $\overline{F}(n)$ (e.g., either $\overline{N}(n)$ or $\overline{W}(n)$) defined by

$$\mu_F^{(s)} = \Sigma n^s \overline{F}(n) \quad (3)$$

is used to compute the averages of the distribution:

$$n_s = \mu_F^{(s)}/\mu_F^{(s-1)} \quad (4)$$

In defining $\mu_F^{(s)}$, sums may be truncated at zero since $\overline{F}(n)$ is zero for $n < 1$ for a MWD. The moments $\mu_N^{(s)}$ of $\overline{N}(n)$ and $\mu_W^{(s)}$ of $\overline{W}(n)$ are related, for example, $\mu_W^{(s)} = \mu_N^{(s+1)}/\mu_N^{(s)}$, and with $\overline{F}(n)$ a MWD, the n_s are often either directly given by a physical measurement or may be correlated with the property determined. The average $n_1 = \mu_F^{(1)}/\mu_F^{(0)} = \mu_F^{(1)}$ is the mean of the distribution.

The averages n_s appear so frequently in connection with the MWD that a special terminology has long since developed:

(a) The number average (the mean of $\overline{N}(n)$) is given by

$$n_n = \mu_N^{(1)}/\mu_N^{(0)} = \Sigma n \bar{N}(n) \quad (5)$$

$$n_n = \mu_W^{(0)}/\mu_W^{(-1)} = [\Sigma n^{-1} \bar{W}(n)]^{-1} \quad (6)$$

(b) The weight average (the mean of $W(n)$) is

$$n_w = \mu_N^{(2)}/\mu_N^{(1)} = \Sigma n^2 \bar{N}(n) / \Sigma n \bar{N}(n) \quad (7)$$

$$n_w = \mu_W^{(1)}/\mu_W^{(0)} = \Sigma n \bar{W}(n) \quad (8)$$

(c) The z average is

$$n_z = \mu_N^{(3)}/\mu_N^{(2)} = \mu_W^{(2)}/\mu_W^{(1)} \quad (9)$$

(d) The z + 1 average is

$$n_{z+1} = \mu_N^{(4)}/\mu_N^{(3)} = \mu_W^{(3)}/\mu_W^{(2)} \quad (10)$$

Higher averages ($z + 2, \dots$) may be defined by obvious generalization. It can be shown that $n_n \leq n_w \leq n_z \leq \dots$

Two of these averages have simple physical significance: n_n , the mean of $\bar{N}(n)$, is the total number of repeat units $\Sigma n N(n)$ divided by the number of molecules $\Sigma N(n)$, and determines colligative properties (e.g., osmotic pressure and vapor pressure lowering); n_w , the mean of $\bar{W}(n)$, is the weighted sum $\Sigma n c(n)$ divided by the total concentration $\Sigma c(n)$, with $c(n)$ the concentration (weight per unit volume) of chains with n units, and is given by measurements sensitive to the masses of the molecules present (e.g., light scattering and sedimentation).

The breadth of a MWD is characterized by the variance σ_F^2 (the positive root of σ_F^2 is called the standard deviation). With a MWD, the dimensionless reduced variance

$$D_F = \sigma_F^2 / (\mu_F^{(1)})^2 = [\mu_F^{(2)} / (\mu_F^{(1)})^2] - 1 \quad (11)$$

called the polydispersity index is used more frequently than σ_F^2 . Thus,

$$D_N = (n_w/n_n) - 1 = [\mu_N^{(2)} / (\mu_N^{(1)})^2] - 1 \quad (12)$$

$$D_W = (n_z/n_w) - 1 = [\mu_W^{(2)} / (\mu_W^{(1)})^2] - 1 \quad (13)$$

$$D_Z = (n_{z+1}/n_z) - 1 = [\mu_Z^{(2)} / (\mu_Z^{(1)})^2] - 1 \quad (14)$$

where D_N and D_W are related to the breadth of the $\bar{N}(n)$ and $\bar{W}(n)$ distributions, respectively, and D_Z is a useful generalization.

Many MWDs of interest are asymmetric about their mean, that is, skewed toward high or low n . The coefficient of skewness γ_F , which involves $\mu_F^{(3)}$, provides a quantitative measure of

the asymmetry of a distribution. As with σ_F , a dimensionless skewness index is convenient in discussions of a MWD:

$$S_F = \sigma_F^3 \gamma_F / (\mu_F^{(1)})^3 = \mu_F^{(3)} / (\mu_F^{(1)})^3 - 3\mu_F^{(2)} / (\mu_F^{(1)})^2 + 2 \quad (15)$$

so that

$$S_N = (D_W + 1)(D_N + 1)^2 - 3(D_N + 1) + 2 \quad (16)$$

$$S_W = (D_Z + 1)(D_W + 1)^2 - 3(D_W + 1) + 2 \quad (17)$$

For a symmetric distribution, $S_F = 0$. Positive and negative S_F indicate a distribution skewed toward large and small n , respectively.

Indices involving higher moments can be utilized to characterize other properties of a distribution and, in principle, a distribution is known completely if all of its moments are known. In practice, the experimentalist never has such luxury of data and rarely has information for indices beyond D_Z or S_W .

In many applications, the average of a function $\Phi(n)$ of n is needed:

$$\overline{\Phi} = \Sigma \Phi(n) n^{b+1} \overline{N}(n) / \Sigma n^{b+1} \overline{N}(n) \quad (18)$$

where b is often an integer. Of course, an equivalent relation with $n \overline{N}(n)$ replaced by $n_n \overline{W}(n)$ can also be used. A frequent objective is to express $\overline{\Phi}$ in terms of the averages n_n , n_w , n_z , In some applications, $\Phi(n)$ obeys a power law $\Phi(n) = \phi n^v$ with integer or noninteger v , so that $\overline{\Phi} = \phi \mu_W^{(v+b)} / \mu_W^{(b)}$, e.g., with $v = 1$ and $b = 2$, $\overline{\Phi} = \phi n_z$. With integer v and b , $\overline{\Phi}$ involves only n_n , n_w , n_z ,, but with noninteger v or b , the quantity

$$n_{(a)} = [\mu_W^{(a)}]^{1/a} = [\Sigma n^a \overline{W}(n)]^{1/a} = [n_n^{-1} \Sigma n^{1+a} \overline{N}(n)]^{1/a} \quad (19)$$

which appears cannot be reduced to n_n , n_w , n_z , ... unless the MWD is known. Since an early application to polymers in which $n_{(a)}$ appeared involved the intrinsic viscosity, $n_{(a)}$ is sometimes called the "viscosity average." Examples of $\overline{\Phi}$ with integral and nonintegral power laws and more general expressions are given below.

