Definitions of terms relating to individual macromolecules, macromolecular assemblies, polymer solutions, and amorphous bulk polymers (IUPAC Recommendations 2014)

Abstract: This document defines terms relating to the properties of individual macromolecules, macromolecular assemblies, polymer solutions, and amorphous bulk polymers. In the section on polymer solutions and amorphous bulk polymers, general and thermodynamic terms, dilute solutions, phase behaviour, transport properties, scattering methods, and separation methods are considered. The recommendations are a revision and expansion of the IUPAC terminology published in 1989 dealing with individual macromolecules, macromolecular assemblies, and dilute polymer solutions. New terms covering the principal theoretical and experimental developments that have occurred over the intervening years have been introduced. Polyelectrolytes are not included.

Keywords: amorphous polymers; bulk polymers; IUPAC Polymer Division; macromolecular assemblies; macromolecules; polymer phase behaviour; polymer solutions; polymer thermodynamics; scattering properties; separation methods; transport properties.

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Preamble

This document is part of a series published by the Subcommittee on Polymer Terminology and formerly by the Commission on Macromolecular Nomenclature dealing with definitions of terms in polymer science [1]. The recommendations presented here are a revision and expansion of the terminology dealing with individual macromolecules, their assemblies and dilute polymer solutions [2]. In particular, the terms dealing with polymer solutions have been augmented by those related to semi-dilute and concentrated polymer solutions, and amorphous bulk polymers. The areas now covered are individual macromolecules, assemblies of macromolecules, polymer solutions and amorphous bulk polymers, general and thermodynamic terms, dilute solutions, phase behaviour, transport properties, scattering properties, and separation methods. For terms related to other aspects of macromolecules and polymer materials, the reader is referred to the Compendium of Polymer Terminology and Nomenclature [1]. Polyelectrolytes are not included in the present definitions.

1 Individual macromolecules

1.1 relative molecular mass, \( M_r \)

- molecular weight

Ratio of the mass of a molecule to the unified atomic mass unit [3].

Note 1: The unified atomic mass unit is one-twelfth of a carbon-12 atom in its nuclear and electronic ground state [3].

Note 2: Relative molecular mass or molecular weight is a pure number and must not be associated with any units.

Note 3: The term “molecular” may also be used for an entity consisting of more than one molecule, such as a complex, an aggregate, a micelle, etc.

Note 4: See molar mass and relative molar mass.

1.2 degree of polymerization (DP), \( X \)

Number of monomeric units in a macromolecule, an oligomer molecule, a block, or a chain.

1.3 chain (in polymer science)

Whole or part of a macromolecule, an oligomer molecule, or a block, comprising a linear or branched sequence of constitutional units between two boundary constitutional units, each of which may be either an end-group, a branch point, or an otherwise-designated characteristic feature of the macromolecule [4].
Note 1: Except in linear single-strand macromolecules, the definition of a chain may be somewhat arbitrary. The following definitions in this section that involve “chains” have been developed based on single-strand chains. However, they can sometimes be applied to other types of chain, such as ladder or spiro chains.

Note 2: A cyclic macromolecule has no end-groups but may nevertheless be regarded as a chain.

Note 3: Any integer number of branch points may be present between the chosen boundary units.

1.4 chain segment

- segment

Group of contiguous skeletal atoms in a chain, including their side groups, if any, such that the chain itself can be represented as a chain of segments.

1.5 short-range intramolecular interaction

Steric or other interaction involving atoms or groups or both situated within a few skeletal bonds of each other along a chain.

Note 1: The interacting atoms or groups are typically separated by fewer than 10 consecutive skeletal bonds in a chain.

Note 2: If no ambiguity between intramolecular interaction and intermolecular interaction can arise, the word “intramolecular” may be omitted.

1.6 long-range intramolecular interaction

Interaction between segments, widely separated in sequence along a chain, that occasionally approach one another during molecular flexing.

Note 1: This type of interaction is closely related to the excluded volume of a segment, the latter quantity reflecting net interactions involving segments from all the molecules in a solution and the solvent molecules.

Note 2: If no ambiguity between intramolecular interaction and intermolecular interaction can arise, the word “intramolecular” may be omitted.

1.7 conformer

One of a set of stereoisomers, each of which is characterized by a conformation corresponding to a distinct energy minimum [3].

1.8 rotamer

- rotational isomer

One of a set of conformers arising from restricted rotation about one single bond [3].
1.9 rotational isomeric state (in polymer science)

- bond-conformational state (in polymer science)

Rotamer defined by a relative rotation about a skeletal bond of a single-strand chain.

Note 1: A rotational isomeric state is conventionally defined over a sequence of three contiguous skeletal bonds with reference to the dihedral (or torsion) angle ($\phi$) between the planes defined by the first two bonds and the second two bonds. For example, for a chain composed of single C–C skeletal bonds, $\phi \approx 0^\circ$ can be used to define the (planar) trans ($t$) rotational isomeric state, and $\phi \approx \pm 120^\circ$ to define the gauche± ($g_{\pm}$) rotational isomeric states.

Note 2: Alternative notations exist. For example, $\phi = 180^\circ$, $\pm 60^\circ$, respectively, can be used to denote the $t$ and $g_{\pm}$ states, which can also be given the symbols T, $G^+$, and $G^-$ [5]. The trans and gauche states or conformers are also known as the “antiperiplanar conformers” and “synclinal conformers” [3, 6]. The notation used in Note 1 is that introduced by Flory and co-workers [5] and is now the one most frequently used in polymer science.

Note 3: The energies of rotational isomeric states are determined by short-range intramolecular interactions.

1.10 chain conformation

Conformation of a chain as defined by its sequence of bond-conformational states.

Note: If no ambiguity results, the word “chain” can be omitted.

1.11 unperturbed dimensions

Dimensions of a macromolecule subject hypothetically to only short-range intramolecular interactions, or subject to short-range and long-range intramolecular interactions and in a theta state of a polymer solution or in the amorphous bulk state.

Note: For linear flexible macromolecules, dimensions are usually expressed as the various averages (moments) of the distributions of the end-to-end distance and the radius of gyration and, for nonlinear flexible macromolecules, the moments of the distribution of the radius of gyration are normally used.

1.12 unperturbed conformational state

Chain conformation corresponding to unperturbed dimensions.

1.13 perturbed dimensions

Dimensions of a macromolecule in a polymer solution not in a theta state.

Note: See Note to Definition 1.11 for an explanation of the meaning of “dimensions”.

1.14 radius of gyration, $s$, unit: nm or SI unit: m

For a macromolecule composed of $n$ mass elements, of masses $m_i$, $i = 1, 2, ..., n$, located at fixed distances $s_i$ from the centre of mass, the radius of gyration is the square-root of the mass average of $s_i^2$ over all mass elements, i.e.,
\[
\sqrt{\frac{\sum_{i=1}^{n} m_i s_i^2}{\sum_{i=1}^{n} m_i}}
\]

Note: The mass elements are usually taken as the masses of the skeletal groups constituting the macromolecule, e.g., \(-\text{CH}_2-\) in poly(methylene).

1.15 **unperturbed radius of gyration**, \(s_o\), unit: nm or SI unit: m

Radius of gyration of a macromolecule in an unperturbed conformational state.

1.16 **root-mean-square radius of gyration**, \(<s^2>^{1/2}, R_g\), unit: nm or SI unit: m

For a flexible macromolecule composed of \(n\) mass elements, of masses \(m_i, i = 1, 2, \ldots, n\), located at statistical-mechanical mean-square distances \(<s_i^2>\) from the centre of mass, the root-mean-square radius of gyration is the square-root of the mass average of \(<s_i^2>\) over all mass elements, i.e.,

\[
<s^2>^{1/2} = \left(\frac{\sum_{i=1}^{n} m_i <s_i^2>}{\sum_{i=1}^{n} m_i}\right)^{1/2}
\]

Note 1: The mass elements are usually taken as the masses of the skeletal groups constituting the macromolecule, e.g., \(-\text{CH}_2-\) in poly(methylene).

Note 2: \(<s_i^2>\) is the statistical mechanical average of \(s_i^2\) over all chain conformations.

Note 3: The radius of gyration is a parameter characterizing the size of a macromolecule as a time-averaged spherical domain in laboratory coordinates.

1.17 **mean-square radius of gyration**, \(<s^2>\), unit: nm\(^2\) or SI unit: m\(^2\)

For a flexible macromolecule composed of \(n\) mass elements, of masses \(m_i, i = 1, 2, \ldots, n\), located at statistical-mechanical mean-square distances \(<s_i^2>\) from the centre of mass, the mean-square radius of gyration is the mass average of \(<s_i^2>\) over all mass elements, i.e.,

\[
<s^2> = \left(\frac{\sum_{i=1}^{n} m_i <s_i^2>}{\sum_{i=1}^{n} m_i}\right)
\]

1.18 **root-mean-square unperturbed radius of gyration**, \(<s_o^2>^{1/2}, s_o\), unit: nm or SI unit: m\(^2\)

Root-mean-square radius of gyration of a macromolecule having unperturbed dimensions.

Note 1: The traditionally used symbol \(<s_o^2>^{1/2}\) is not recommended as it signifies the square root of the unperturbed average, namely, \(< >^{1/2}\) of \(s^2\) rather than the root-mean-square, namely, \(< >^{1/2}\) of the unperturbed squared radius, \(s_o^2\).

1.19 **mean-square unperturbed radius of gyration**, \(<s_o^2>\), unit: nm\(^2\) or SI unit: m\(^2\)

Mean-square radius of gyration of a macromolecule having unperturbed dimensions.
1.20 **end-to-end vector**, \( r \), unit: nm or SI unit m

Vector connecting the two ends of a linear *chain* in a particular *conformation*.

1.21 **unperturbed end-to-end vector**, \( r_o \), unit: nm or SI unit m

Vector connecting the two ends of a linear *chain* in a particular *conformation*, with the chain having *unperturbed dimensions*.

1.22 **end-to-end distance**, \( r \), unit: nm or SI unit m

Magnitude of the *end-to-end vector*.

1.23 **unperturbed end-to-end distance**, \( r_o \), unit: nm or SI unit m

Magnitude of the *unperturbed end-to-end vector*.

1.24 **root-mean-square end-to-end distance**, \(<r^2>^{1/2}\), unit: nm or SI unit m

Square root of the statistical-mechanical mean-square *end-to-end distance* of a linear *chain* averaged over all *chain conformations*.

*Note:* If no ambiguity results, the term “end-to-end distance” can be used.

1.25 **mean-square end-to-end distance**, \(<r^2>\), unit: nm\(^2\) or SI unit m\(^2\)

Statistical-mechanical mean-square *end-to-end distance* of a linear *chain* averaged over all *chain conformations*.

1.26 **root-mean-square unperturbed end-to-end distance**, \(<r_o^2>^{1/2}\), unit: nm or SI unit m

Root-mean-square *end-to-end distance* of a *chain* having *unperturbed dimensions*.

*Note:* If no ambiguity results, the term “unperturbed end-to-end distance” can be used.

1.27 **mean-square unperturbed end-to-end distance**, \(<r_o^2>\), unit: nm\(^2\) or SI unit m\(^2\)

Mean-square *end-to-end distance* of a *chain* having unperturbed dimensions.

*Note:* \(<r_o^2>\) of a hypothetical, sufficiently long, linear *chain* of identical single skeletal bonds having *rotational isomorphic states* that are independent of each other is given by the equation

\[
<r_o^2> = n l^2 \frac{(1+\cos \theta)(1+<\cos \phi>)}{(1-\cos \theta)(1-<\cos \phi>)}
\]  

(1)

where \( n \) is the number of skeletal bonds of length \( l \) and valence-angle supplement \( \theta \), and \(<\cos \phi>\) is the average of the cosine of the dihedral angles \( \phi \) defined over sequences of three contiguous skel-
etal bonds. This equation is useful for understanding the significance of characteristic ratio, steric factor, and effective bond-length.

