
**Nanotechnologies — Characterization
of multiwall carbon nanotubes —
Mesoscopic shape factors**

*Nanotechnologies — Caractérisation des nanotubes en carbone
multicouches — Facteurs de forme mésoscopique*

STANDARDSISO.COM : Click to view the full PDF of ISO/TS 11888:2017



STANDARDSISO.COM : Click to view the full PDF of ISO/TS 11888:2017



COPYRIGHT PROTECTED DOCUMENT

© ISO 2017, Published in Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

	Page
Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms, definitions and abbreviated terms	1
3.1 Terms and definitions	1
3.2 Abbreviated terms	3
4 Sample preparation methods	3
4.1 Ball mill cutting	3
4.2 Dispersion method	3
4.3 Sample preparation for SEM	3
4.4 Alternative sample preparation method	3
5 Experimental procedure	4
5.1 Measurements of the SBPL using SEM	4
5.1.1 SEM	4
5.1.2 Measurement methods for the SBPL	4
5.2 Measuring inner and outer diameters of MWCNTs using TEM	5
6 Test report	5
Annex A (normative) Formulae for terms and definitions in Clause 2, Annex B, Annex C and Annex D	6
Annex B (informative) Viscometry	11
Annex C (informative) Dynamic light scattering and depolarized dynamic light scattering	12
Annex D (informative) Case study and reports	14
Bibliography	18

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

This second edition cancels and replaces the first edition (ISO/TS 11888:2011), which has been technically revised.

Introduction

Multiwall carbon nanotubes (MWCNTs) synthesized by chemical vapour deposition (CVD) are of growing interest for use in polymer composites and conductive coatings. In many cases, MWCNTs synthesized by CVD have static (permanent) bend points randomly distributed along their axis. Physical and chemical properties of mass-produced MWCNTs are strongly dependent on the statistical distribution of mesoscopic shapes and sizes of the individual MWCNT (see ISO/TS 80004-3), among other parameters, that comprise the product.^{[4][6]} It is therefore crucial to characterize the mesoscopic shapes of MWCNTs in order to ensure that the final properties are reproducible for use in a wide range of materials, including composites and other dispersions, as well as for Environment, Health and Safety (EHS) issues.^[7]

This document provides methods for the characterization of mesoscopic shape factors of MWCNTs, including sample preparation procedures. In particular, it provides a statistical method for characterizing MWCNTs produced by the CVD method. During MWCNT synthesis, axial structures are not perfectly linear but include static bend points.

This document provides methods for determining a statistical quantity, representing a maximum straight length that is not deformed by permanent bending called the “static bending persistence length” (SBPL). The SBPL gives information regarding the relationship between the MWCNT mesoscopic shape and size. If two MWCNTs of equal length have different SBPLs, their overall sizes (e.g. radius of gyration or an equivalent diameter such as a hydrodynamic diameter) will also be different from one another. In practical applications, the variation in SBPL affects both chemical reactivity and physical properties.^{[4][5][6]}

Electrical conductivity and dimensional stability of MWCNT-polymer compounds are also strongly dependent on the SBPL of the MWCNT used to make them.^{[4][5][6]} Various properties might be affected by SBPL, including electrical percolation threshold,^{[6][8]} toxicity,^[7] thermal conductivity,^[9] rheological property^[10] and field emission property.^[11] SBPL could be useful for estimating the loading of a MWCNT-polymer matrix to achieve electrical conductivity (percolation limit) and should also assist with modelling the mechanical properties of MWCNT-polymer composites with different loadings.

Prior to commencing any work, users are advised to familiarize themselves with the latest guidance on handling and disposal of MWCNTs, particularly in relation to the use of appropriate personal protective equipment. Information on current practices is available in ISO/TR 12885.

STANDARDSISO.COM : Click to view the full PDF of ISO/TS 11888:2017

Nanotechnologies — Characterization of multiwall carbon nanotubes — Mesoscopic shape factors

1 Scope

This document describes methods for the characterization of mesoscopic shape factors of multiwall carbon nanotubes (MWCNTs). Techniques employed include scanning electron microscopy (SEM), transmission electron microscopy (TEM), viscometry, and light scattering analysis.