In some cases, it is useful to employ the integral or cumulative distribution $I_F(n)$ defined by

$$I_F(n) = \sum_{m=0}^n \overline{F}(m) \quad (20)$$

(Note that the summation range is limited in this case.) Thus, $I_W(n)$ is the weight fraction of polymer with n or fewer repeating units.

3. Examples of Molecular Weight Distribution Functions

In broad terms, three types of MWD functions are of interest: (a) those calculated theoretically using a model for the polymerization process; (b) those determined empirically, usually in numerical form, for a particular sample by suitable experiment (e.g. size-exclusion or elution chromatography, fractionation or sedimentation); and (c) analytic expressions, believed to be reasonable (but not necessarily accurate) representations of the MWD, and having some aspects of mathematical convenience. The second type of MWD is of limited value for theoretical purposes, such as the computation of $\overline{\Phi}$ in terms of n_n , n_w , n_z , ... and $n_{(a)}$, but even if the MWD is available only in numerical form, it is useful both for a qualitative insight into the nature of the MWD, and to provide experimental measures of n_n , n_w , n_z , ..., by numerical analysis. It is then sometimes possible to represent the true MWD by one of the empirical or theoretical functions. The theoretical functions may be used to predict the MWD, given the polymerization conditions, or may serve, together with an experimental estimate of the MWD, to permit assessment of a polymerization process.

Several MWD functions frequently encountered in the study of polymers are given in Table 1, together with expressions for n_n , n_w , n_z , ... and $n_{(a)}$. In each case, only $\overline{N}(n)$ is presented, since $n_n \overline{W}(n) = n \overline{N}(n)$. The averages n_n , n_w , n_z , ... and $n_{(a)}$ are given in preference to the equivalent quantities $\mu_N^{(1)}$, $\mu_N^{(2)}$, ... or $\mu_N^{(1)}$, D_N , S_N , ..., as a matter of convenience and familiarity to specialists (but $n_{(a)}^a$ is, in fact, $\mu_W^{(a)} = \mu_N^{(a+1)}/\mu_N^{(1)}$).

Examples of several MWD functions are given in Fig. 1 for a range of D_N as bilogarithmic plots of $\overline{W}(n)/\overline{W}(n_n)$ versus n/n_n . Although this presentation distorts the shape of $\overline{W}(n)$, it is useful for the wide range of variables of interest. The curves in Fig. 1 were all calculated with $n_n = 100$, but they may be used to obtain $\overline{W}(n)$ for other n_n as well, except in some cases at very low n_n (e.g., substantial deviation obtains for the Flory-Schulz MWD with $n_n = 2$).

⟨POSITION FOR FIGURE 1 AND TABLE 1⟩

3.1 One-Parameter Functions

The theory of step-growth (condensation) polymerization for flexible chain polymers led to the Flory-Schulz distribution. In the theory, p enters as the extent of reaction; it can also be

considered as an arbitrary parameter, chosen to force $\bar{N}(n)$ to give the correct n_n (i.e., $p = 1 - n_n^{-1}$) or, alternatively, the correct polydispersity index, for example $D_N = p$. The skewness index S_N is $p + p^2$. The relation

$$\sum n^s p^{n-1} = \frac{d}{dp} [p \sum n^{s-1} p^{n-1}] \quad (21)$$

is useful in the summations encountered since, for integral s , any such sum can eventually be reduced to terms involving $\sum p^{n-1} = (1-p)^{-1}$ multiplied by functions of p .

The exponential function is an approximate form for the Flory-Schultz distribution when n_n is large. It is sometimes more convenient analytically, for example, in the calculation of $n_{(a)}$, and stands in relation to two and three-parameter exponential functions discussed below. For this distribution, $D_N = 1$, $D_W = 1/2$ and $S_N = 2$.

The Poisson distribution is realistic for certain types of polymerizations, such as anionic polymerizations for which the termination rate is nil and initiation is much faster than propagation. Since $D_N = n_n^{-1}$, the distribution is very narrow for realistic values of n_n . The relation

$$\sum n^s v n^{n-1} / (n-1)! = \frac{d}{dv} [v \sum n^{s-1} v^{n-1} / (n-1)!] \quad (22)$$

is useful in summations with the Poisson distribution, since by continued differentiation, any such sum with integral s can be reduced to terms involving $\sum v n^{n-1} / (n-1)! = \exp v$ multiplied by functions of v .

3.2 Two-Parameter Functions

For some addition polymerizations, the Schulz-Zimm distribution is a realistic representation of $N(n)$. More frequently, it is used as a mathematically convenient, and often reasonable, representation of $\bar{N}(n)$, without attempt to relate the parameters to polymerization variables. The Schulz-Zimm distribution is a generalized form of the one-parameter exponential relation, to which it reduces if the parameter h is unity. Since $D_N = h^{-1}$, $D_W = (h+1)^{-1}$ and $D_Z = (h+2)^{-1}$, ..., the Schulz-Zimm distribution is sharper or broader than the one-parameter exponential distribution as h is greater or smaller than unity, respectively. The skewness index of $\bar{N}(n)$ is positive ($S_N = 2/h^2$). In many cases (including calculation of n_n , n_w , n_z , ... and $n_{(a)}$) use is made of the standard form (after conversion of sums to the integrals)

$$\int_0^{\infty} du u^{t-1} \exp(-ku) = \Gamma(t)/k^t \quad (23)$$

where $\Gamma(t)$ is the gamma function. The convenience of this relation is, in fact, one of the principal reasons that the Schulz-Zimm function finds widespread use.