1.28 characteristic ratio, $C_n (C_\infty$ when $n \to \infty)$

Ratio of the mean-square unperturbed end-to-end distance of a linear chain to $n<l^2>$, where $n$ is the number of skeletal bonds in the chain and $<l^2>$ is the mean-square skeletal bond length, i.e.,

$$C_n = \frac{<r^2>}{n<l^2>}$$

**Note 1:** $<l^2> = \sum_{i=1}^{n} l_i^2 / n$. For a chain of identical skeletal bonds of length $l$, $<l^2> = F$.

**Note 2:** For a hypothetical, sufficiently long linear chain of identical single skeletal bonds having rotational isomeric states that are independent of each other, eq. 1 in Definition 1.27 shows that the value of $C_n$ depends on the values of $\cos \theta$ and $<\cos \phi>$. In general, for actual chains, the value of $C_n$ is still characteristic of the values of the valence angles of the skeletal bonds and of the dihedral bond-conformational angles, although it may be difficult to write an analytical expression for $C_n$.

1.29 freely rotating chain

Hypothetical chain, free from short-range and long-range intramolecular interactions, consisting of infinitely thin rectilinear skeletal bonds, with the dihedral angles of sequences of three contiguous skeletal bonds assuming all values with equal probability.

1.30 root-mean-square end-to-end distance of a freely rotating chain, $<r^2_{o,f}>^{1/2}$, unit: nm or SI unit: m

Root-mean-square end-to-end distance of a linear freely rotating chain.

**Note:** If no ambiguity results, the term “freely rotating end-to-end distance” can be used.

1.31 mean-square end-to-end distance of a freely rotating chain, $<r^2_{o,f}>$, unit: nm$^2$ or SI unit m$^2$.

Mean-square end-to-end distance of a linear freely rotating chain.

**Note:** $<r^2_{o,f}>$ of a hypothetical, sufficiently long, linear freely rotating chain of identical single skeletal bonds is given by the equation

$$<r^2_{o,f}> = nl^2 \left( \frac{1+\cos \theta}{1-\cos \theta} \right)$$

where $n$ is the number of skeletal bonds of length $l$ and valence-angle supplement $\theta$.

1.32 steric factor, $\sigma$

Square root of the ratio of the mean-square unperturbed end-to-end distance of a chain to that of the freely rotating chain of the same structure, in the limit of infinite chain length, i.e.,
\[ \sigma = \left( \frac{<r_\sigma^2>}{<r_\phi^2>} \right)^{1/2} \]

**Note 1:** The steric factor is a type of characteristic ratio relating to *chain* structure, cf., *characteristic ratio*.

**Note 2:** The value of the steric factor reflects the effect of hindrance to free rotation. For a hypothetical, sufficiently long chain of identical single skeletal bonds having *rotational isomeric states* that are independent of each other, eqs. 1 and 2 in Definitions 1.27 and 1.31, respectively, show that the value of \( \sigma \) depends on the value of \( <\cos \phi> \). In general, for actual chains, the value of \( \sigma \) is still characteristic of the values of the dihedral bond-conformational angles, although it may be difficult to write an analytical expression for \( \sigma \).

**Note 3:** The value of \( \sigma \) can be used as a measure of the stiffness of a linear chain.

### 1.33 Effective Bond Length, \( b \), unit: nm or SI unit: m

Square root of the ratio of the *unperturbed mean-square end-to-end distance* of a linear *chain* to its number of skeletal bonds, i.e.,

\[ b = \left( \frac{<r^2>}{n} \right)^{1/2} \]

**Note 1:** The effective bond length is a type of characteristic ratio relating to chain structure, cf., *characteristic ratio*.

**Note 2:** \( b^2 \) is the unperturbed mean-square end-to-end distance per skeletal bond. For a hypothetical, sufficiently long chain of identical single skeletal bonds having *rotational isomeric states* that are independent of each other, eq. 1, in Definition 1.27 shows that the value of \( b \) depends on the values of \( l, \cos \theta \) and \( <\cos \phi> \). In general, for actual chains, the value of \( b \) is still characteristic of the values of the lengths and valence angles of the skeletal bonds and of the dihedral bond-conformational angles, although it may be difficult to write an analytical expression for \( b \).

### 1.34 Freely Jointed Chain

- **Random-Walk Chain**
- **Random-Flight Chain**

Hypothetical linear *chain* consisting of infinitely thin rectilinear *segments* (links) uniform in length, each of which can take all orientations in space with equal probability, independently of its neighbours.

**Note 1:** In a freely jointed chain, two or more links can occupy the same volume simultaneously.

**Note 2:** The *root-mean-square end-to-end distance* of a freely jointed chain consisting of \( m \) links, each of length \( l' \) is given by the equation

\[ <r^2>^{1/2} = m^{1/2}l' \]  

### 1.35 Contour Length, \( r_{max} \), unit: nm or SI unit: m

- **Fully Extended Chain Length**

Maximum *end-to-end distance* of a *chain*.

**Note 1:** For a *chain* of identical single skeletal bonds, the contour length is equal to the end-to-end distance of the chain in which the bonds all adopt the planar *trans* rotational isomeric state. For a chain of a more complex structure, only an approximate value of the contour length may be evaluated.
Note 2: The contour length of a freely jointed chain consisting of \( m \) links of length \( l' \) is given by the equation

\[
r_{\text{max}} = ml'
\]

(4)

Note 3: The sum of the lengths of all skeletal bonds of a single-strand polymer molecule is occasionally termed “contour length”. The use of the term in this sense is discouraged.

1.36 equivalent freely jointed chain

Hypothetical freely jointed chain with the same mean-square end-to-end distance and contour length as an actual linear chain having unperturbed dimensions.

Note: The number of links, \( m \), and their length, \( l' \), are evaluated from the mean-square end-to-end distance, \( <r_o^2> \), and contour length, \( r_{\text{max}} \), of the actual chain using eqs. 3 and 4 in Definitions 1.34 and 1.35, with

\[
m = \frac{r_{\text{max}}^2}{<r_o^2>} \quad \text{and} \quad l' = \frac{<r_o^2>}{r_{\text{max}}}
\]

For example, for polymethylene at room temperature, one freely jointed link is equivalent to about 10 actual C–C skeletal bonds.

1.37 Kuhn segment

- statistical segment
- equivalent freely jointed link

Segment or link of an equivalent freely jointed chain.

1.38 Kuhn segment length, \( l' \), \( l'_k \); unit: nm or SI unit: m

- statistical segment length
- freely jointed link length

Length of a Kuhn segment.

1.39 self-avoiding random-walk chain

Freely jointed chain subject to the condition that the segments cannot intersect one another.

Note 1: In the model of a self-avoiding chain, segments are considered to have a finite volume such that two or more cannot occupy the same volume simultaneously.

Note 2: The self-avoiding random-walk chain model is used to represent a polymer chain with excluded volume.

1.40 macromolecular coil

Depiction of a macromolecule in which its segments are distributed about some point in space.

Note: The point in space is usually chosen as the molecular centre of mass or a chain end.
1.41 statistical coil

*Macromolecular coil* adopted by a flexible macromolecule in solution, or in amorphous bulk polymer.

*Note:* A statistical coil can refer to a flexible macromolecule having *perturbed dimensions* or in the *theta state*.

1.42 random coil

- Gaussian coil

*Statistical coil* adopted by a linear, single-strand macromolecule in solution in the *theta state*, or in amorphous bulk polymer.

*Note:* The probability density of *end-to-end vectors* of a macromolecule forming a random coil follows a Gaussian distribution.

1.43 worm-like chain

- *Kratky–Porod chain*

Hypothetical, infinitely thin linear *chain* of continuous curvature, with the direction of curvature at any point being random.

*Note:* The model can be used to describe chains of different degrees of flexibility, from *freely jointed chains* to rigid rods, and is particularly useful for representing stiff, single-strand, and multi-strand chains.

1.44 persistence length, $a$, unit: nm or SI unit: m

For a linear *chain*, the average projection of the *end-to-end vector* on the tangent to the chain contour at a chain end in the limit of infinite chain length.

*Note 1:* The persistence length is the basic characteristic of the *worm-like chain*.

*Note 2:* The persistence length is equal to one-half of the *Kuhn segment length* of the equivalent freely jointed chain ($a = l'/2$).

1.45 chain stiffness

Parameter describing the *end-to-end distance* of a linear, single-strand macromolecular *chain* having *unperturbed dimensions* relative to that of a model macromolecular chain not subject to short-range interactions.

*Note:* The *steric factor*, $a$, *Kuhn segment length*, $l'$, and *persistence length*, $a$, are all measures of chain stiffness.

1.46 short-chain branch

Oligomeric offshoot from a macromolecular *chain* [1].

1.47 long-chain branch

Macromolecular offshoot from a macromolecular *chain* [1].
1.48 \( g \)-factor, \( g \)

- radius of gyration contraction factor
- contraction factor
- geometric contraction factor

Ratio of the mean-square radius of gyration of a branched molecule, \(<s'_g^2>\), to that of an otherwise identical linear molecule, \(<s'_l^2>\), of the same relative molecular mass in the same solvent at the same temperature, i.e.,

\[ g = \frac{<s'_g^2>}{<s'_l^2>} \]

Note: The \( g \)-factor is a quantity characterizing the effects of long-chain branches on the size of a branched molecule. Compare Definition 1.49.

1.49 \( g' \)-factor, \( g' \)

- viscosity contraction factor
- hydrodynamic contraction factor

Ratio of the intrinsic viscosity of a branched molecule, \([\eta_b]\), to that of an otherwise identical linear molecule, \([\eta_l]\), of the same relative molecular mass in the same solvent at the same temperature, i.e.,

\[ g' = \frac{[\eta_b]}{[\eta_l]} \]

Note: The \( g' \)-factor is a quantity characterizing the effects of long-chain branches on the size of a branched molecule. Compare Definition 1.48.

2 Assemblies of macromolecules

2.1 compositional heterogeneity

Variation in elemental composition from molecule to molecule usually found in copolymers.

2.2 constitutional heterogeneity

Variation in constitution from molecule to molecule in polymers with molecules uniform with respect to elemental composition.

Note: An example is a polymer composed of linear and branched molecules; another example is a statistical copolymer comprising two isomeric constitutional units.

2.3 uniform polymer

- molecularly uniform polymer

Polymer composed of molecules uniform with respect to relative molecular mass and constitution.

Note 1: A polymer comprising a mixture of linear and branched chains, all of uniform relative molecular mass, is not uniform.

Note 2: A copolymer comprising linear molecules of uniform relative molecular mass and uniform elemental composition, but different sequence arrangement of the various types of monomeric units, is not uniform (e.g., a copolymer comprising molecules with random arrangement as well as block arrangement of monomeric units).
Note 3: A polymer uniform with respect only to either relative molecular mass or constitution may be termed “uniform”, provided a suitable qualifier is used (e.g., “a polymer uniform with respect to relative molecular mass”).

Note 4: The adjectives “monodisperse” and “polydisperse” are deeply rooted in the literature despite their being non-descriptive and self-contradictory. The terms “uniform” and “non-uniform” are now the preferred adjectives. See also dispersity, Definition 2.26.

2.4 non-uniform polymer

- molecularly non-uniform polymer

Polymer comprising molecules non-uniform with respect to relative molecular mass or constitution, or both.

Note: See Definition 2.3, Notes 1–4.

2.5 molar mass, $M$, unit: $\text{g mol}^{-1}$ or SI unit: $\text{kg mol}^{-1}$

Mass divided by amount of substance.

Note 1: In the present context, “amount of substance” is the number of molecules divided by the Avogadro constant, $N_A = 6.022 141 79 (30) \times 10^{23} \text{mol}^{-1}$ [3].

Note 2: If the unit $\text{g mol}^{-1}$ unit is used, the numerical values of molar mass, relative molecular mass and relative molar mass are equal.