This document also includes additional terms needed to define the characterization of static bending persistence length (SBPL). Measurement methods are given for the evaluation of SBPL, which generally varies from several tens of nanometres to several hundred micrometres.

Well-established concepts and mathematical expressions, analogous to polymer physics, are utilized for the definition of mesoscopic shape factors of MWCNTs.

2 Normative references

There are no normative references in this document.

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the following terms, definitions and abbreviated terms apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <http://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

NOTE Formulae for some of these terms and definitions are given in [Annex A](#).

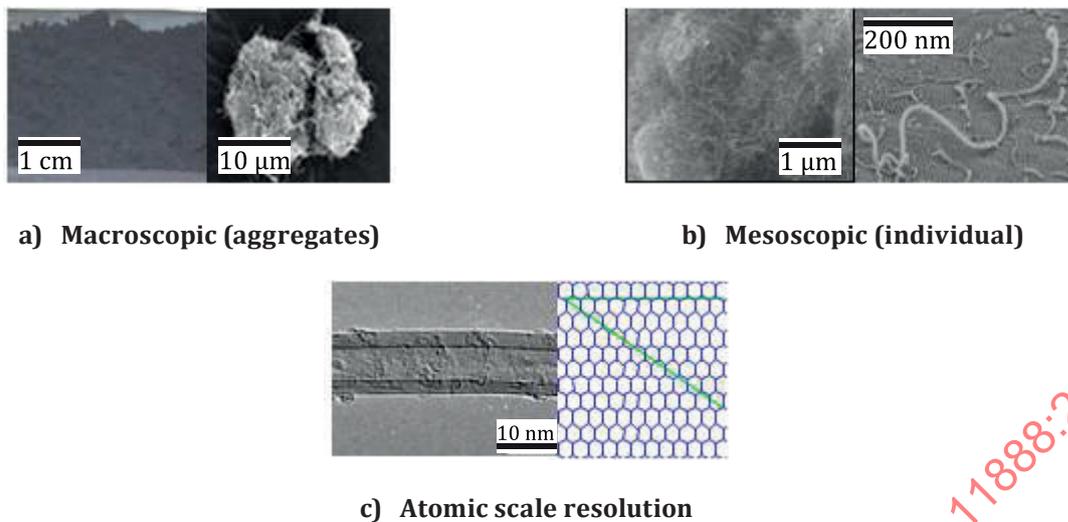
3.1.1

mesoscopic shape

description of shape at the observation scale for an individual multiwall carbon nanotube (MWCNT)

Note 1 to entry: Mesoscopic shape factors describe the average size and shape of individual MWCNTs, while “macroscopic” describes the shape and size of MWCNT aggregates or agglomerates. “Atomic scale resolution” describes the shape of an MWCNT at the atomic level (see [Figure 1](#)).

Note 2 to entry: See Reference [\[4\]](#).



NOTE SOURCE: 2010 ACS

Figure 1 — Shape of MWCNTs at various scales

3.1.2

regular shape

⟨MWCNTs⟩ property of having a regular pattern along the tube axis

Note 1 to entry: Correlations in the direction of the tangent show a periodical shape for MWCNTs of regular shape. Both straight and coil-shaped MWCNTs are typically classified as MWCNTs of regular shape.

3.1.3

random shape

⟨MWCNTs⟩ property of having static or permanent bend points distributed randomly (Gaussian) along their tube axis

3.1.4

static bending persistence length

SBPL

$$l_{sp}$$

maximum straight length without static bending

3.1.5

contour length

$$L$$

total length of an MWCNT along its axis

3.1.6

weighted average contour length

$$\bar{L}_w$$

average of contour length which is assigned a weight

3.1.7

end-to-end distance

$$R$$

straight distance between the two ends of an MWCNT

3.1.8

bending ratio

$$D_b$$

ratio between mean-squared end-to-end distance and squared contour length

3.1.9**intrinsic viscosity**[η]

description of an MWCNT's contribution to the viscosity of MWCNT dispersion

3.2 Abbreviated terms

CVD	chemical vapour deposition
DDLS	depolarized dynamic light scattering
DLS	dynamic light scattering
DMF	dimethylformamide
SBPL	static bending persistence length
SEM	scanning electron microscopy
TEM	transmission electron microscopy

4 Sample preparation methods**4.1 Ball mill cutting**

Place 200 mg of MWCNTs and 20 ml of ethanol and zirconia balls (5,2 mm) into a zirconia pot (150 ml) and ball mill 500 r/min for 2 h.