The normal (or Gaussian) function represents the MWD as symmetric about the median n_m , with halfwidth β . It is not often used to represent the MWD, despite the considerable body of work on its properties in standard probability theory, partly because its mathematical convenience is lost unless its breadth is narrow enough that the effects of truncation for $n < 0$ do not substantially affect summations of interest. (This has been assumed to be the case for the entries in Table 1.) In such cases, it is sometimes used as a mathematically convenient empirical alternative to the Poisson distribution. It has been used to represent either $\bar{N}(n)$ or $\bar{W}(n)$, as convenient to the problem at hand. With the former, one has $D_N = \beta^2/n_m^2$, and $S_N = 0$.

The logarithmic normal distribution is a variation of the normal distribution designed to eliminate the troublesome truncation mentioned above, and can represent a distribution with a long high-molecular-weight tail. Most frequently, $\bar{W}(\ln n)$ is represented as being normally distributed, with the result for $\bar{N}(n)$ given in Table 1. For this distribution, $D_N = D_W = D_Z = \exp(\beta^2 - 1)$, so that S_N is positive for $D_N > 0$. In using the logarithmic normal distribution, the standard form

$$\int_0^{\infty} du u^{v-1} \exp[-(\alpha^{-1} \ln u/u_0)^2] = \alpha \pi^{1/2} u_0^v \exp(v^2 \alpha^2/4) \quad (24)$$

is frequently encountered.

3.3 Three-Parameter Function

Although not often used in its most general form, a three-parameter exponential function has been adopted for some purposes. Inspection of the entries in Table 1 reveals the progression in the one, two and three parameter family of exponential functions. A special form of the three-parameter exponential function has been used, with $h = m - 1$ ($h > 0$), which has the merit that the integral weight distribution for the resultant two-parameter relation is especially simple

$$I_W(n) = 1 - \exp[-yn^m] \quad (25)$$

3.4 Other Distribution Functions

All of the $\bar{N}(n)$ given in Table 1 are unimodal, that is, have only one maximum. In some cases,

especially with mixtures, it is useful to construct MWD functions by combination of two or more unimodal functions.

4. Use of the Molecular Weight Distribution Function

Applications of MWD functions to interpret physical properties abound; only a few illustrative examples will be given, with emphasis on results useful in the next section. These will involve calculations of a physically meaningful average $\overline{\Phi}$ of a function $\Phi(n)$ that depends on n and the concentration $c(n)$ (weight/vol) of n -mers. In a polydisperse mixture, $c = \sum c(n)$ is the total concentration, and $\overline{W}(n) = c(n)/c$.

In the following, we assume that the polymer is heterodisperse only in chain length. Otherwise, multivariate distributions may be needed to represent the material (e.g., the bivariate number fractions $\overline{N}(n,\gamma)$ for components with n repeating units and property γ , which could be the number of long chain branches, etc.).

4.1 Osmotic Pressure

For a dilute solution, the osmotic pressure Π involves sums over the components:

$$\Pi/RT = (c/m_0)\sum n^{-1}\overline{W}(n) + c^2\sum_{m,n} B(m,n)\overline{W}(m)\overline{W}(n) + \dots \quad (26)$$

$$\Pi/RTc = (n_n m_0)^{-1} + B^\Pi c + \dots \quad (27)$$

where the term proportional to c has been reduced to a standard average (i.e., n_n^{-1}), but the

average $B^\Pi = \sum_{m,n} B(m,n)\overline{W}(m)\overline{W}(n)$ of the second virial coefficient $B(m,n)$ cannot be evaluated without representation for $B(m,n)$. To illustrate the calculation of B^Π , it is convenient to let $B(m,n) = [B(m,m)B(n,n)]^{1/2}$ and $B(n,n) = bn^{-\gamma}$ (with $0 < \gamma < 1/4$). The former results in $B^\Pi = [\sum B^{1/2}(n,n)\overline{W}(n)]^2$, and use of the latter gives a relation involving $n_{(a)}$, with $a = -\gamma/2$:

$$B^\Pi = bn_n^{-\gamma}\Psi^\Pi \quad (28)$$

$$\Psi^\Pi = (n_n/n_{(-\gamma/2)})^\gamma \quad (29)$$

With the Schulz-Zimm distribution, $\Psi^\Pi = h^\gamma[\Gamma(1+h-\gamma/2)/\Gamma(1+h)]^2$. Other more realistic models have been studied to represent more complex behavior of B^Π .

4.2 Light Scattering

For a dilute polymer solution, the Rayleigh ratio R_0 at zero scattering angle involves sums over the components (for isotropic solute, with all solute elements having identical refractive index,

e.g., see (Berry 2000)):

$$R_0/K = m_0 c \Sigma n \overline{W}(n) - 2(m_0 c)^2 \Sigma \Sigma_{m,n} B(m,n) m n \overline{W}(m) \overline{W}(n) \quad (30)$$

$$Kc/R_0 = (n_w m_0)^{-1} + 2B^{LS} c + \dots \quad (31)$$

where the term proportional to c is expressed as a standard average (e.g., n_w), but where evaluation of

$$B^{LS} = n_w^{-2} \Sigma \Sigma_{m,n} B(m,n) m n \overline{W}(m) \overline{W}(n) \quad (32)$$

requires a model for $B(m,n)$. If the expression introduced above is employed, then

$$B^{LS} = n_w^{-2} [\Sigma B^{1/2}(n,n) n \overline{W}(n)]^2 \quad (33)$$

and

$$B^{LS} = b n_w^{-\gamma} \Psi^{LS} \quad (34)$$

$$\Psi^{LS} = (n_w/n_{(1-\gamma/2)})^{\gamma-2} \quad (35)$$

in which Ψ^{LS} contains $n_{(a)}$ with $a = 1 - \gamma/2$. Use of the Schulz-Zimm distribution gives $\Psi^{LS} = (h+1)^\gamma [\Gamma(2+h-\gamma/2)/\Gamma(2+h)]^2$, so that for this model, $B^{LS}/B^\Pi = [(1+h-\gamma/2)/(1+h)]^2$, which demonstrates the general result that $B^{LS} \leq B^\Pi$.