Note 3: The term “molar” may also be used for entities consisting of more than one molecule, such as complexes, aggregates, micelles, etc.

2.6 relative molar mass, $M_r$

Molar mass divided by 1 g mol$^{-1}$ [3].

Note 1: The quantity 1 g mol$^{-1}$ is sometimes called the standard molar mass.

Note 2: Relative molar mass and molecular weight have identical numerical values.

2.7 molar-mass average, $M_k$, unit: $\text{g mol}^{-1}$ or SI unit: $\text{kg mol}^{-1}$

- molecular-weight average, $M_{w,k}$
- relative-molar-mass average, $M_{r,k}$
- relative-molecular-mass average, $M_{r,k}$

Any average of the molar mass, molecular weight, relative molar mass, or relative molecular mass for a non-uniform polymer, with the symbol $k$ specifying the type of average.

Note 1: The various symbols that $k$ can be are given in terms 2.8 to 2.12. For example, with $k = n$, number-average quantities are defined.

Note 2: An infinite number of molar-mass averages can in principle be defined, but only a few types of averages are directly accessible experimentally. The most important averages are defined in terms of simple moments of the distribution functions and are obtained by methods applied to systems in thermodynamic equilibrium, such as osmometry, static light scattering, and sedimentation equilibrium. Hydrodynamic methods, as a rule, yield more complex molar-mass averages.

Note 3: Any molar-mass average can be defined in terms of mass fractions or mole fractions. In this document, the most important molar-mass averages are defined in terms of the mass fraction, $w_M$, of the...
species of molar mass $M$. These definitions are most closely related to experimental determinations of molar-mass averages.

Note 4: The last three names are synonyms. The quantities are dimensionless (pure numbers) and are not associated with any units.

2.8 number-average molar mass, $M_n$, unit: g mol$^{-1}$ or SI unit: kg mol$^{-1}$

$$M_n = \frac{1}{\sum_i (\frac{w_i}{M_i})}$$

- number-average molecular weight, $M_{r,n}$
- number-average relative molar mass, $M_{r,n}$
- number-average relative molecular mass, $M_{r,n}$

$$M_{r,n} = \frac{1}{\sum_i (\frac{w_i}{M_i})}$$

Note 1: For definitions of symbols, see Definition 2.7.

Note 2: The last three names are synonyms. The quantities are dimensionless (pure numbers) and are not associated with any units.

2.9 mass-average molar mass, $M_m$, $M_w$, unit: g mol$^{-1}$ or SI unit kg mol$^{-1}$

$$M_m = M_w = \sum_i w_i M$$

- mass-average molecular weight, $M_{r,m}$, $M_{r,w}$
- mass-average relative molar mass, $M_{r,m}$
- mass-average relative molecular mass, $M_{r,m}$

$$M_{r,m} = M_{r,w} = \sum_i w_i M_i$$

Note 1: For definitions of symbols, see Definition 2.7.

Note 2: The last three names are synonyms. The quantities are dimensionless (pure numbers) and are not associated with any units.

2.10 $z$-average molar mass, $M_z$, SI unit: g mol$^{-1}$ or kg mol$^{-1}$

$$M_z = \frac{\sum_i w_i M^2}{\sum_i w_i M}$$
- z-average molecular weight, $M_{r,z}$
- z-average relative molar mass, $M_{r,z}$
- z-average relative molecular mass, $M_{r,z}$

\[
M_{r,z} = \frac{\sum_{M} w_M M^2}{\sum_{M} w_M M^1}
\]

Note 1: For definitions of symbols, see Definition 2.7.
Note 2: The last three names are synonyms. The quantities are dimensionless (pure numbers) and are not associated with any units.

2.11 (z + 1)-average molar mass, $M_{z+1}$, unit: g mol$^{-1}$ or SI unit: kg mol$^{-1}$

\[
M_{z+1} = \frac{\sum_{M} w_M M^3}{\sum_{M} w_M M^2}
\]

- (z + 1)-average molecular weight, $M_{r,z+1}$
- (z + 1)-average relative molar mass, $M_{r,z+1}$
- (z + 1)-average relative molecular mass, $M_{r,z+1}$

\[
M_{r,z+1} = \frac{\sum_{M} w_M M^3}{\sum_{M} w_M M^2}
\]

Note 1: For definitions of symbols, see Definition 2.7.
Note 2: The last three names are synonyms. The quantities are dimensionless (pure numbers) and are not associated with any units.

2.12 viscosity-average molar mass, $M_{\eta}$, unit: g mol$^{-1}$ or SI unit kg mol$^{-1}$

\[
M_{\eta} = \left[ \sum_{M} w_M M^a \right]^{1/a}
\]

- viscosity-average molecular weight, $M_{\eta,v}$
- viscosity-average relative molar mass, $M_{\eta,v}$
- viscosity-average relative molecular mass, $M_{\eta,v}$

\[
M_{\eta,v} = \left[ \sum_{M} w_M M^a \right]^{1/a}
\]

where $a$ is the exponent in the Mark–Houwink equation, $[\eta] = KM^a$.

Note 1: For definitions of symbols, see Definition 2.7.
Note 2: The last three names are synonyms. The quantities are dimensionless (pure numbers) and are not associated with any units.

Note 3: The exponent $a$ is different from the adjustable parameter of some of the distribution functions and from the persistence length.
2.13 apparent molar mass, $M_{\text{app}}$, SI unit: g mol$^{-1}$ or kg mol$^{-1}$

- apparent molecular weight, $M_{\text{app}}$
- apparent relative molar mass, $M_{\text{app}}$
- apparent relative molecular mass, $M_{\text{app}}$

Molar mass, molecular weight, relative molar mass, or relative molecular mass calculated from experimental data without the application of appropriate corrections.

Note 1: The last three names are synonyms. The quantities are dimensionless (pure numbers) and are not associated with any units.

Note 2: Examples of corrections are those for finite polymer concentration, association, preferential solvation, compositional heterogeneity, constitutional heterogeneity, and also from experimental data obtained from an instrument (often an SEC instrument) calibrated using standard samples of known molar masses of a polymer constitutionally different from that being analysed.

2.14 polymolecularity correction

Correction applied to a relationship between a property and the molar mass or relative molecular mass, determined experimentally for a polymer non-uniform with respect to relative molecular mass, in order to obtain the corresponding relationship for a polymer uniform with respect to relative molecular mass.

2.15 average degree of polymerisation, $X_k$

Any average of the degree of polymerization of a polymer, where $k$ specifies the type of average.

Note: For a homopolymer, Definitions 2.7–2.12 apply directly to averages of the degree of polymerisation when $X$ is substituted for $M_r$ in the formulae.

2.16 distribution function (in polymer science)

- distribution (in polymer science)

Normalized function giving the relative amount of a portion of a polymer with a specific value, or a range of values, of a random variable or variables.

Note 1: A distribution function may be discrete, i.e., take on only certain specified values of the random variable(s), or continuous, i.e., take on any intermediate value of the random variable(s), in a given range. Most distributions in polymer science are intrinsically discrete, but it is often convenient to regard them as continuous or to use distribution functions that are inherently continuous.

Note 2: A distribution function may be an integral (or cumulative) distribution function or distribution, i.e., one giving the proportion of the population for which a random variable is less than or equal to a given value. Alternatively it may be a differential distribution function (or probability density function) or distribution, i.e., one giving the (maybe infinitesimal) proportion of the population for which the random variable(s) is (are) within a (maybe infinitesimal) interval of its (their) range(s).

Note 3: Normalization requires that: (i) for a discrete differential distribution function, the sum of the function values over all possible values of the random variable(s) be unity; (ii) for a continuous differential distribution function, the integral over the entire range of the random variable(s) be unity; (iii) for an integral (cumulative) distribution function, the function value at the upper limit of the random variable(s) be unity.
2.17 number-distribution function, $f_n$

- differential number-distribution function
- number distribution
- differential number distribution

Differential distribution function in which the relative amount of a portion of a substance with a specific value, or a range of values, of the random variable(s) is expressed in terms of mole fraction.

2.18 cumulative number-distribution function, $F_n$

- integral number-distribution function
- cumulative number distribution
- integral number distribution

Cumulative distribution function in which the relative amount of a portion of a substance with values of the random variable or variables less than or equal to a given value or given values is expressed in terms of mole fraction.

2.19 mass-distribution function, $f_m, f_w$

- differential mass-distribution function
- mass distribution
- differential mass distribution

Differential distribution function in which the relative amount of a portion of a substance with a specific value, or a range of values, of the random variable(s) is expressed in terms of mass fraction.

2.20 cumulative mass-distribution function, $F_m, F_w$

- integral mass-distribution function
- cumulative mass distribution
- integral mass distribution

Cumulative distribution function in which the relative amount of a portion of a substance with values of the random variable or variables less than or equal to a given value or given values is expressed in terms of mass fraction.

*Note*: It is the differential and cumulative mass-distribution functions that are usually determined experimentally.

2.21 Schulz–Zimm distribution

Continuous distribution with differential number-distribution function of the form

$$f_n(X)\,dX = \frac{a^b}{\Gamma(b)} X^{b-1} \exp(-aX)\,dX$$
where $X$ is the degree of polymerisation, $a$ and $b$ are positive adjustable parameters, and $\Gamma(b)$ is the gamma function of argument $b$.

**Note 1:** This distribution is equivalent to the Pearson Type III distribution [7].

**Note 2:** For a sample of polymer in which the values of degree of polymerisation and relative molar mass are directly proportional to each other, the Schulz–Zimm differential mass-distribution function is

$$f_m(X) dX = \frac{a^{b-1}}{\Gamma(b+1)} X^b \exp(-aX) dX$$

### 2.22 Most probable distribution

- *Flory distribution*
- *Schulz–Flory distribution*

Discrete distribution with differential number-distribution function of the form

$$f_n(X) = a(1-a)^{X-1}$$

where $X$ is the degree of polymerisation and $0 < a \leq 1$.

**Note 1:** For large values of $X$, the most probable distribution converges to the particular case of the Schulz–Zimm distribution with $b = 1$.

**Note 2:** For a sample of polymer in which the values of degree of polymerisation and relative molar mass are directly proportional to each other, the most probable differential mass-distribution function is

$$f_m(X) = a^2 X(1-a)^{X-1}$$

### 2.23 Poisson distribution

Discrete distribution with differential number-distribution function of the form

$$f_n(X) = \frac{e^{-a} a^{X-1}}{(X-1)!}$$

where $X$ is the degree of polymerisation and $a \geq 0$.

**Note:** For a sample of polymer in which the values of degree of polymerisation and relative molar mass are directly proportional to each other, the Poisson differential mass-distribution function is

$$f_m(X) = \frac{Xe^{-a} a^{X-1}}{(a+1)(X-1)!}$$

### 2.24 Tung distribution

Continuous distribution with differential number-distribution function of the form

$$f_n(X) dX = \frac{a^{\left[1-(1/b)\right]} bX^{b-2} \exp(-aX^b)}{\Gamma\left[1-(1/b)\right]} dX$$
where \( X \) is the degree of polymerisation, \( a \geq 0 \) and \( b > 1 \).

**Note:** For a sample of polymer in which the values of degree of polymerisation and relative molar mass are directly proportional to each other, the Tung differential mass-distribution function is

\[
f_n(X)\,dX = \frac{abX^{b-1}\exp(-aX^b)}{\Gamma[1-(1/b)]}\,dX
\]

### 2.25 logarithmic normal distribution

- **log-normal distribution**

Continuous distribution with differential number-distribution function of the form

\[
f_n(X)\,dX = \frac{b}{aX^2\sqrt{\pi}}\exp\left(-\frac{1}{a^2}\left[\frac{\ln\left(\frac{X}{b}\right)}{b}\right]^2-\frac{a^2}{4}\right)\,dX
\]

where \( X \) is the degree of polymerisation and \( a, b \geq 0 \).