Pour the ball-milled MWCNT dispersion from the zirconia pot into a 50 ml conical centrifuge tube at 5 000 r/min.

Centrifuge the ball-milled MWCNT dispersion to separate the MWCNTs and then freeze-dry the separated MWCNTs for 24 h. Dry the MWCNTs at 300 °C for 30 min while exposed to air to remove unwanted volatile components.

Grind the dried MWCNTs by pestle and mortar.

NOTE When higher r/min and longer ball-milling time are applied than those described here, the structure of MWCNTs might be destroyed.

4.2 Dispersion method

Disperse 0,02 g of milled MWCNTs in 200 ml dimethylformamide (DMF) using an ultra-sonicator at 40 W for 3 h. Pour the MWCNT dispersion into a 50 ml conical centrifuge tube and centrifuge at 3 000 r/min for 30 min. Filter the dispersion with a paper filter (pore size 10 μ m) to eliminate any non-dispersed parts that might remain.

NOTE DMF is the best solvent for CNT dispersion (see Reference [4,5]).

4.3 Sample preparation for SEM

Use additional DMF to dilute the MWCNT dispersion to 10 \times . Drop 1 ml of the 10 \times dispersion onto a 0,02 μ m ceramic filter and filter it under vacuum. Dry the ceramic filter, containing the MWCNTs, at 60 °C for 24 h.

4.4 Alternative sample preparation method

Following the methods in order (4.1, 4.2 and 4.3) is recommended for Method 1 (see 5.1.2.1) and Method 3 (see 5.1.2.3). As-synthesized MWCNTs can be used for Method 2 (see 5.1.2.2).

5 Experimental procedure

5.1 Measurements of the SBPL using SEM

5.1.1 SEM

5.1.1.1 General

High-resolution SEM images allow closely spaced features to be examined at a high magnification.

5.1.1.2 Preparing SEM images

Cut the ceramic filter containing the MWCNTs into small pieces and place on a sample holder, to which conductive tape is applied. Dry the sample holder under vacuum at 40 °C for 1 h. Sputter coat the dried sample with iridium for 1 min. Gold, platinum, or carbon may be used if an iridium source is not available. Take three or more SEM images at a magnification of 10 000×. Take three or more representative high-resolution images at 20 000×. This procedure is recommended for Method 1 (5.1.2.1) and Method 3 (5.1.2.3).

Alternatively, place an as-synthesized MWCNT on a sample holder, to which conductive tape is applied. Dry the sample holder under vacuum at 40 °C for 1 h. Sputter coat the dried sample with iridium for 1 min. Gold or platinum may be used if an iridium source is not available. Take three or more SEM images at a magnification of 10 000×. Take three or more representative high-resolution images at 20 000×. This procedure is recommended for Method 2 (see 5.1.2.2).

NOTE 1 Sputter coating for more than 1 min can cause a slight change in the bending of the MWCNT.

5.1.2 Measurement methods for the SBPL

5.1.2.1 Method 1

From the SEM images, determine the contour lengths and end-to-end distances of at least 100 different individual MWCNTs. Classify the data using an interval of 100 nm for contour length. For each contour length range, calculate the mean-squared end-to-end distance.

Obtain the bending ratio for each contour length range by dividing the mean-squared end-to-end distance by the squared average contour length [see Formula (A.3)]. When the contour length is greater than 1 μm, the value of contour length from the top view image may be underestimated by up to 15 %.[1] When more accurate values are required, measure the contour length and end-to-end distance using a 3D image, which can be obtained by several side view images.[1]

Plot the bending ratio with respect to the reciprocal contour length, measure the gradient and determine the SBPL using Formula (A.4). When the linear relationship between bending ratio and reciprocal contour length reaches the asymptotic limit, the resulting slope equals two times the SBPL.

NOTE 1 For MWCNTs of random shape, the end-to-end distance varies at constant contour length.[1] Therefore, various values of end-to-end distance could be measured for each contour length range. The distribution of end-to-end distance of MWCNT is Gaussian for each contour length range when MWCNTs are of random shape. To obtain the mean-squared end-to-end distance, the mean value of the squared end-to-end distance is calculated.