For data extrapolated to infinite dilution, the dependence on scattering angle ϑ is given by $R_q^0(n) = K n m_0 c(n) P(u)$, where $u = R_G^2(n) q^2$ depends on n through the root-mean-square radius of gyration R_G ; $q = (4\pi/\lambda) \sin \vartheta/2$ is the modulus of the scattering vector. Evaluation of

$$R_q^0 = \Sigma R_q^0(n) = K c m_0 \Sigma n P(u) \overline{W}(n) \quad (36)$$

requires a model for $P(u)$. However, for any (isotropic) scatterer, $P(u) = 1 - u/3 + \dots$, and

$$Kc/R_q^0 = (n_w m_0)^{-1} [1 + (q^2/3) n_w^{-1} \Sigma R_G^2(n) n \overline{W}(n) + \dots] \quad (37)$$

With several molecular models, $R_G^2(n) = r n^\nu$, so that

$$R_G^2 = n_w^{-1} \Sigma R_G^2(n) n \overline{W}(n) = r n_z^{1+\varepsilon} \omega \quad (38)$$

with $\omega = (n_z/n_w)(n_{(2+\varepsilon)}/n_z)^{2+\varepsilon}$, where $\varepsilon = \nu - 1$ and involves $n_{(a)}$ with $a = 2 + \varepsilon$. For integral ν , R_G^2 may be expressed in terms of standard averages. For example, with flexible coil chains under Flory-theta conditions ($B^{LS} = B^\Pi = 0$), $\nu = 1$ and $R_G^2 = r n_z$, and for rodlike chains, $\nu = 2$ and $R_G^2 = r n_z n_{z+1}$. With flexible chains under conditions with $B^{LS} > 0$, ν will usually be nonintegral, with $0 < \varepsilon \leq 0.2$. In this case, a specific $\overline{W}(n)$ is needed to evaluate w , for example, with the Schulz-Zimm distribution, $\omega = \Gamma(3+h+\varepsilon)/(h+2)^\varepsilon \Gamma(3+h)$.

Over a wider range of q , for the flexible coil under conditions with $B^{LS} = 0$, $P(u) = (2/u^2)[u$

$-1 + \exp(-u)]$, and for a rodlike chain, $P(u) = x^{-2}[x\text{Si}(2x) - \sin^2 x]$, where $x^2 = 3u$ and Si is the sine integral. Each of these contain terms that require evaluation of a function that is not a power-law relation. Thus, for the coil, making use of the relation $R_G^2(n) = rn$,

$$R_q^0 = Kcn_w m_0 \{ 2/(q^2 r n_w) - 2/(q^4 r^2 n_n n_w) + 2/(q^4 r^2 n_w) [\Sigma n^{-1} \exp(-rq^2 n) \overline{W}(n)] \} \quad (39)$$

This expression is more useful if the final term can be represented in terms of standard averages. With the Schulz-Zimm distribution, use can be made of the standard integral given above (with $k = rq^2 + y$ and $t = h$) to give

$$Kc/R_q^0 = (2m_0)^{-1} q^2 r \{ 1 - (q^2 r n_n)^{-1} [1 - (1 + q^2 r n_n/h)^h] \}^{-1} \quad (40)$$

Thus, for $h = 1$, $Kc/R_q^0 = (n_w m_0)^{-1} (1 + q^2 r n_z) 3$. A similar treatment can be given for rodlike chains, or molecules of other shapes, and for the scattering from anisotropic molecules (e.g., see (Berry 2000)).

4.3 Intrinsic Viscosity

The specific viscosity $\eta_{sp}(n)$ of a very dilute solution is given by $\eta_{sp}(n) = [\eta](n)c(n)$, where the intrinsic viscosity $[\eta](n)$ usually obeys a power-law relation $[\eta](n) = kn^\alpha$, so that $n_{(a)}$ appears, with $a = \alpha$:

$$[\eta] = \eta_{sp}/c = \Sigma [\eta](n) \overline{W}(n) = kn_{(\alpha)}^\alpha \quad (41)$$

The data in Table 1 relate $n_{(a)}$ to the standard averages for several distribution functions. For α in the usual range 0.5–0.8 for flexible-chain polymers, $n_n < n_{(\alpha)} < n_w$. For rodlike chains, α is about 1.8, and $n_{(\alpha)} = n_w (n_z/n_w)^{4/9}$.

4.4 Size-Exclusion Chromatography

In size-exclusion chromatography, the relative concentration $H(V_e)$ of the eluent is determined as a function of elution volume V_e (e.g., H is some observable proportional to c , such as differential refractive index or an optical density at an appropriate wavelength). Frequently, V_e can be represented as a universal function of $[\eta]M$ for a given column, independent of the polymer. Of course, if the relation between $[\eta]$ and M is known, then (after correction for unwanted axial diffusional broadening, see below) the chromatogram can be used to compute $\overline{W}(n)$, since $\overline{W}(n) = H(V_e)/\Sigma H(V_e)$, where the sum extends over all V_e , each of which corresponds to an n to be computed from $[\eta]M$. With a sample for which the relation between $[\eta]$ and M is unknown, reasonable estimates of D_N , D_w and D_z may still be obtained by arbitrary approximation of the power-law exponent $\alpha = \partial \ln[\eta]/\partial \ln M$ by an estimate α_A and calculation of