**Note:** For a sample of polymer in which the values of degree of polymerisation and relative molar mass are directly proportional to each other, the logarithmic normal differential mass-distribution function is

\[
f_n(X)\,dX = \frac{b}{aX\sqrt{\pi}}\exp\left(-\frac{1}{a^2}\left[\frac{\ln\left(\frac{X}{b}\right)}{b}\right]^2\right)\,dX
\]

### 2.26 molar-mass dispersity, \( D_M \)

- molecular-weight dispersity
- relative-molar-mass dispersity
- relative-molecular-mass dispersity

Ratio of the mass-average molar mass, \( M_m \), molecular weight, relative molar mass, or relative molecular mass, \( M_{r,m} \), to the number-average molar mass, \( M_n \), molecular weight, relative molar mass, or relative molecular mass, \( M_{r,n} \) [8].

\[
D_M = \frac{M_m}{M_n} = \frac{M_{r,m}}{M_{r,n}}
\]

**Note:** Use of the term “polydispersity index”, or other terms involving the word “polydispersity”, for \( M_m/M_n, M_{r,m}/M_{r,n} \) is strongly discouraged.

### 2.27 degree-of-polymerisation dispersity, \( D_X \)

Ratio of the mass-average degree of polymerisation, \( X_m \), to the number-average degree of polymerisation, \( X_n \) [8].

\[
D_X = \frac{X_m}{X_n}
\]

**Note:** Use of the term “polydispersity index”, or other terms involving the word “polydispersity”, for \( X_m/X_n \) is strongly discouraged.
2.28 dispersity, $D$

Ratio of $M_m$ to $M_n$, or the ratio of $X_m$ to $X_n$ for a homopolymer or an alternating copolymer of sufficiently large molar mass, such that the effects of the distinct structures of the end-groups of the constituent macromolecules can be neglected, giving $X_n$ directly proportional to $M_n$, $X_m$ directly proportional to $M_m$ and $D_m = D_X = D$ [8].

Note 1: Dispersity is a measure of the dispersion (or spread) of a molar-mass, molecular-weight, relative-molar-mass, relative-molecular-mass, or degree-of-polymerization distribution function. For a uniform polymer, $D = 1$; for a polymer of sufficiently high $X_n$ having a Poisson distribution of molar masses, molecular weights, relative-molar-masses, or relative-molecular-masses, $D \approx 1$; and for a polymer of sufficiently high $X_n$ having a most-probable distribution of molar masses, molecular weights, relative-molar-masses, or relative-molecular-masses, $D \approx 2$.

Note 2: For a copolymer that is not an alternating copolymer $X_n$ cannot be considered to be directly proportional to $M_n$, nor $X_w$ directly proportional to $M_w$. It is then necessary to state whether $D_m$ or $D_X$ is being used.

3 Polymer solutions and amorphous bulk polymers

3.1 General and thermodynamic terms

3.1.1 dilute solution (in polymer science)

Solution in which the sum of the volumes of the domains occupied by the dissolved macromolecules or entities is substantially less than the total volume of the solution.

Note 1: The term "domain" refers to the smallest volume that contains a macromolecule or dissolved entity in its average shape.

Note 2: The definition is consistent with the definition given in the “Gold Book” [3]. The present definition is preferred in polymer science because of the importance of the concept of macromolecular domains.

3.1.2 cross-over concentration, $c^*$, unit: g cm$^{-3}$ or SI unit: kg m$^{-3}$

- overlap concentration

Concentration at which the sum of the volumes of the domains occupied by the dissolved macromolecules or entities is approximately equal to the total volume of the solution.

Note 1: For the meaning of the term “domain”, see Definition 3.1.1, Note 1.

Note 2: The cross-over concentration is not uniquely defined because different measurement techniques give different values.

Note 3: In physical chemistry, the symbol $c$ refers usually to amount concentration, but in polymer science it is generally used for mass concentration. The molar mass of a polymer is described by a distribution function rather than having a single value, hence, the amount concentration for a polymer solution cannot be precisely defined.

3.1.3 semi-dilute solution

Polymer solution in the concentration range at which the domains occupied by the dissolved macromolecules or entities start to overlap.

Note: The semi-dilute solution behaviour sets in at concentrations larger than the overlap concentration, $c^*$. 

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3.1.4 concentrated solution

Polymer solution in the concentration range at which the domains occupied by the dissolved macromolecules or entities overlap to such an extent that it is not possible to distinguish the individual domains from one another.

Note: The limiting maximum mass concentration is the density of the bulk amorphous polymer.

3.1.5 entanglement (in polymer science)

Entanglement, involving one or more macromolecular chains, of duration at least equal to the period of observation.

Note: A volume element, in which the chains of two or more macromolecules are entangled, acts as a temporary junction point of a transient polymer network, such as can occur in a semi-dilute solution or a concentrated solution.

3.1.6 mesh size (in polymer science), $\xi$, unit: nm or SI unit: m

Average distance between two adjacent entanglements on a given macromolecule in a semi-dilute solution, a concentrated solution, or bulk amorphous polymer.

3.1.7 blob

Hypothetical spherical volume element occupied by a subchain of a macromolecule between two neighbouring entanglements on the same macromolecule.

Note 1: The size of a blob is a scaling function of concentration and temperature.

Note 2: It is assumed that the behaviours of portions of a macromolecule separated by more than the size of a blob are not correlated with each other.

3.1.8 scaling law

Equation of the type $y = k x^a$, relating two physical quantities, $x$ and $y$, in which the value of the exponent $a$ can be predicted by theory.

Note 1: The constant $k$ cannot be predicted from theory and must be determined experimentally.

Note 2: It has been shown that scaling laws are particularly useful in the description of semi-dilute polymer solutions.

3.1.9 free volume, $v_f$, SI unit: m$^3$ kg$^{-1}$

Difference between specific volume of an amorphous polymer and that of its perfect crystalline form.

3.1.10 polymer–solvent interaction

Sum of the effects of all intermolecular interactions between polymer and solvent molecules in solution that are reflected in the values of the Gibbs and Helmholtz energies of mixing.
3.1.11 mean-field theory

Theory reducing the difficult exact evaluation of interactions in a multi-body system to a simpler but approximate evaluation of an average effective interaction of one body with its surroundings.

3.1.12 Flory–Huggins theory

- Flory–Huggins–Staverman theory

Statistical thermodynamic mean-field theory of polymer solutions, first formulated independently by Flory, Huggins, and Staverman, in which the thermodynamic properties of the solution are derived from a simple concept of combinatorial entropy of mixing and a reduced Gibbs-energy parameter, the $\chi$ parameter.

*Note:* Modified slightly from the definition in ref. [9].

3.1.13 chi parameter, $\chi$

- $\chi$ parameter
- chi interaction parameter
- $\chi$ interaction parameter

Numerical parameter employed in the Flory–Huggins theory, to account for the contribution of the non-combinatorial entropy of mixing and the enthalpy of mixing to the Gibbs energy of mixing.

*Note:* Modified slightly from the definition in ref. [9].

3.1.14 solubility parameter (of a polymer), $\delta$, unit: $\mu$Pa$^{1/2}$ = J$^{1/2}$ cm$^{-3/2}$ or SI unit: Pa$^{1/2}$ = J$^{1/2}$ m$^{-3/2}$

Parameter used in predicting the solubility of non-electrolytes (including polymers) in a given solvent. For a substance B:

$$\delta_B = \left( \frac{\Delta_{vap} E_{m,B}}{V_{m,B}} \right)^{1/2}$$

where $\Delta_{vap} E_{m}$ is the molar energy of vaporization at zero pressure and $V_{m}$ is the molar volume [3].

*Note 1:* For a polymer, the value of the solubility parameter is usually taken to be the value of the solubility parameter of the solvent producing the solution with maximum intrinsic viscosity or maximum swelling of a network of the polymer.

*Note 2:* For a substance of low molecular weight, the value of the solubility parameter can be estimated most reliably from the enthalpy of vaporization and the molar volume.

*Note 3:* The solubility of a substance B can be related to the square of the difference between the solubility parameters for supercooled liquid B and solvent at a given temperature, with appropriate allowances for entropy of mixing. Thus, a value of the solubility parameter of B can be estimated from the solubilities of solid B in a series of solvents of known solubility parameters.

3.1.15 preferential sorption

- selective sorption

Equilibrium phenomenon, operative in polymer solutions in multicomponent solvents, and in polymer networks swollen by multicomponent solvents, producing differences in solvent composition between that in
the polymer-containing regions and that in the pure solvent which is in thermodynamic equilibrium with the polymer-containing regions.

**3.1.16 selective solvent**

Medium that is a solvent for at least one component of a mixture of polymers, or for at least one type of block of a block or graft polymer, but a nonsolvent or poor solvent (see Definition 3.2.5, Note 2) for the other component(s) or other type(s) of block(s).

**3.1.17 co-solvency**

Dissolution of a polymer in a solvent comprising more than one component, each component of which, by itself, is a nonsolvent for the polymer.

**3.1.18 co-nonsolvency**

Decrease in solubility of a polymer in a solvent comprising more than one component, each component of which by itself is a solvent for the polymer.

*Note:* Poly(N-isopropylacrylamide) in water/methanol [9] and poly(vinyl alcohol) in dimethylsulfoxide/water [10] are examples of systems in which co-nonsolvency occurs.

**3.2 Dilute solutions**

**3.2.1 osmotic pressure, \( \Pi \), SI unit: Pa**

Excess pressure required to maintain osmotic equilibrium between a solution and the pure solvent separated by a membrane permeable only to the solvent

\[
\Pi = -\frac{RT}{V_s'} \ln a_s
\]

where \( V_s' \) and \( a_s \) are, respectively, the partial molar volume and activity of the incompressible solvent [3].

*Note:* For ideal dilute solutions, \( \Pi = c \frac{RT}{M_n} \), where the solute entities are individually moving molecules, ions, etc., regardless of their nature, \( c \) is the mass concentration of the solutes, and \( M_n \) is the number-average molar mass of the solutes.

**3.2.2 osmometer**

Apparatus for measuring osmotic pressure.

**3.2.3 osmometry**

Measurement of the osmotic pressure of a solution using an osmometer.

*Note:* The osmometry of a dilute solution of polymer is an absolute method for determining the number-average molar mass of the polymer and the osmotic virial coefficients of the solution.
3.2.4 osmotic virial coefficient, $A_i$, where $i = 1, 2, \ldots$, SI unit: mol kg$^{-1}$ m$^{3}$ kg$^{-1}$

- virial coefficient of the chemical potential

Coefficient in the expansion of the chemical potential of the solvent, $\mu_s$, in powers of the mass concentration, $c$, of the solute, i.e.,

$$\mu_s - \mu_s^0 = -\Pi V_s' = -RT\left(A_1 c + A_2 c^2 + A_3 c^3 + \ldots\right)$$

where $\mu_s^0$ is the chemical potential of the solvent in the reference state at the temperature of the system and ambient pressure, $\Pi$ is the osmotic pressure and $V_s'$ is the partial molar volume of the solvent. In solvents comprising more than one component, the definition applies to any solvent component.

**Note 1:** The first osmotic virial coefficient is the reciprocal number-average molar mass, i.e., $A_1 = 1 / M_n$.

The values of the second and higher virial coefficients, $A_2, A_3, \ldots$, respectively, are characteristic of polymer–solvent and polymer–polymer interactions.

**Note 2:** The factor $RT$ is sometimes included in the virial coefficients, to give

$$\mu_s - \mu_s^0 = -\Pi V_s' = -V_s'(A_1 c + A_2 c^2 + A_3 c^3 + \ldots), \quad \text{where} \quad A_i = RT A_i$$

**Note 3:** To evaluate $M_n$ and $A_2$, $\Pi/c$ is often plotted versus $c$, so that

$$\frac{\Pi}{c} = \left(\frac{\Pi}{c}\right)_0 \left(1 + \Gamma_2 c + \Gamma_3 c^2 + \ldots\right), \quad \text{where} \quad \left(\frac{\Pi}{c}\right)_0 = \frac{RT}{M_n}, \quad \text{and} \quad \Gamma_i = M_n A_i$$

3.2.5 thermodynamic quality of solvent

- quality of solvent

Qualitative characterization of the polymer–solvent interaction.