NOTE 2 Because well-dispersed MWCNTs are filtered prior to SEM imaging, 100 MWCNTs are sufficiently representative of the shape of the MWCNTs in the sample. This is supported by DLS and DDLS measurements as well as intrinsic viscosity measurements.[1] An approximate value for the SBPL can be obtained using Method 2 or Method 3.

5.1.2.2 Method 2

Measure the radius of curvature of at least 100 individual tubes from the SEM images of as-synthesized MWCNTs, then calculate the mean value of the radius of curvature. This mean radius is approximately equal to the value of SBPL.

5.1.2.3 Method 3

From the SEM image, select at least 10 MWCNTs with a contour length in the range of $2,0 \mu\text{m} \pm 0,2 \mu\text{m}$. Measure the end-to-end distance of each MWCNT. The approximate value of SBPL can be obtained from the mean-squared end-to-end distance and the squared average contour length [see [Formula \(A.3\)](#) and [Formula \(A.4\)](#)].

NOTE 1 Method 1 is the most accurate method but it is time consuming. The SBPL estimated by Method 2 has up to 20 % deviation compared to Method 1 (Method 2 has a tendency to underestimate the SBPL). The SBPL estimated by Method 3 has up to 100 % deviation compared to the value obtained by Method 1. The order of magnitude of SBPL has consequences for many applications such as transparent conductive film, electrode and polymer composites.

NOTE 2 The values of SBPL obtained by Method 1, Method 2, and Method 3 can be confirmed by the viscometry method ([Annex B](#)) and/or the light scattering method ([Annex C](#)).

5.2 Measuring inner and outer diameters of MWCNTs using TEM

Place a droplet of the diluted MWCNT/DMF dispersion onto a carbon-coated copper grid. Dry the grid at $60 \text{ }^\circ\text{C}$ for 24 h. Take TEM images at 10 000x magnification. Take three or more high-resolution images at 1 000 000x to 3 000 000x of the MWCNT.

In order to obtain averages, measure the inner and outer diameters at not less than three different positions along the axis for at least 10 different MWCNTs. At least 30 total measurements are required.

6 Test report

The test report shall contain the following information (see [Annex D](#)):

- a) a full description of the sample preparation method(s) used;
- b) average inner and outer diameter (m);
- c) method used to determine SBPL;
- d) SBPL (m);
- e) all information necessary for evaluating the SBPL.

The test report may also include information relating to weighted average contour length and bending ratio (optional).

Annex A
(normative)

Formulae for terms and definitions in [Clause 2](#), [Annex B](#), [Annex C](#) and [Annex D](#)

A.1 Formulae for terms and definitions in [Clause 2](#)

A.1.1

static bending persistence length

SBPL

l_{sp}

maximum straight length without static bending

The overall size of MWCNTs of random shape scale with the square root of its contour length, L , as expressed by [Formula \(A.1\)](#) for the case $L \gg l_{sp}$.^[4,5,6]

$$\langle R^2 \rangle = 2l_{sp}L + 2l_{sp}(e^{-L/l_{sp}} - 1) \tag{A.1}$$

l_{sp} is SBPL. The following terms apply to MWCNTs of random shape.

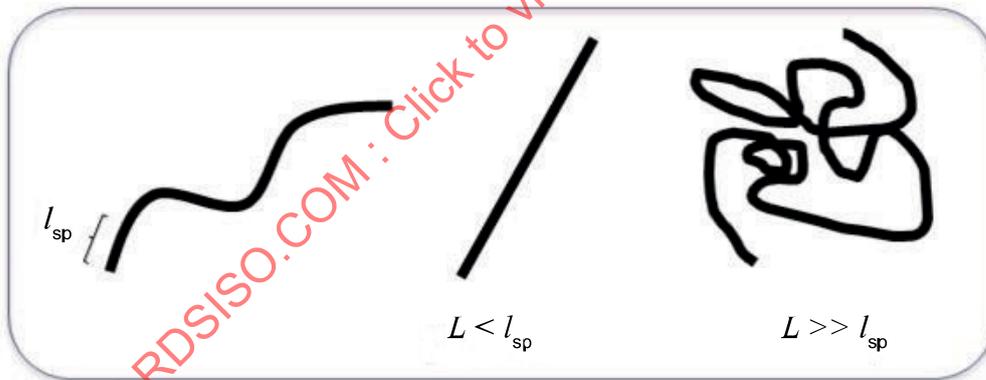


Figure A.1 — SBPL of an MWCNT

A.1.2

bending ratio

D_b

ratio between mean-squared end-to-end distance and squared contour length

The bending ratio, D_b , is determined by the number of static bend points and their distribution along the MWCNT axis. D_b is expressed as in [Formula \(A.2\)](#).^[4,5,6]