$([\eta]M)^{1/(1+\alpha_A)}$ from the observed $[\eta]M$. It is often found that estimates of D_N , etc., do not depend strongly on the estimate for α_A (Frequently, α_A is equated with α_C , the value of α for the polymer used to calibrate the column, as is the case if one uses a correlation for M vs V_e for a standard polymer to analyze data on an unknown material.) The nature of this dependence can be illustrated by calculation of the experimental quantities

$$A_\delta^{(s)} = \Sigma([\eta]M)^{s/(1+\alpha_A)} \overline{W}(n) \quad (42)$$

that are available if the calibration between $[\eta]M$ and V_e is known. Thus, an apparent n_w/n_n ratio would be calculated as

$$(n_w/n_n)_{APP} = A_\delta^{(1)}/A_\delta^{(-1)} \quad (43)$$

where $\delta = (\alpha - \alpha_A)/(\alpha + \alpha_A)$. With the power-law relation $[\eta] = kn^\alpha$, this calculation gives $A_\delta^{(1)}/A_\delta^{(-1)} = [n_{(1+\delta)}/n_{-(1+\delta)}]^{1+\delta}$, so that for the Schulz-Zimm distribution

$$(n_w/n_n)_{APP} = (n_w/n_n) \Gamma(h+2+\delta) \Gamma((h-\delta)/\Gamma(h+2)) \Gamma(h) \quad (44)$$

Consequently, $(n_w/n_n)_{APP}$ is close to n_w/n_n with a reasonable estimate for α_A for example, in error by 17% for $h = 1$ and $\delta = 0.1$ (which represents a large deviation of α_A from α).

In some cases, in order to obtain some estimate of n_n , etc., for a polymer with unknown power-law parameters; the coefficient k is also approximated by an estimate k_A to permit calculation of the experimental quantities $B_\delta^{(s)} = (k_A)^{-s/(1+\alpha_A)} A_\delta^{(s)}$ and apparent averages $(n_s)_{APP} = B_\delta^{(s)}/B_\delta^{(s-1)}$ (e.g., this obtains if the correlation of M vs V_e for a standard polymer is used to analyze the data for the unknown polymer, so that k_A and α_A are put equal to the corresponding parameters k_C and α_C for the standard). In this case, with the Schulz-Zimm distribution,

$$(n_s)_{APP}/n_s = (k/k_A)^{1/(1+\alpha_A)} (n_n/h)^\delta \frac{h+s(1+\delta)}{h+s} \frac{\Gamma(h+s(1+\delta))}{\Gamma(h-\delta+s(1+\delta))} \quad (45)$$

As an example, if data on benzene solutions of poly(vinyl acetate) were analyzed with the $M - V_e$ relation for polystyrene (in benzene), then for a polymer with $h = 1$, $(n_w)_{APP} = 1.54(n_n)^{-0.05} n_w$, illustrating the error that can be introduced by this procedure.

4.5 Photon Correlation Light Scattering

Time-resolved light scattering using photon correlation methods give the intensity autocorrelation functions $g^{(2)}(\tau, \Delta\tau)$ of the count rate in sampling intervals of duration $\Delta\tau$. For appropriate experimental conditions (including extrapolation to infinite dilution):

$$[g^{(2)}(\tau, \Delta\tau) - 1]^{1/2} = A \Sigma Q_q(n) \exp(-\tau/\tau_q(n)) \quad (46)$$

where $\tau_q^{-1}(n)$ is given by $q^2 D_T(n)$, with $D_T(n)$ the translational diffusion coefficient, and $Q_q(n)$ is the fraction of the scattering due to the component with coherence time $\tau_q(n)$. For independent scatterers (i.e., infinite dilution), $Q_q(n) = R_q^0(n)/R_q^0$. Thus, analysis of $[g^{(2)}(\tau, \Delta\tau) - 1]^{1/2}$ requires the extensive use of models (e.g., random-flight, rodlike) to permit evaluation of the dependence of $Q_q(n)$ and $\tau_q(n)$ on n in data interpretation. For example, the first cumulant K_1 , equal to $-(1/2)\partial \ln[g^{(2)}(\tau) - 1]/\partial \ln \tau$ as τ goes to zero, can be evaluated for a Schulz-Zimm MWD to give

$$K_1 = \frac{kTq^2}{4\pi\eta_s(rn_w)^{1/2}} (1 + q^2 rn_n/3h)^{1/2} \frac{\Gamma(h + 3/2)h^{1/2}}{(h + 1)^{1/2}\Gamma(h + 1)} \quad (47)$$

if $P(u)$ is approximated by the Guinier relation $\exp(-u/3)$, and the expression $D_T(n) = kT/(6\underline{d}\pi\eta_s R_G^2(n))$ for the random-flight chain is used, with $R_G^2(n) = rn$ and $\underline{d} \approx 2/3$. The result reveals the effects of intra molecular interference (e.g., the factor $(1 + q^2 rn_n/3h)$, which is approximately unity for $q^2 \ll rn_n/3$) and the complex dependence on polydispersity, even for the most primitive features of $g^{(2)}(\tau)$. The intra molecular interference effects may be suppressed if conditions are used with $q^2 R_G^2 \ll 1$. Then, for a Schulz-Zimm MWD, and with $R_G^2(n) = rn^{1+\epsilon}$,

$$K_1 = \frac{kTq^2}{6\pi\eta_s} \left\{ \underline{d} rn_w^\alpha H_{(1-\alpha)}(h + 1) \right\}^{-1} \quad (48)$$

where $\alpha = (1 + \epsilon)/2$, $H_\mu(x) = x^\mu \Gamma(x)/\Gamma(x + \mu)$, with $\Gamma(\dots)$ the gamma function, and $h^{-1} = M_w/M_n - 1$. For example, since $H_0(x) = 1$, K_1 is inversely proportional to M_w if $\alpha = 1$, approximating the behavior for a rodlike chain. In general, the factor involving h is close to unity unless the MWD is very broad, e.g., that factor increases from unity for a monodisperse sample to 1.12 for $M_w/M_n = 11$.