**Note 1:** The thermodynamic quality of a solvent depends on the Gibbs and Helmholtz energies of mixing of solvent and polymer.

**Note 2:** A solution of a polymer in a “good” solvent is characterized by a higher value of the second osmotic virial coefficient than a solution of the same polymer in a “poor” solvent.

3.2.6 theta state

- $\theta$ state

State of a polymer solution for which the second osmotic virial coefficient is zero.

**Note 1:** In some respects, a polymer solution in the theta state resembles an ideal solution and the theta state may be referred to as a pseudo-ideal state. However, a solution in the theta state must not be identified with an ideal solution.

**Note 2:** The solvent involved is often referred to as a theta solvent.

**Note 3:** It is assumed that the degree of polymerization of the polymer is high.

**Note 4:** In the theta state, the distances between pairs of segments in a flexible polymer chain follow Gaussian distributions and the chain has unperturbed dimensions.
3.2.7 **theta temperature**, θ, SI unit: K

- **θ temperature**

Temperature at which a polymer solution is in the *theta state*.

3.2.8 **excluded volume of a segment**

- **segmental excluded volume**

Volume from which a segment of a macromolecule in solution effectively excludes all other segments, i.e., those belonging to the same macromolecule as well as those belonging to other macromolecules.  
*Note:* The excluded volume of a segment depends on the *thermodynamic quality of the solvent*, and is not a measure of the geometrical volume of that segment.

3.2.9 **excluded volume of a macromolecule**

- **macromolecular excluded volume**

Volume from which a macromolecule in a *dilute solution* effectively excludes all other macromolecules.  
*Note:* The excluded volume of a macromolecule depends on the *thermodynamic quality of the solvent* and is not a measure of the geometrical volume of that macromolecule.

3.2.10 **thermodynamically equivalent sphere**

Hypothetical sphere, impenetrable to other thermodynamically equivalent spheres, displaying the same excluded volume as an actual macromolecule.

3.2.11 **expansion factor**, α, α_s, α_D, α_η

- **chain expansion factor**

Ratio of a linear dimensional characteristic of a macromolecule in a given solvent at a given temperature to the same dimensional characteristic in the *theta state* at the same temperature.  
*Note 1:* The most frequently used expansion factors are: expansion factor of the mean-square end-to-end distance, \( \alpha_e = \langle r^2 \rangle / \langle r_\theta^2 \rangle \); expansion factor of the mean-square radius of gyration, \( \alpha_s = \langle s^2 \rangle / \langle s_\theta^2 \rangle \); expansion factor of the translational diffusion, \( \alpha_D = \langle r_D^2 \rangle / \langle r_D^\theta \rangle \); where \( r_D \) is the *equivalent hydrodynamic radius* in translational diffusive flow and \( r_{D,\theta} \) is the corresponding radius in the *theta state* at the same temperature as that used to measure \( r_D \); expansion factor of the intrinsic viscosity, \( \alpha_\eta = [\eta] / [\eta_\theta] \), where \([\eta]\) is the intrinsic viscosity and \([\eta_\theta]\) is the intrinsic viscosity in the theta state at the same temperature as that used to measure \([\eta]\).

*Note 2:* Expansion factors defined by different linear dimensional characteristics are not exactly equal, nor need they have constant relative values as a function of relative molecular mass.
3.3 Phase behaviour

3.3.1 miscibility

Capability of a mixture to form a single phase over certain ranges of temperature, pressure, and composition [9].

Note 1: Whether or not a single phase exists depends on the chemical structures, molar-mass distributions functions, and molecular constitutions of the components present.

Note 2: The existence of a single phase may be confirmed by light scattering, X-ray scattering, and neutron scattering measurements.

Note 3: For a two-component mixture, the necessary and sufficient condition for the existence of a stable or metastable equilibrium of a homogeneous single phase is

$$\left( \frac{\partial^3 \Delta_{\text{mix}} G}{\partial \phi^3} \right)_{T, p} \geq 0$$

where $\Delta_{\text{mix}} G$ is the Gibbs energy of mixing and $\phi$ the composition, where $\phi$ is usually the volume fraction of one of the components. The borderline (spinodal) between (meta)stable and unstable states is defined by the above second derivative equalling zero (see Definition 3.3.4). If the compositions of two conjugate (coexisting) phases become identical upon change of temperature or pressure, the third derivative also equals zero (defining a critical state or critical point).

Note 4: If a mixture is thermodynamically metastable, it will demix if suitably nucleated (see Definition 3.3.6). If a mixture is thermodynamically unstable, it will demix by spinodal decomposition or by nucleation and growth if suitably nucleated, provided there is minimal kinetic hindrance, such as that caused by the mixture having a high viscosity.

3.3.2 critical point (in polymer science)

Point in the isobaric temperature-composition plane for a binary mixture where the compositions of all coexisting phases become identical [9].

Note 1: An alternative, more general definition “critical solution point” exists [3].

Note 2: Unless otherwise specified, atmospheric pressure is assumed.

Note 3: In a phase diagram, the slope of the tangent to the spinodal is zero at a critical point.

Note 4: At a critical point, binodals and spinodals coincide.

Note 5: Although the definition holds strictly for binary mixtures, it is often erroneously applied to multi-component mixtures.

Note 6: See Definition 3.3.1, Note 3.

3.3.3 binodal

- binodal curve
- coexistence curve

Curve in the isobaric temperature-composition plane for a mixture defining the region of composition and temperature across which a transition occurs from miscibility of the components to conditions where single-phase mixtures are metastable or unstable [9].

Note: Binodal compositions are defined by pairs of points on the curve defining the dependence of Gibbs energy of mixing on composition that have common tangents, corresponding to compositions of equal chemical potentials of each of the two components in two phases.
3.3.4 spinodal

- spinodal curve

Curve in the isobaric temperature-composition plane for a mixture defining the region of composition and temperature for a mixture across which a transition occurs from conditions where single-phase mixtures are metastable to conditions where single-phase mixtures are unstable and undergo phase separation by spinodal decomposition [9].

Note 1: The spinodal curve for a binary mixture is defined as the geometrical locus of all states with

\[ \frac{\partial^2 \Delta_{\text{mix}} G}{\partial \phi^2}_{T,p} = 0 \]

where \( \Delta_{\text{mix}} G \) is the Gibbs energy of mixing and \( \phi \) the composition, where \( \phi \) is usually the volume fraction of one of the components.

Note 2: In the unstable region bounded by the spinodal curve, separation into phase domains is spontaneous, i.e., no nucleation step is required to initiate the separation process.

3.3.5 spinodal decomposition

- spinodal phase-demixing

Diffusion-limited, phase-domain separation in a mixture initiated by delocalized concentration fluctuations occurring in an unstable region of a mixture bounded by a spinodal curve. 

Note 1: Modified slightly from the definition in ref. [9].

Note 2: See Definition 3.3.4, Note 1. Spinodal decomposition occurs when the magnitude of Gibbs energy fluctuations with respect to composition are zero.

3.3.6 nucleation of phase separation

Initiation of the formation of phase domains through the presence of heterogeneities in concentrations [9].

Note: In a metastable region of a phase diagram (see Definition 3.3.1, Note 4), phase separation is initiated only by nucleation.

3.3.7 cloud point

Point in the isobaric temperature-composition plane of a binary or multicomponent mixture at which a decrease in transparency is observed due to the turbidity caused by phase separation.

Note 1: Modified slightly from the definition in ref. [9].

Note 2: A cloud point is characterized by the first appearance of turbidity or cloudiness.

Note 3: A cloud point can be induced by varying temperature or composition.

Note 4: A cloud point induced by varying temperature is heating-rate or cooling-rate dependent.

3.3.8 cloud-point curve

Curve of temperature vs. composition defined by the cloud points over range of compositions of two substances [9].
3.3.9 cloud-point temperature

Temperature at a cloud point.

3.3.10 lower critical solution temperature (LCST)

Critical temperature below which a mixture is miscible at any composition [9].

*Note 1:* The LCST depends upon pressure and the molar-mass distribution functions of the constituent polymer(s).

*Note 2:* For a mixture containing or consisting of polymeric components, these may be different polymers or species of different molar mass of the same polymer.

*Note 3:* The LCST occurs near the minimum on the cloud point curve.

*Note 4:* An LCST exists for mixtures in which solubility decreases with temperature.

*Note 5:* The occurrence of an LCST is less common than that of an upper critical solution temperature. It cannot be explained by simple polymer solution theories, such as the Flory–Huggins theory. However, it occurs for several polymer/solvent pairs and frequently for polymer blends.

3.3.11 upper critical solution temperature (UCST)

Critical temperature above which a mixture is miscible at any composition [9].

*Note 1:* Above the UCST and below the LCST, if it exists, a single phase exists for all compositions.

*Note 2:* The UCST depends upon the pressure and molar-mass distribution functions of the constituent polymer(s).

*Note 3:* For a mixture containing or consisting of polymeric components, these may be different polymers or species of different molar mass of the same polymer.

*Note 4:* The UCST occurs near the maximum on the cloud point curve.

*Note 5:* A UCST exists for mixtures in which solubility increases with temperature.

*Note 6:* A UCST exists for the majority of polymer containing mixtures, and it can be explained by simple polymer solution theories, such as the Flory–Huggins theory.

3.3.12 miscibility gap

Area within the coexistence curve of an isobaric phase diagram (temperature vs. composition) or an isothermal phase diagram (pressure vs. composition) [9].

*Note:* A miscibility gap is observed at temperatures below a UCST or above an LCST. Its location depends on pressure. In the miscibility gap, there are at least two phases coexisting.

3.4 Transport properties

3.4.1 translational diffusion

Process by which the equilibrium statistical distribution of positions of molecules or entities in space is maintained or restored due to their translational Brownian motion.

3.4.2 translational frictional coefficient (in polymer science), \( f \), SI unit: \( \text{kg s}^{-1} \)

- **frictional coefficient** (in polymer science)

Frictional force, \( F \), per unit velocity, \( u \), experienced by an isolated spherical body moving unidirectionally in a viscous isotropic fluid, i.e., \( F = fu \).
Note 1: More generally, $f$ is defined as the tensor that correlates the vectorial frictional force, $F$, on a body in a viscous fluid and the vectorial velocity, $u$, with $F = fu$. However, the more general definition is not needed in polymer science as experimental determinations of the translational frictional coefficient all employ situations in which $F$ and $u$ are collinear and $F = fu$.

Note 2: $f$ is related to the translational diffusion coefficient, $D$, of an isolated body by the Einstein equation $D = kT/f$, where $k$ is the Boltzmann constant and $T$ the thermodynamic temperature.

### 3.4.3 Translational Diffusion Coefficient (in Polymer Science), $D$, SI Unit: $m^2 s^{-1}$

- **Diffusion Coefficient** (in Polymer Science)

Proportionality constant relating the flux per unit area, $J_n$, in unidirectional flow of amount, $n$, of entities B to their concentration gradient in the direction ($x$) of flow, $dc_B/dx$, i.e., $J_n = -Ddc_B/dx$.

**Note 1**: More generally [3], $D$ is defined using vectorial flow as the proportionality constant, relating the flux per unit area, $J_n$, of amount, $n$, of entities B to their concentration gradient, $\nabla c_B$, i.e., $J_n = -D\nabla c_B$. However, the more general definition is not needed in polymer science as experimental determinations of the translational diffusion coefficient all employ unidirectional flow.

**Note 2**: The unit $\mu m^2 s^{-1}$ is sometimes useful for $D$.

### 3.4.4 Rotational Diffusion

Process by which the equilibrium statistical distribution of the overall orientation of molecules or particles is maintained or restored due to their rotational Brownian motion [10].