$$D_b \equiv \frac{\langle R^2 \rangle}{L^2} \equiv \sum_{i=1}^k \varphi_i^2 \quad (\text{A.2})$$

where

- $\varphi_i = N_i / N$ (each segment, i , consists of N_i unit segments);
- N is the total number of unit segments in an MWCNT;
- N_i is the number of unit segments in the i -direction segments;
- $k = m + 1$ where m is the number of static bend points;
- $\langle R^2 \rangle$ is mean-squared end-to-end distance;
- L is contour length.

SBPL is defined by [Formula \(A.3\)](#).^[4,5,6] Using SBPL is more convenient than using bending ratio because the former does not depend on contour length as it is obtained in an asymptotic limit.^[4,5,6] $2l_{sp}$ can be obtained from the slope when D_b is plotted versus $1/L$. When contour length is long enough, $1/L$ approaches zero.

$$D_b \equiv \frac{\langle R^2 \rangle}{L^2} \equiv \left(\frac{2l_{p0}}{L} \right) \left(\frac{1 + \cos(\theta)}{1 - \cos(\theta)} \right) = C \left(\frac{2l_{p0}}{L} \right) \equiv \frac{2l_{sp}}{L} \quad (\text{A.3})$$

where

- C is a constant;
- θ is a static bent angle between the direction of $(i+1)^{\text{th}}$ segment and the axis direction of i^{th} segment when i^{th} segment and $(i+1)^{\text{th}}$ segment is a neighbour (θ is 90°);
- l_{p0} is a segment length, assuming all segments in an MWCNT have equal length.

A.1.3

weighted average contour length

\bar{L}_w

average of contour length which is assigned a weight

NOTE Weighted average contour length, \bar{L}_w , is used for evaluating SBPL in SEM, DLS and viscometry analysis.

$$\bar{L}_w \equiv \frac{\sum_{i=1}^N N_i L_i^2}{\sum_{i=1}^N N_i L_i} \quad (\text{A.4})$$

where

N is the total number of individual MWCNT nano-objects;

N_i is the number of MWCNT having a length of L_i .

Weighted average end-to-end distance, \bar{R}_w , can be obtained by combining [Formula \(A.2\)](#) and [Formula \(A.4\)](#), which is used for the estimation of intrinsic viscosity in [Annex B](#).

A.1.4

intrinsic viscosity

$[\eta]$

description of an MWCNT's contribution to the viscosity of MWCNT dispersion

Intrinsic viscosity, $[\eta]$, is defined by [Formula \(A.5\)](#), [Formula \(A.6\)](#), and [Formula \(A.7\)](#).^[4,5]

$$[\eta] = 2,20 \times 10^{21} \frac{f}{M_{aw}} \left\langle \bar{R}_w^2 \right\rangle^{3/2} \quad (\text{A.5})$$

$$f = \left[1 + 0,926 \Delta (D_b)^{1/2} \right]^{-1} \quad (\text{A.6})$$

$$\Delta = \ln \left(\frac{2l_{sp}}{D_0} \right) - 2,431 \quad (\text{A.7})$$

A.2 Formulae for other terms and definitions

A.2.1

dynamic bending persistence length

l_p

maximum straight length that is not bent by thermal energy

Where MWCNTs are dispersed, the value for dynamic bending persistence length depends on the type of solvent used. The Kratky-Porod expression for l_p is given in [Formula \(A.8\)](#).

$$\left\langle R^2 \right\rangle = 2l_p L + 2l_p (e^{-L/l_p} - 1) \quad (\text{A.8})$$

where

$\left\langle R^2 \right\rangle$ is mean-squared end-to-end distance, which is the mean value of squared end-to-end distance;

L is contour length, which is the total length of an MWCNT along its axis.