5. Determination of the Molecular Weight Distribution

Methods of characterizing a MWD may involve physical separation of components, with subsequent analysis of n_n , n_w , ... and the total concentration for each aliquot, or measurement of physical properties (e.g., osmotic pressure and light scattering) that depend on gradients of $c(n)$ induced by Brownian motion or external fields to give either $\overline{W}(n)$ or, more usually, n_n , n_w , ... for the entire sample.

Several examples of the latter have been cited in the preceding: osmotic pressure and light scattering yield $M_n = n_n m_0$ and $M_w = n_w m_0$, respectively, and for a random-flight coil, $R_G^2 = rn_z$ provides a means to estimate n_z if r is known. In principle, the shape of the scattering function

Kc/R_q^0 at infinite dilution can be used to determine n_n , n_w and n_z if it is known that the polymer is linear and obeys random-flight statistics (see Sect. 3.2)—in practice, the range of q available (limited, since $\vartheta < \pi$) is usually too small to permit necessary evaluation of Kc/R_q^0 , and in any case, the departure from random-flight statistics may be severe for $R_G q \gg 1$. Another treatment of this kind involves the intensity autocorrelation function $g^{(2)}(\tau, \Delta\tau)$. Unfortunately, analysis of $g^{(2)}(\tau, \Delta\tau)$ in terms of $\overline{W}(n)$ is complex, even with the infinite dilution approximation, requires extensive use of models (e.g., random-flight and rodlike, and is not well suited for accurate evaluation of $\overline{W}(n)$).

Measurements that employ an external field to create concentration gradients that are studied in situ include equilibrium and velocity sedimentation thermal diffusion and a few other more specialized techniques. In sedimentation equilibrium, under appropriate conditions for a solute with molecular weight $M = nm_0$, the concentration at a position r along a centrifugal field with angular velocity ω for a solution confined between positions b and m is

$$c^{(r)}(n) = c_0 A M \exp(-ABM) / [1 - \exp(-BM)] \quad (49)$$

with c_0 the initial concentration, $A = (r^2 - m^2)/(b^2 - m^2)$, and $B = (\partial\rho/\partial c)\omega^2(b^2 - m^2)/RT$ where ρ is the solution density. For a heterodisperse solute the average (measurable) concentration at r is $c^{(r)} = \Sigma c^{(r)}(n)$ so that analysis of $c^{(r)}$ as a function of r provides a means to study $\overline{N}(n)$, either by inversion of $c^{(r)}$ to obtain $\overline{N}(n)$ or by analysis of $c^{(r)}$ to deduce n_w , n_z , etc. In practice, deviations from the idealized $c^{(r)}(n)$ given above caused by solution compressibility (especially with organic solvents) and hydrodynamic and thermodynamic interactions among the solute molecule makes the analysis less attractive. Moreover, the method is inherently time consuming. Consequently, it is used much less frequently than size-exclusion chromatography (see below).

Sedimentation velocity affords an alternative centrifugal coefficient $s(n)$, equal to $M(\partial\rho/\partial c)D_T(n)/RT$ for a solution at infinite dilution. The spreading of the boundary between solution and solvent as the boundary moves down the cell (for positive $\partial\rho/\partial c$) contains information on $\overline{N}(n)$. In practice, conversion of the experimental data $\partial c^{(r)}/\partial r$ to $\overline{N}(n)$ is hampered by the factors mentioned above in connection with sedimentation equilibrium, and the procedure is seldom used for quantitative estimate of $\overline{N}(n)$ owing to the more easily used size-exclusion chromatography.

Methods involving physical separation of components for subsequent analysis may be

discrete or continuous (as with chromatography). Of the discrete methods, separation of the components of a polymer in a dilute solution by successive adjustments of the thermodynamic conditions, with removal and analyses at each step is frequently used. The thermodynamic conditions may be altered by addition or removal (e.g., by evaporation) of a reagent or by change in the temperature.

The change may cause successive phase separation from solution of components with successively smaller n (fractional precipitation) or dissolution of components with successively higher n (fractional solution). In either case, the recovered component can be characterized by its weight fraction \bar{W} and properties, for example, n_n, n_w, \dots . Elaborate methods have been developed to reconstruct $\bar{N}(n)$ from such data, to take account of the inevitable overlap of components in each fraction. For example, in one scheme, the cumulative weight fraction $I_w(n)$ is approximated by the experimental cumulative weight $M_w = n_w m_0$:

$$I_w(n) \approx I_i(n) = (1/2)\bar{W}_i(n_w) + \sum_{j=1}^{i-1} \bar{W}_j(n_w) \quad (50)$$

Differentiation of $I_w(n)$ then gives $W(n) = dI_w(n)/dn$; more elaborate schemes have been used.

In many cases, chromatographic methods have supplanted discrete fractionations. Chromatographic methods based on solubility, molecular size, adsorption, thermal diffusion, sedimentation and other properties have been developed. Space prohibits discussion of any but the presently much used size exclusion chromatography (SEC), which finds use in both preparative and analytical applications. Nonetheless, other chromatographic methods are frequently used, such as column elution fractionation. If only relative concentrations are determined, the correlation between $[\eta]M$ and V_e will permit construction of $\bar{W}(n)$ from the chromatogram $S(V_e)$ (e.g., relative concentration as a function of V_e , if the relation between $[\eta]$ and M is known) or, if not, the data may be used to estimate D_N , etc., and apparent averages $(n_s)_{APP}$ of the distribution as discussed above.