### 3.4.5 Rotational Frictional Coefficient (in Polymer Science), $\zeta$, SI Unit: $J s$

Torque, $T$, per unit angular velocity, $\omega$, required for rotation of a body about a given axis in a viscous isotropic fluid, i.e., $T = \zeta \omega$.

**Note 1**: $\zeta$ is related to the rotational diffusion coefficient, $\Theta$, of an isolated body in a viscous isotropic fluid by the equation $\Theta = kT/\zeta$, where $k$ is the Boltzmann constant and $T$ the absolute temperature.

**Note 2**: A body whose shape is described by principal axes, a, b, and c, of different lengths has three different rotational frictional coefficients denoted by $\zeta_a$, $\zeta_b$, and $\zeta_c$, relating to rotation about the axes a, b, and c, respectively, and three different rotational diffusion coefficients, $\Theta_a$, $\Theta_b$, and $\Theta_c$, where, for an isolated body in a viscous isotropic fluid, $\Theta_a = kT/\zeta_a$, $\Theta_b = kT/\zeta_b$, and $\Theta_c = kT/\zeta_c$.

### 3.4.6 Rotational Diffusion Coefficient (in Polymer Science), $\Theta$, SI Unit: $s^{-1}$

For rotation about a given axis, the proportionality constant relating the rate of change of amount concentration, $c_B$, of entities B subtending an angle $\theta$ to the direction $\theta = 0$ to the rate of change of the fraction of entities per unit volume, $f(\theta)$, with respect to $\theta$, i.e., $(dc_B/dt)_\theta = \Theta df(\theta)/d\theta$.

**Note**: This definition is taken from [10, 11] and is equivalent to that given in [3].

### 3.4.7 Streaming Birefringence

- **Flow Birefringence**

Birefringence induced by flow in liquids, solutions, and dispersions of optically anisotropic, anisometric, or deformable molecules or entities due to a non-random orientation of the molecules or entities.

**Note**: Streaming birefringence can be used to determine rotational diffusion coefficients.
3.4.8 sedimentation coefficient (in polymer science), s, SI unit: s

Velocity of sedimentation, \( u \), per unit acceleration of the centrifugal force field, \( r \omega^2 \), where \( \omega \) is the angular velocity and \( r \) the distance from the centre of rotation. That is, \( s = u/(r \omega^2) \).

Note 1: The unit \( 10^{-13} \) s is useful for \( s \); this unit has been referred to as a “svedberg” (Sv). 1 Sv = \( 10^{-13} \) s = 0.1 ps.

Note 2: Sedimentation in polymer science is usually studied using an ultracentrifuge.

Note 3: The molar mass of a uniform polymer may be evaluated from measured values of \( s \) and the translational diffusion coefficient, \( D \), in dilute solution, with

\[
M = \frac{R T s}{D (1 - \bar{V} \rho_0)}
\]

where \( R \) is the gas constant, \( T \) the thermodynamic temperature, \( \bar{V} \) the partial specific volume of the polymer, and \( \rho_0 \) the density of the solvent. For a non-uniform polymer with respect to molar mass an average molar mass will be evaluated.

3.4.9 sedimentation equilibrium

Equilibrium established in a centrifugal field when, due to back-diffusion, there is no net flux of any component across any plane perpendicular to the centrifugal force.

Note: At sedimentation equilibrium, the flux due to sedimentation is balanced by the flux in the opposite direction due to the concentration gradient created by the sedimentation.

3.4.10 equilibrium sedimentation method

- sedimentation-equilibrium method

Experimental method by which the distribution of the concentration of the solute or dispersed component in a dilute solution or dispersion along the centrifuge cell is measured at sedimentation equilibrium, and the results are interpreted in terms of the molar masses of the solute species or their distribution functions, or both.

3.4.11 sedimentation-velocity method

Experimental method by which the velocity(ies) of sedimentation of solute component(s) or dispersed particles is (are) measured and the result is expressed in terms of its (their) sedimentation coefficient(s).

3.4.12 Archibald’s method

Experimental sedimentation method based on the fact that at the meniscus and at the bottom of an ultracentrifuge cell there is zero flux of solute across a plane perpendicular to the radial direction and the equations characterizing sedimentation equilibrium always apply, even though the system as a whole may be far from sedimentation equilibrium.

Note: The use of the term “approach to sedimentation equilibrium” for Archibald’s method is discouraged as the whole solution or dispersion in the ultracentrifuge cell is not near to sedimentation equilibrium.
3.4.13 equilibrium sedimentation in a density gradient

- sedimentation equilibrium in a density gradient

Equilibrium sedimentation method using a multicomponent solvent forming a density gradient in a centrifugal field.

Note: Equilibrium sedimentation in a density gradient can be used to determine the compositional heterogeneity of copolymers.

3.4.14 isopycnic

Adjective describing components of a multicomponent system with equal partial specific volumes [3].

3.4.15 relative viscosity, \( \eta_r \)

- viscosity ratio

Ratio of the viscosity of the solution, \( \eta \), to the viscosity of the solvent, \( \eta_0 \), i.e.,

\[ \eta_r = \frac{\eta}{\eta_0} \]

3.4.16 relative viscosity increment, \( \eta_{inc} \)

Ratio of the difference between the viscosities of solution and solvent to the viscosity of the solvent, i.e.,

\[ \eta_{inc} = \frac{(\eta - \eta_0)}{\eta_0} \]

Note: The use of the term “specific viscosity” for this quantity is discouraged, since the relative viscosity increment does not have the attributes of a specific quantity.

3.4.17 reduced viscosity, unit: cm\(^3\) g\(^{-1}\) or SI unit: m\(^3\) kg\(^{-1}\)

- viscosity number

Ratio of the relative viscosity increment to the mass concentration of the solute, \( c \), i.e.,

\[ \eta_{inc} / c \]

Note: \( \eta_{inc} / c \) and the quantities in the following Definitions 3.4.18 and 3.4.19 are neither viscosities nor pure numbers. The names of the terms are to be looked on as deeply entrenched traditional names. Any replacements using a consistent terminology would cause unnecessary confusion in the polymer literature.

3.4.18 inherent viscosity, \( \eta_{inh} \), unit: cm\(^3\) g\(^{-1}\) or SI unit: m\(^3\) kg\(^{-1}\)

- logarithmic viscosity number, \( \eta_{ln} \)

Ratio of the natural logarithm of the relative viscosity to the mass concentration of the solute, \( c \), i.e.,

\[ \eta_{inh} = \eta_{ln} = (\ln \eta_r) / c \]

Note: See Note under Definition 3.4.17.
3.4.19 intrinsic viscosity, \([\eta]\), unit: \(\text{cm}^3\ \text{g}^{-1}\) or SI unit: \(\text{m}^3\ \text{g}^{-1}\)

- **limiting viscosity number**

Limiting value of the reduced viscosity or the inherent viscosity at infinite dilution of the solute, i.e.,

\[
[\eta] = \lim_{c \to 0} (\eta_{\text{inc}} / c) = \lim_{c \to 0} \eta_{\text{inh}}
\]

**Note:** See Note to Definition 3.4.17.

3.4.20 Huggins equation

Equation describing the dependence of the reduced viscosity, \(\eta_{\text{inc}} / c\), of dilute solutions on the mass concentration of solute, \(c\), with

\[
\eta_{\text{inc}} / c = [\eta] + k_H [\eta]^2 c
\]

where \(k_H\) is the Huggins coefficient and \([\eta]\) is the intrinsic viscosity.

3.4.21 Huggins coefficient, \(k_H\)

Parameter in the Huggins equation.

3.4.22 Kraemer equation

Equation describing the dependence of the inherent viscosity, \(\eta_{\text{inh}}\), of a dilute solution on the mass concentration of the solute, \(c\), with

\[
\eta_{\text{inh}} = (\ln \eta_{\text{i}}) / c = [\eta] + k_K [\eta]^2 c
\]

where \(k_K\) is the Kraemer coefficient and \([\eta]\) is the intrinsic viscosity.

3.4.23 Kraemer coefficient, \(k_K\)

Parameter in the Kraemer equation.

3.4.24 Mark–Houwink equation

- **Mark–Houwink–Kuhn–Sakurada equation**

Equation describing the dependence of the intrinsic viscosity of a polymer on its molar mass, molecular weight, relative molar mass, or relative molecular mass and having the form

\[
[\eta] = K M_v^a \quad \text{or} \quad [\eta] = K M_{v,v}^a
\]

where \(K\) and \(a\) are constants, the values of which depend on the nature of the polymer and solvent as well as on temperature, \(M_v\) is the viscosity-average molar mass, or viscosity-average molecular weight, and \(M_{v,v}\) is the viscosity-average relative molar mass, or viscosity-average relative molecular mass.
Note 1: The use of this equation with molecular weight, relative molar mass, or relative molecular mass, rather than with molar mass, is recommended, since in the last case the constant $K$ assumes awkward and variable dimensions owing to the fractional and variable value of the exponent $a$.

Note 2: The values of the constants $K$ and $a$ are preferably established using uniform polymers of various molecular weights or polymers with narrow molecular-weight distribution functions.

3.4.25 hydrodynamic interaction

In a solution or dispersion, the perturbation of the flow of the solvent continuum or dispersing medium continuum around a solute molecule, a segment of a dissolved macromolecule or dispersed entity caused by the presence of the other solute molecules, segments, or dispersed entities.

3.4.26 free-draining

- freely draining

Adjective describing the undisturbed flow of solvent through the domain of a dissolved macromolecule.

Note: Free-draining flow occurs in the limit of zero hydrodynamic interaction.

3.4.27 impermeable

- non-free-draining

Adjective describing the flow behaviour of a macromolecule in solution or a dispersed entity when, due to hydrodynamic interaction, the solvent or dispersion medium within the domain of the macromolecule or dispersed entity is essentially immobilised and moves with the dissolved macromolecule or dispersed entity.

3.4.28 partial free-draining

- partially draining

Adjective describing the flow behaviour of a macromolecule in solution or a dispersed entity when, due to hydrodynamic interaction, the solvent within the domain of the macromolecule or a dispersed entity becomes progressively more immobilised with respect to the macromolecule or a dispersed entity in the direction from its outer fringes inward.

Note: Free-draining and impermeable behaviour are two extremes of the concept of partial free-draining behaviour.

3.4.29 hydrodynamically equivalent sphere

Hypothetical sphere that experiences the same frictional forces as an actual polymer molecule or dispersed entity and is impermeable to the surrounding fluid and the other hydrodynamically equivalent spheres or dispersed entities present in the solution or dispersion.

Note 1: The concept of a hydrodynamically equivalent sphere is relevant to the impermeable flow behaviour of a macromolecule or dispersed entity.

Note 2: The size of a hydrodynamically equivalent sphere may be different for different types of motion, e.g., for diffusive and viscous flows.
3.4.30 equivalent hydrodynamic volume

Volume of the hydrodynamically equivalent sphere.

Note: The molar equivalent hydrodynamic volume determined using measurements of *intrinsic viscosity*, $[\eta]$, is $V_\varphi$, where $V_\varphi = [\eta]M/N_A$, with $M$ the molar mass and $N_A$ the Avogadro constant.

3.4.31 equivalent hydrodynamic radius

Radius of the hydrodynamically equivalent sphere.

3.4.32 Stokes equation

For an isolated dissolved molecule or dispersed entity, an equation relating the translational frictional coefficient, $f$, to the *equivalent hydrodynamic radius* in translational diffusive flow, $r_o$, and to the viscosity of the solvent continuum or the dispersion medium continuum, $\eta_o$, with

$$ f = 6\pi \eta_o r_o. $$

3.4.33 Stokes–Einstein equation

For an isolated dissolved molecule or dispersed entity, an equation relating the translational diffusion coefficient, $D$, to the *equivalent hydrodynamic radius* in translational diffusive flow, $r_o$, and to the viscosity of the solvent continuum or the dispersion medium continuum, $\eta_o$, with

$$ D = k T / (6 \pi \eta_o r_o^3) $$

where $k$ is the Boltzmann constant and $T$ the thermodynamic temperature.