A.2.2

apparent persistence length

l_{ap}

measured value of persistence length of an MWCNT by dynamic light scattering

When an MWCNT in a dispersion is exposed to thermal energy, its overall size and shape changes. The apparent persistence length, l_{ap} , is determined by the contributions of SBPL, l_{sp} , static bent angle, θ , and dynamic bent angle, $\Delta\theta$, according to [Formula \(A.9\)](#).

l_{ap} can be measured by DLS (see [Annex C](#)).

$$l_{ap} = l_{sp} \left(\frac{1 + \cos(\theta + \Delta\theta)}{1 - \cos(\theta + \Delta\theta)} \right) \left(\frac{1 - \cos(\theta)}{1 + \cos(\theta)} \right) \quad (\text{A.9})$$

The dynamic bent angle is the change of bent angle by thermal energy. The dynamic bent angle is usually less than 2° at moderate temperatures, so apparent persistence length can be approximated by the SBPL.

A.2.3

apparent molecular weight

M_a

description of the molecular weight of an MWCNT, assuming the individual MWCNT is a molecule

Apparent molecular weight, M_a , is defined by [Formula \(A.10\)](#):

$$M_a = \rho N_{\text{avo}} \left(\frac{\pi \left(\frac{-2}{D_0} - \frac{-2}{D_1} \right) L}{4} \right) \quad (\text{A.10})$$

where

ρ is the density of graphene layers of an individual MWCNT;

N_{avo} is Avogadro's number;

\bar{D}_0 is the average outer diameter of an MWCNT;

\bar{D}_1 is the average inner diameter of an MWCNT.

A.2.4

weighted average apparent molecular weight

\bar{M}_{aw}

average of apparent molecular weight which is assigned a weight

The weighted average apparent molecular weight, \bar{M}_{aw} , is defined by [Formula \(A.11\)](#):

$$\bar{M}_{aw} \equiv \frac{\sum_{i=1}^N N_i M_{ai}^2}{\sum_{i=1}^N N_i M_{ai}} \quad (\text{A.11})$$

where

- N is the total number of individual MWCNTs;
- N_i is the number of MWCNTs having apparent molecular weight, M_{ai} ;
- \overline{M}_{aw} is used for the estimation of intrinsic viscosity in [Annex B](#).

A.2.5

relative viscosity

η_r

ratio of the viscosity of a dispersion to the viscosity of the solvent used

Relative viscosity, η_r , can be estimated by the ratio between the time during which MWCNT dispersion passes the viscometer capillary, t_{MWCNT} , and the time during which pure DMF containing no MWCNT passes the viscometer capillary, t_{DMF} .

$$\eta_r = \frac{t_{\text{MWCNT}}}{t_{\text{DMF}}} \quad (\text{A.12})$$

A.2.6

specific viscosity

η_s

ratio of the viscosity of a dispersion to the viscosity of the solvent used minus one

Specific viscosity, η_s , can be obtained from relative viscosity using [Formula \(A.13\)](#):

$$\eta_s = \eta_r - 1 \quad (\text{A.13})$$

Annex B (informative)

Viscometry

B.1 General

Intrinsic viscosity of MWCNT dispersion can be estimated by weighted average apparent molecular weight, \bar{M}_{aw} , weighted average contour length, \bar{L}_w , and SBPL, l_{sp} . If there are known values of \bar{M}_{aw} and \bar{L}_w , l_{sp} can be estimated from the measured value of intrinsic viscosity. The viscometry method confirms the SBPL values obtained by measurement methods in [5.1.2](#).

B.2 Mesoscopic shape factor from intrinsic viscosity measurement

Clean the viscometer with DMF three times.

Using a viscometer with a capillary diameter of 0,46 mm is recommended because the resolution is inadequate for larger diameters and MWCNT aggregation can occur for smaller diameters.

Measure the time during which pure DMF containing no MWCNTs passes the viscometer capillary. Using additional DMF, dilute the MWCNT dispersion (prepared in accordance with [4.2](#)) to 0,001 wt.% to 0,005 wt.%. Pour the diluted MWCNT dispersion into the viscometer. Measure the time during which 0,001 wt.% to 0,005 wt.% MWCNT dispersion passes the viscometer capillary.