In some cases, dual detectors are used with SEC to determine the relative concentration (e.g., from the difference in refractive indices between eluent and solvent) and, say, the light scattering intensity R_q at small scattering angle (and low concentration) as functions of the elution volume V_e . In this case, after correction for axial diffusion (see below), $\bar{W}(n)$ may be determined directly, assuming a single, identical repeating unit on all chains. In addition, use of

a multi-angle light scattering photometer will give the distribution of R_G^2 if the chains are long enough to permit a reliable estimate of the angular dependence of the light scattering.(e.g., see Berry and Cotts 1999) Analysis is also possible with random or alternating copolymers. The determination of the MWD for randomly branched polymers, such as those obtained in certain free radical polymerizations has been a vexing problem since the early history of the study of the MWD of macromolecules. In this case, a bivariate distribution with respect to both molecular weight and the number p of branch nodes per chain would be desirable (assuming all branch nodes have the same functionality, or number of branches). Of course, even that does not fully describe the system, as a variety of chain structures may have the same M and p . Remarkably, an analysis of the distribution of species in size elution chromatography shows that under ideal conditions, the species at a given elution volume V_e are narrowly distributed with respect to M , but more polydisperse with respect to p , e.g., M_w/M_n is much closer to unity than p_w/p_n for the chains at a given V_e .(Shiga and Kato 1986) Consequently, determination of M_w as a function of V_e permits a reasonable estimate of the MWD. Complementary determination of R_G^2 provides information that may be used to estimate the average number of branches on the molecules as a function of M_w .

Axial diffusion on the column can broaden the observed chromatogram. In this case, the observed chromatogram $S(V_e)$ is related to the chromatogram $S^{(c)}(V_e)$ corrected for axial diffusion by

$$S(V_e) = \sum_{u=V_1}^{V_2} S^{(c)}(V_e)g(V_e - u) \quad (51)$$

where $g(V_e - V)$ is a spreading function, and the sum runs over the entire elution volume range V_1 to V_2 . Frequently, a Gaussian function with mean V_e and variance $(2H)^{-1}$ is used for $g(V_e - u)$, so that in principle the Fourier transform

$$S^{(c)}(V_e) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} ds \exp(s^2/4H)S(s)\exp(-isV_e) \quad (52)$$

can be used to compute $S^{(c)}(V_e)$ from $S(V_e)$ if the spreading parameter H is known. Rigorous evaluation of $S^{(c)}(V_e)$ from experimental $S(V_e)$ is seldom easy, but an approximation leads to the useful result (see Tung 977)

$$S^{(c)}(V_e) = [H/(H - b_1)]^{1/2}S(V_e) \exp[b_1^2/4(H - b_1)] \quad (53)$$

where $(2b_1 = -d^2 \ln S(x)/dx^2)_{x=V_e}$. Given H (which may vary with V_e), $S^{(c)}(V_e)$ may be

estimated for each $S(V_e)$.

6. Conclusions

The preceding has presented several functions commonly used to approximate the molecular weight distribution of linear homopolymers, applications of these to the analysis of experiments designed to determine the MWD or, more often, certain parameters of that distribution such as M_n , M_w , etc., and certain experimental procedures for the determination of the MWD without the aid of an analytical representation of the distribution. It should be acknowledged that many important issues in the characterization of the molecular features of the chains in a polymeric ensemble are not included in this discussion: the frequency and nature of chain branching; the sequence distribution of different monomers on the chains if not homopolymers; the sequence distribution of stereo isomers of the monomers (even in the case of chains otherwise chemically homogeneous); any distribution of chain ends; etc. An analytical description of these requires a multivariant distribution function, e.g., the distribution of molecular weight and branch density at a minimum for a branched chain polymer. The experimental determination of such multivariant distribution functions is usually difficult, if not impossible with current methods, and may render determination of the MWD or its characterizing parameters problematic in some cases. For example, with a copolymer of unknown sequence distribution, the use of a light scattering detector to analyze the eluent in an SEC separation may not yield correct estimates for M_w the eluent owing to issues involved in the analysis of such data for copolymers. (Berry 2000) One might attempt to use a preliminary separation by average chemical composition prior to an SEC analysis to improve the SEC analysis, in which case it might be possible to obtain useful estimates of M_w by light scattering on the eluent if the monomer sequence distribution among the chains of like composition is random (or strictly alternating). For branched chains, as discussed in the preceding, simultaneous analysis of R_G^2 and M on the eluent by light scattering may allow some evaluation of the bivariate distribution of molecular weight and chain branching given a model for the type of chain branching present. In any case, it seems reasonable to anticipate that improved methods to determine multivariate distributions characteristic of many polymers of interest will continue to develop to augment information on the MWD.

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Table I

Some frequently used molecular weight distribution functions

Name	$\bar{N}(n)^a$	Parameter	n_n	n_w	n_z	n_{z+1}	$n_{(a)}^b$
Flory-Schulz	$(1-p)p^{n-1}$	p	$\frac{1}{1-p}$	$\frac{1+p}{1-p}$	$\frac{1+4p+p^2}{(1-p)(1+p)}$	$\frac{1+11p+11p^2+p^3}{(1-p)(1+4p+p^2)}$	c
Exponential	$y \exp(-yn)$	y	1/y	$\frac{2}{y}$	$\frac{3}{y}$	$\frac{4}{y}$	$\frac{[\Gamma(2+a)]^{1/a}}{y}$
Poisson	$[v^{n-1}/(n-1)!] \exp(-v)$	v	1+v	$\frac{1+3v+v^2}{1+v}$	$\frac{1+7v+6v^2+v^3}{1+3v+v^2}$	$\frac{1+15v+25v^2+10v^3+v^4}{1+7v+6v^2+v^4}$	c
Schulz-Zimm ^d (two-parameter exponential)	$y^h n^{h-1} \exp(-yn)/\Gamma(h)$	h, y	h/y	$\frac{1+h}{y}$	$\frac{2+h}{y}$	$\frac{3+h}{y}$	$\frac{\Gamma(1+a+h)}{y\Gamma(1+h)}$
Normal (Gaussian) ^c	$[2\pi\beta^2]^{-1/2} \exp[-(n-n_m)^2/2\beta^2]$	n_m, β	n_m	$n_m[1+(\beta/n_m)^2]$	$n_m \frac{1+3(\beta/n_m)^2}{1+(\beta/n_m)^2}$	$n_m \frac{1+6(\beta/n_m)^2+3(\beta/n_m)^4}{1+3(\beta/n_m)^2}$	c
Logarithmic normal	$(n/n)[2\pi\beta^2]^{-1/2} \exp[-(\ln n/n_m)^2/2\beta^2]$	n_m, β	$n_m \exp(\beta^2/2)$	$n_m \exp(3\beta^2/2)$	$n_m \exp(5\beta^2/2)$	$n_m \exp(7\beta^2/2)$	$n_m \exp[(a+2)\beta^2/2]$
Three-parameter exponential ^d	$my^{h/m} n^{h-1} \exp(-yn^m)/\Gamma(h/m)$	h, y, m	$\frac{\Gamma[(h+1)/m]}{y^{1/m}\Gamma(h/m)}$	$\frac{\Gamma[(h+2)/m]}{y^{1/m}\Gamma(h/m)}$	$\frac{\Gamma[(h+3)/m]}{y^{1/m}\Gamma(h/m)}$	$\frac{\Gamma[(h+4)/m]}{y^{1/m}\Gamma(h/m)}$	$\frac{\Gamma[(h+1+a)/m]^{1/a}}{y^{1/m}\Gamma(h/m)}$