Note: The Stokes–Einstein equation is derived by combining the Stokes equation with the Einstein equation $D = k T / f$. (See Definition 3.4.2.)

3.4.34 Perrin equation

For an isolated dissolved molecule or dispersed entity, an equation relating the rotational diffusion coefficient, $\Theta$, to the *equivalent hydrodynamic radius* in rotational diffusive flow, $r_o$, and to the viscosity of the solvent continuum or the dispersion medium continuum, $\eta_o$, with

$$ D = k T / (6 \pi \eta_o r_o^4) $$

where $k$ is the Boltzmann constant and $T$ the thermodynamic temperature.

3.4.35 pearl-necklace model

- bead-rod model

Model describing the flow behaviour of a dissolved *chain* macromolecule in terms of a freely jointed sequence of beads, each of which offers hydrodynamic resistance to the flow of the surrounding solvent continuum and is connected to the next bead by a rigid rod that offers no hydrodynamic resistance.
3.4.36 Kirkwood–Riseman theory

Theory, based on the *pearl-necklace model*, that describes the translational diffusive and viscous flows of an isolated linear macromolecule in solution in the *theta state* and accounts for the gradual change from *free-draining* behaviour at lower molecular weights to *impermeable* behaviour at higher molecular weights.

**Note:** The Kirkwood–Riseman theory is usually applied in the *impermeable* limit when it essentially relates the *equivalent hydrodynamic radius* to the *root-mean-square unperturbed radius of gyration*, \( \langle s^2 \rangle \), with

\[
r_D = 0.675 \langle s^2 \rangle^{1/2}
\]

and

\[
r_\eta = 0.256 \langle s^2 \rangle^{1/2}
\]

where \( r_D \) and \( r_\eta \) are the *equivalent hydrodynamic radii* in translational diffusive flow and viscous flow.

3.4.37 Flory–Fox assumption

Assumption that the *Kirkwood–Riseman theory* can be applied to linear isolated macromolecules in solution, independent of whether they are in the *theta state*.

**Note:** The Kirkwood–Riseman relationships between \( r_D \) and \( r_\eta \) and the *root-mean-square radius of gyration*, \( \langle s^2 \rangle \), are then

\[
r_D = 0.675 \langle s^2 \rangle^{1/2} = 0.675 \langle s^2 \rangle^{1/2} \alpha_D
\]

and

\[
r_\eta = 0.256 \langle s^2 \rangle^{1/2} = 0.256 \langle s^2 \rangle^{1/2} \alpha_\eta
\]

where \( r_D \) and \( r_\eta \) are the *equivalent hydrodynamic radii* in translational diffusive flow and viscous flow, and \( \alpha_D \) and \( \alpha_\eta \) are the corresponding *expansion factors*.

3.4.38 Flory–Fox equation

Equation relating intrinsic viscosity, \( \eta \), and molar mass, \( M \), to the *mean-square radius of gyration*, \( \langle s^2 \rangle \), with

\[
[\eta] M = \Phi' \langle s^2 \rangle^{3/2}
\]

where \( \Phi' \) is a parameter the value of which depends on the molar-mass distribution, macromolecular constitution, and *chain expansion*.

**Note 1:** \([\eta] M/N_A \), where \( N_A \) is the Avogadro constant, is the *equivalent hydrodynamic volume* in viscous flow, \( V_\eta' \), with \( V_\eta' = 4\pi r_\eta^3 / 3 \). Hence, the Flory–Fox equation is consistent with the *Kirkwood–Riseman theory* and the Flory–Fox assumption. (See Notes to Definitions 3.4.36 and 3.4.37.)

**Note 2:** For a solution in the *theta state*, \( \Phi' \) is denoted \( \Phi_\theta' \) and its value is given by the *Kirkwood–Riseman theory*, with \( \Phi_\theta' = 4.22 \times 10^2 \text{ mol}^{-1} \).

**Note 3:** The Flory–Fox equation is sometimes written in terms of \( \langle r^2 \rangle \), the *mean-square end-to-end distance*, instead of \( \langle s^2 \rangle \), with

\[
[\eta] M = \Phi \langle r^2 \rangle^{3/2}
\]

where \( \Phi = \Phi' / 6^{3/2} \).
The latter equality assumes that \(<r^2> = 6<s^2>\), which is only exactly true in the theta state. In this case,

\[ [\eta] M = \Phi \langle r^2 \rangle^{3/2} \]

where \( \Phi = \Phi' / 6^{3/2} = 2.87 \times 10^{-3} \text{ mol}^{-1} \).

Note 4: \( \Phi \) is known as the viscosity function or the Flory function. See Definition 3.4.39.

3.4.39 viscosity function, \( \Phi \), SI unit: \( \text{mol}^{-1} \)

- Flory function

Coefficient connecting the intrinsic viscosity, the mean-square radius of gyration, and the molar mass of a chain macromolecule, according to the equation

\[ [\eta] = \Phi 6^{1/2}\langle s^2 \rangle^{3/2} / M. \]

3.4.40 bead-spring model

Model describing the flow behaviour of a dissolved chain macromolecule in terms of a freely jointed sequence of beads, each of which offers frictional resistance to the flow of the surrounding solvent and is connected to the next bead by a spring which does not contribute to the frictional resistance but which is responsible for the elastic and deformational properties of the chain.

3.4.41 Rouse theory

Molecular theory for treating polymer chain dynamics based on the bead-spring model assuming the beads (segments) have zero excluded volume and there is no hydrodynamic interaction between the beads.

3.4.42 Rouse chain

Hypothetical polymer chain satisfying the assumptions made in the Rouse theory.

3.4.43 reptation

Snake-like movement of a polymer chain in a semi-dilute or concentrated solution or bulk amorphous polymer through the hypothetical tube created by neighbouring chains.

3.4.44 tube model

Model to describe the motion of a polymer chain confined in the hypothetical tube created by neighbouring chains.

Note 1: In the tube model, the polymer chain moves along the hypothetical tube defined by the neighbouring polymer chains. The tube is continually undergoing tube renewal.

Note 2: The tube model is an essential concept for reptation.
3.4.45 tube renewal

Dynamic renewal of tubes by the disentanglement and re-entanglement of polymer chains.

3.4.46 primitive chain

Polymer chain allowed to undergo reptation along the tube created by neighbouring chains.

Note: The chain can be depicted as a connected sequence of blobs.

3.5 Scattering properties

Preamble—coherent elastic scattering of radiation

A beam of radiation traversing a medium may be attenuated and partially scattered. The definitions given are for those cases in which the attenuation of the incident beam is due only to scattering, the energy of scattering quanta is the same as that of quanta in the primary beam (elastic scattering) and phase relationships between independent scatterers are retained (coherent scattering). This section deals with light scattering (LS), small-angle X-ray scattering (SAXS), and small-angle neutron scattering (SANS). In light scattering, the polarization of light is relevant; only plane-polarized light is considered here, and it is called vertically polarized (v) if the electric vector of the beam is perpendicular to the plane containing the source, sample, and detector, and horizontally polarized (h) if the electric vector lies in that plane. Unpolarized light is considered to be a mixture of equal parts of v and h light.

3.5.1 uniform dispersion

Dispersion of particles of identical size, shape, and constitution.

3.5.2 non-uniform dispersion

Dispersion of particles not identical with respect to size, shape, or constitution.

3.5.3 static light scattering (SLS)

Experimental method based on the measurement of the time-averaged intensity of light scattered from a polymer solutions or a dispersion of particles at various angles with respect to the incident beam.

Note 1: SLS is an absolute method, i.e., one not requiring calibration, for the determination of the molar mass of a macromolecular substance or dispersion of particles.

Note 2: Measurement of the angular dependence of the time-averaged intensity of light scattered from a dilute solution of macromolecules or a dilute dispersion of particles that are not negligibly small with respect to the wavelength of the incident light can be used to evaluate an average radius of gyration of the solute macromolecules or dispersed particles.

Note 3: Measurement of the concentration dependence of the intensity of light scattered from a dilute solution of macromolecules or a dilute dispersion of particles yields information on the thermodynamic interaction between the solute and solvent or dispersed particles and dispersion medium in terms of the second osmotic virial coefficient and, less frequently, higher virial coefficients.
3.5.4 dynamic light scattering (DLS)

- quasi-elastic light scattering (QELS)
- photon-correlation spectroscopy (PCS)

Experimental method based on the measurement of the time autocorrelation function of the intensity of light scattered from a polymer solution or a dispersion of particles.

*Note:* The basic information that can be obtained from the time autocorrelation function [12] of a polymer solution or a dispersion is: (i) for a *uniform polymer* or a *uniform dispersion*, the diffusion coefficient of the macromolecules or the dispersed particles; (ii) for a *non-uniform polymer* or a non-uniform dispersion, the distribution function of diffusion coefficients of the macromolecules or the dispersed particles.

3.5.5 small molecule

Molecule much smaller than the wavelength of the radiation in the solvent used.

*Note:* For a molecule to be considered to be small, the lengths of all of its dimensions must be less than about one-twentieth of the wavelength employed.

3.5.6 small particle

Particle much smaller than the wavelength of the radiation in the dispersion medium used.

*Note:* For a particle to be considered to be small, the lengths of all of its dimensions must be less than about one-twentieth of the wavelength employed.

3.5.7 large molecule

Molecule of size similar to or larger than the wavelength of the radiation in the solvent used.

*Note:* A molecule is treated as large if the length of its largest dimension exceeds about one-twentieth of the wavelength employed.

3.5.8 large particle

Particle of size similar to or larger than the wavelength of the radiation in the dispersion medium used.

*Note:* A particle is treated as large if the length of its largest dimension exceeds about one-twentieth of the wavelength employed.

3.5.9 Rayleigh scattering

Scattering of light by molecules or particles that are much smaller than the wavelength of the radiation used [3].

*Note 1:* Rayleigh scattering is exhibited by *small molecules* and *small particles* and can be exhibited by *large molecules* and *large particles*, provided they are not large enough to exhibit *Mie scattering*.

*Note 2:* In Rayleigh scattering, the intensity of scattered radiation at a given angle and distance from the point of scattering is proportional to $\lambda^{-4}$, where $\lambda$ is the wavelength of the incident radiation.
3.5.10 Mie scattering (in polymer science)

Scattering of light by molecules or particles of size larger than approximately one-half of the wavelength of the radiation used.

Note 1: For homogeneous spheres, the phenomenon is rigorously described by the theory developed by Mie.
Note 2: The definition is consistent with the more general definition given in [3].

3.5.11 scattering angle, $\theta$

- angle of observation

Angle between the forward direction of the incident beam and a straight line connecting the scattering point and the detector.

3.5.12 scattering vector, $\mathbf{q}$

- momentum transfer

Vector difference between the wave propagation vectors of the incident and the scattered beams, both of magnitude $2\pi/\lambda$, where $\lambda$ is the wavelength of the scattered radiation in the solvent or dispersion medium used.

Note: The magnitude of the scattering vector, $|\mathbf{q}| = (4\pi/\lambda) \sin(\theta/2)$, where $\lambda$ is the wavelength of the scattered radiation in the medium and $\theta$ is the scattering angle.

3.5.13 refractive index increment, $\partial n/\partial c$, unit: see Note 1

Rate of change of the solution refractive index, $n$, with solute concentration, $c$.

Note 1: The solute concentration is most frequently expressed in terms of mass concentration, molality, or volume fraction. If expressed in terms of mass concentration or molality, the corresponding refractive index increments are referred to as “specific refractive index increments” or “molal refractive index increments”, respectively. The unit of $\partial n/\partial c$ is that of the reciprocal of the concentration used, usually cm$^3$ g$^{-1}$ for mass concentration and g mol$^{-1}$ for molality. The corresponding SI units are m$^3$ kg$^{-1}$ and kg mol$^{-1}$.

Note 2: Following use of the full name, the abbreviated name “refractive increment” may be used.

3.5.14 isorefractive

Adjective describing components of a multicomponent system having refractive index increments with respect to each other equal to zero.

3.5.15 Rayleigh ratio, $R(\theta)$ or $R_\theta$, unit: cm$^{-1}$ or SI unit: m$^{-1}$

- cross-section (in small-angle neutron scattering)

Quantity used to characterize the scattered intensity at the scattering angle, $\theta$, defined as $R(\theta) = i_r^2/(I_o f V_o)$, where $I_o$ is the intensity of the incident radiation, $i_r$ is the intensity of scattered radiation from the observed
scattering volume, $V_\theta$, at an angle $\theta$ and a distance $r$ from the point of scattering. The factor $f$ takes account of polarization phenomena.

**Note 1:** The value of $f$ depends upon the type of radiation employed:

- (i) for static light scattering, depending upon the polarization of the incident beam, $f = 1$ for vertically polarized light, $f = \cos^2 \theta$ for horizontally polarized light, $f = (1 + \cos^2 \theta)/2$ for unpolarized light;
- (ii) for small-angle neutron scattering, $f = 1$;
- (iii) for small-angle X-ray scattering, $f \approx 1$, if $\theta < \text{ca. } 5^\circ$.

**Note 2:** In physics texts, the factor, $f$, may not be included in the definition of the Rayleigh ratio.

**Note 3:** Except for some potential minor correction factors, $V_\theta$ is proportional to $1/\sin(\theta)$.

### 3.5.16 excess Rayleigh ratio, $\Delta R(\theta)$ or $\Delta R_\theta$

Unit: cm$^{-1}$ or SI unit: m$^{-1}$

Difference between the Rayleigh ratio for a dilute solution or dilute dispersion and that for the pure solvent or the dispersion medium at the same scattering angle.

**Note:** Cf. Definition 3.5.17.

### 3.5.17 excess scattering

Difference between the scattering intensity for a dilute solution or a dilute dispersion and that for the pure solvent or the dispersion medium at the same scattering angle.

**Note:** Cf. Definition 3.5.16.

### 3.5.18 turbidity, $\tau$

Unit: cm$^{-1}$ or SI unit: m$^{-1}$

Measure of the apparent absorbance of the incident radiation due to scattering per unit distance of the incident beam path, with

$$\tau = - \frac{1}{d} \ln \left( \frac{I}{I_0} \right)$$

where $I_0$ is the intensity of the incident radiation, $I$ is the intensity of the transmitted (non-scattered) radiation, and $d$ is the thickness of the layer of the scattering medium.

**Note:** For small particles direct proportionality exists between turbidity and the Rayleigh ratio.

### 3.5.19 turbidimetric titration

Process in which a precipitant is added incrementally to a highly dilute polymer solution and the intensity of light scattered by, or the turbidity due to, the finely dispersed particles of the polymer-rich phase is measured as a function of the amount of precipitant added.

### 3.5.20 particle scattering function, $P(\theta)$ or $P_\theta$

- particle scattering factor
- form factor

Ratio of the intensity of radiation scattered at scattering angle $\theta$, to the intensity of scattered radiation scattered at $\theta = 0$, i.e.,
\[ P(\theta) = \frac{R(\theta)}{R(0)} \]

**Note:** Mathematically, the form factor is the Fourier transform of the pair correlation function of the scattering entities within a molecule or particle.

### 3.5.21 static structure factor

Function describing the dependence of relative scattering intensity on the magnitude of the scattering vector, \( q \), for a polymer solution or a dispersion.

**Note:** The static structure factor accounts for interference of the scattered radiation within individual macromolecules or individual dispersed particles, described by the form factor, as well as interference of the scattered radiation from different macromolecules or dispersed particles, reflecting the ordering of the positions of the scattering entities.

### 3.5.22 dynamic structure factor

Function describing the temporal dependence of relative scattering intensity on the magnitude of the scattering vector, \( q \).

**Note:** The value of the dynamic structure factor is characteristic of the various modes of motions of the polymer molecules or the dispersed particles and their parts and is also characteristic of the time-dependent interference of scattering, reflecting ordering of the positions of the scattering entities in time. In dynamic light scattering, it can be derived from the time autocorrelation function.

### 3.5.23 Zimm plot

Graphical representation of data on intensity of scattered radiation from large particles in solution, based on the equation

\[ \frac{Kc}{\Delta R(\theta)} = \frac{1}{M_m P(\theta)} + 2A_2 c + ... \]

with \( Kc/\Delta R(\theta) \) plotted versus a linear combination of \( \sin^2(\theta/2) \) and \( c \), where \( \theta \) is the scattering angle and \( c \) the mass concentration of the solute, \( \Delta R(\theta) \) is the excess Rayleigh ratio, \( P(\theta) \) is the particle scattering function that comprises, for a large molecule or a large particle, the z-average radius of gyration and is a polynomial in \( \sin^2(\theta/2) \). \( K \) depends on the solute, the solvent, the temperature, and the type of radiation employed, \( M_m \) is the mass-average molar mass, and \( A_2 \) is the second virial coefficient of the chemical potential.

**Note 1:** The Zimm plot is used for the simultaneous evaluation of \( M_m, A_2 \), and, for a large molecule or a large particle, the z-average mean-square radius of gyration.

**Note 2:** Several modifications of the Zimm plot are in frequent use; the most common one uses the excess scattering instead of the excess Rayleigh ratio.

**Note 3:** The Zimm plot is a two-dimensional representation of the surface \( Kc/\Delta R(\theta) = f[\sin^2(\theta/2),c] \) representing the dependence of \( Kc/\Delta R(\theta) \) on scattering angle, \( \theta \), and concentration, \( c \). It is constructed from values of \( Kc/\Delta R(\theta) \) for solutions of different concentrations, each of which is measured at the same series of scattering angles.
3.5.24 Guinier plot

Graphical representation of data on intensity of scattered radiation from large particles, obtained at different angles but at the same concentration, in which \( \log[\Delta R(\theta)] \) or \( \log[P(\theta)] \) is plotted versus \( \sin(\theta/2) \) or \( q^2 \); \( \Delta R(\theta) \) is the excess Rayleigh ratio, \( P(\theta) \) the particle scattering function, \( \theta \) the scattering angle, and \( q \) the magnitude of the scattering vector.

**Note:** A Guinier plot is usually used for the evaluation of the mean-square radius of gyration.

3.5.25 Kratky plot

Graphical representation of data on intensity of scattered radiation, obtained at different angles but at the same concentration, in which \( \sin^2(\theta/2) \Delta R(\theta) \), is plotted versus \( \sin(\theta/2) \), or \( q^2 \Delta R(\theta) \) is plotted versus \( q \); for definitions of symbols, see Definition 3.5.24.

**Note:** A Kratky plot is used for the determination of molecular shape.

3.5.26 Dissymmetry of scattering, \( z(\theta_1, \theta_2) \)

Ratio of two Rayleigh ratios for different scattering angles, i.e., \( z(\theta_1, \theta_2) = R(\theta_1)/R(\theta_2) \), where \( \theta_1 < \theta_2 \).

**Note:** The angles \( \theta_1 \) and \( \theta_2 \) must be specified; in light scattering it is customary to let \( \theta_2 = 180^\circ - \theta_1 \), and, most frequently, \( \theta_1 = 45^\circ \) and \( \theta_2 = 135^\circ \).

3.5.27 Depolarization of scattered light

Phenomenon consequent upon the electric vectors of the incident and scattered beams being non-coplanar because light scattered from a vertically (horizontally) polarized incident beam contains a horizontal (vertical) component.

**Note:** The phenomenon is due primarily to the anisotropy of the polarizability of the scattering medium.

3.6 Separation methods

3.6.1 Fractionation

Process by means of which macromolecular species differing in some characteristic (chemical composition, relative molecular mass, branching, stereoregularity, etc.) are separated from each other.

3.6.2 Polymer-poor phase

- **Dilute phase**

Phase of a two-phase equilibrium system, consisting of a polymer and low-molecular-weight material, having the lower concentration of polymer.

**Note:** The use of the term “sol phase” is discouraged.
3.6.3 polymer-rich phase

- concentrated phase

Phase of a two-phase equilibrium system, consisting of a polymer and low-molecular-weight material, having the higher concentration of polymer.  
*Note:* The use of the term “gel phase” is discouraged.

3.6.4 precipitation fractionation

- fractional precipitation

Process in which a polymeric substance, consisting of macromolecules differing in some characteristic affecting their solubility, is separated from a solution into fractions by successively decreasing the solution power of the solvent, resulting in the repeated formation of a two-phase system in which the less soluble components are concentrated in the polymer-rich phase.

3.6.5 extraction fractionation

Process in which a polymeric substance, consisting of macromolecules differing in some characteristic affecting their solubility, is separated from a polymer-rich phase into fractions by successively increasing the solution power of the solvent, resulting in the repeated formation of a two-phase system in which the more soluble components are concentrated in the polymer-poor phase.

3.6.6 size-exclusion chromatography (SEC)

Separation technique in which separation mainly according to the equivalent hydrodynamic volume of the molecules or particles takes place in a porous non-adsorbing material with pores of approximately the same size as the effective dimensions in solution of the molecules to be separated.

3.6.7 gel-permeation chromatography (GPC)

*Size-exclusion chromatography* in which the porous non-adsorbing material is a gel.

3.6.8 molar-mass exclusion limit

- molecular-weight exclusion limit

Maximum value of the molar mass or molecular weight of molecules or particles, in a polymer-solvent system or dispersion, that can enter into the pores of the porous non-adsorbing material used in *size-exclusion chromatography.*  
*Note:* For particles with molar mass or molecular weight larger than the exclusion limit separation by size-exclusion chromatography is not effective.
3.6.9 *elution time*, $t_{el}$, SI unit: s

Time elapsed from the injection of the sample into a chromatography bed to the recording of a specified signal of the detector due to the sample having passed through the bed.

3.6.10 *elution volume*, $V_{el}$, unit: cm$^3$ or SI unit: m$^3$

Volume of solvent that has passed through a chromatography bed from the injection of the sample to the recording of a specified signal of the detector due to the sample having passed through the bed.

3.6.11 *retention time*, $t_R$, SI unit: s

*Elution time* at the maximum of an elution peak.

3.6.12 *retention volume*, $V_R$, unit: cm$^3$ or SI unit: m$^3$

*Elution volume* at the maximum of an elution peak.

3.6.13 **universal calibration**

Calibration of *size-exclusion chromatography* columns based on the finding that the *retention volume* of a molecular or particulate species is usually a single-valued function of an appropriate size parameter of the molecule or particle, irrespective of its chemical nature and structure.

*Note:* The product of the *intrinsic viscosity* and *molar mass*, $[\eta]M$, the molar equivalent hydrodynamic volume (see Definition 3.4.30) is widely used as a suitable size parameter.

3.6.14 **spreading function**

Detector signal produced, as a function of *elution time* or *volume*, at the outlet of a chromatography column, by an instantaneous injection of a uniform sample.

3.6.15 **plate number**, $N$

Number, characteristic of the efficiency of a chromatography column in terms of band broadening, defined as $N = 8 \ln 2 (t_R / w_h)^2$, where $t_R$ is the *retention time* of an individual low-molecular-weight compound, and $w_h$ is the time interval corresponding to the length of the line parallel to the base of the peak at 50% of the peak height that terminates at the intersections with the two limbs of the peak.

*Note:* The definition is consistent with the definitions given in [3].

3.6.16 **plate height**, $H$, unit: cm or SI unit: m

- height equivalent to a theoretical plate (HETP)

Length of a chromatography column ($L$) divided by its *plate number* ($N$), i.e., $H = L/N$.

*Note:* The definition is consistent with the definition given in [3].
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References


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