a Number fraction; the weight fraction may be calculated as $\bar{W}(n) = (n/n_n)\bar{N}(n)$

b See text, for definition of $n_{(a)}$

c $n_{(a)}$ may be calculated analytically for any integer a (see text)

d $\Gamma(x)$ is the gamma function; for integer x, $\Gamma(x) = (x-1)!$

e As discussed in text the entries for n_n , etc., are only for $\beta/n_m < 1$

Figure Caption

Figure 1 Examples of $W(n)$ for logarithmic exponential (---), Gaussian (- -) and Schulz-Zimm (—) distribution functions for the indicated $D_N = n_w/n_n - 1$. The latter, with $D_N = 1$ also represents the exponential and Flory-Schulz functions. All curves are calculated with $n_n = 100$, but are essentially unchanged with other n_n , except in some cases for small n_n .

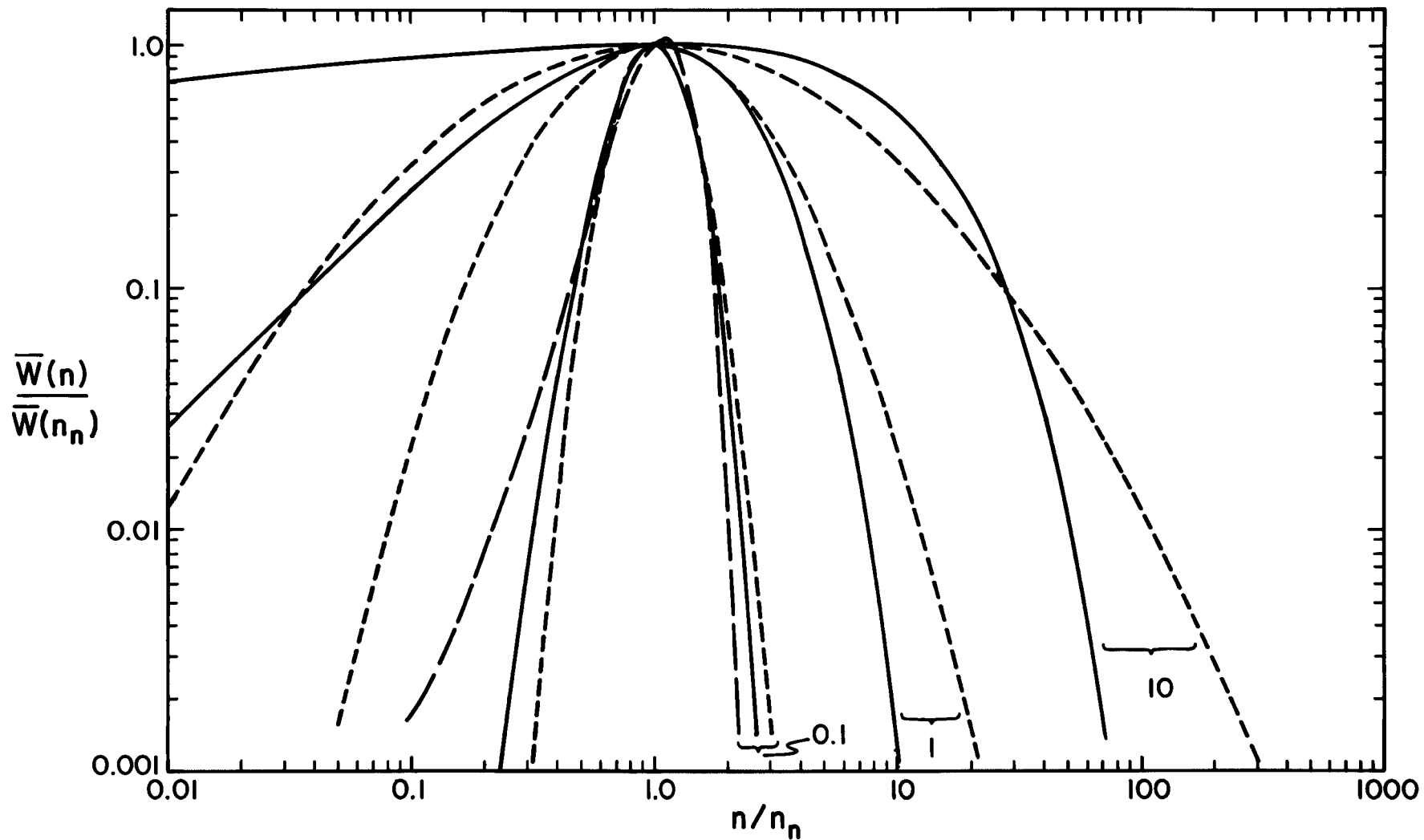


Figure 1 Examples of $\overline{W}(n)$ for logarithmic exponential (---), Gaussian (---) and Schulz-Zimm (—) distribution functions for the indicated $D_N = n_w/n_n - 1$. The latter, with $D_N = 1$ also represents the exponential and Flory-Schulz functions. All curves are calculated with $n_n = 100$, but are essentially unchanged with other n_n , except in some cases for small n_n .