Calculate the relative and specific viscosities of the MWCNT dispersion using [Formula \(A.12\)](#) and [Formula \(A.13\)](#). Divide the specific viscosity by the MWCNT concentration. Plot the quotient with respect to the MWCNT concentration. Determine intrinsic viscosity by extrapolating the quotient to zero MWCNT concentration.

The value obtained for the intrinsic viscosity of the MWCNT dispersion can be used to estimate the SBPL by use of [Formula \(A.5\)](#), [Formula \(A.6\)](#), and [Formula \(A.7\)](#), provided that values for the weighted averaged apparent molecular weight and weighted averaged end-to-end distance are known.

Annex C (informative)

Dynamic light scattering and depolarized dynamic light scattering

C.1 General

Translational and rotational diffusion coefficients of MWCNTs can be measured by dynamic light scattering (DLS) and depolarized dynamic light scattering (DDLS). The diffusion coefficients can be estimated by apparent persistence length, l_{ap} , average outer diameter of MWCNT, $\overline{D_0}$, and weighted average contour length, $\overline{L_w}$. The light scattering method confirms the SBPL values obtained by measurement methods in 5.1.2.

C.2 Mesoscopic shape factor from light scattering measurement

DLS and DDLS are used to measure the translational and the rotational diffusion of MWCNTs. Using a Diode-Pumped Solid State Laser (DPSSL), supply approximately 100 mW at $\lambda_0 = 532$ nm.

NOTE Using higher power can result in an undesirable temperature increase of the MWCNT.

Use a 256-channel digital autocorrelator with a 480 ns minimum delay time to compute the scattered photons time autocorrelation function.

Measure the autocorrelation function at several scattering angles ranging between 30° to 90°. Apply the polarizer and the detector, each having 1:100 000 extinction ratio to the DLS. Rotate the detector with 1° resolution using the motor control unit.

The DLS cell should be controllable to 1 K above a temperature range between 278 K to 393 K. Translational and rotational diffusion coefficients can be obtained from the first cumulant of the average decay rate, Γ , of the electric field autocorrelation. When incident light and detector are both vertically oriented, the translational diffusion coefficient is obtained from the slope of the curve plotted for the average decay rate with respect to the square scattering vector magnitude:

$$q = 4\pi n \sin(\theta_s / 2) / \lambda_0 \quad (\text{C.1})$$

where

- n is dispersion refractive index;
- θ_s is scattering angle;
- λ_0 is incident light wavelength *in vacuo*.

In order to avoid a hydrodynamic interaction effect, a very dilute dispersion of $n_M L^3 = 0,5$ is recommended for DLS measurement, where n_M is the number of MWCNTs. Measure the first cumulant of the average decay rate, Γ , of the electric field autocorrelation function. When the incident light and

detector are both vertical, Γ is expressed as Γ_{Vv} . The translational diffusion coefficient, D_T , is characterized by [Formula \(C.2\)](#).^[12]

$$\Gamma_{Vv} = q^2 D_T \quad (C.2)$$

When the incident light is vertical and the detector is horizontal, Γ is expressed as Γ_{Hv} . The translational diffusion coefficient and rotational diffusion coefficient, D_R , is characterized by [Formula \(C.3\)](#).^[12]

$$\Gamma_{Hv} = q^2 D_T + 6D_R \quad (C.3)$$

There are three unknown factors for the shape and size of MWCNTs: average diameter, SBPL and weighted average contour length. With the average diameter data obtained by an independent method, SBPL and weighted average contour length can be evaluated by comparing [Formula \(C.4\)](#) and [Formula \(C.7\)](#) to experimental data.^[5] In [Annex D](#), experimental data are compared to the calculation data.

$$D_T = \frac{kT}{3\pi\eta_s \bar{L}_w} \quad (C.4)$$

$$\left[1 + \ln(2L_{ap}) - 2,431 + 1,843(N/2L_{ap})^{1/2} + 0,138(N/2L_{ap})^{-1/2} - 0,305(N/2L_{ap})^{-1} \right] \quad (C.5)$$

$$L_{ap} = l_{ap} / \bar{D}_0 \quad (C.5)$$

$$N = \bar{L}_w / \bar{D}_0 \quad (C.6)$$

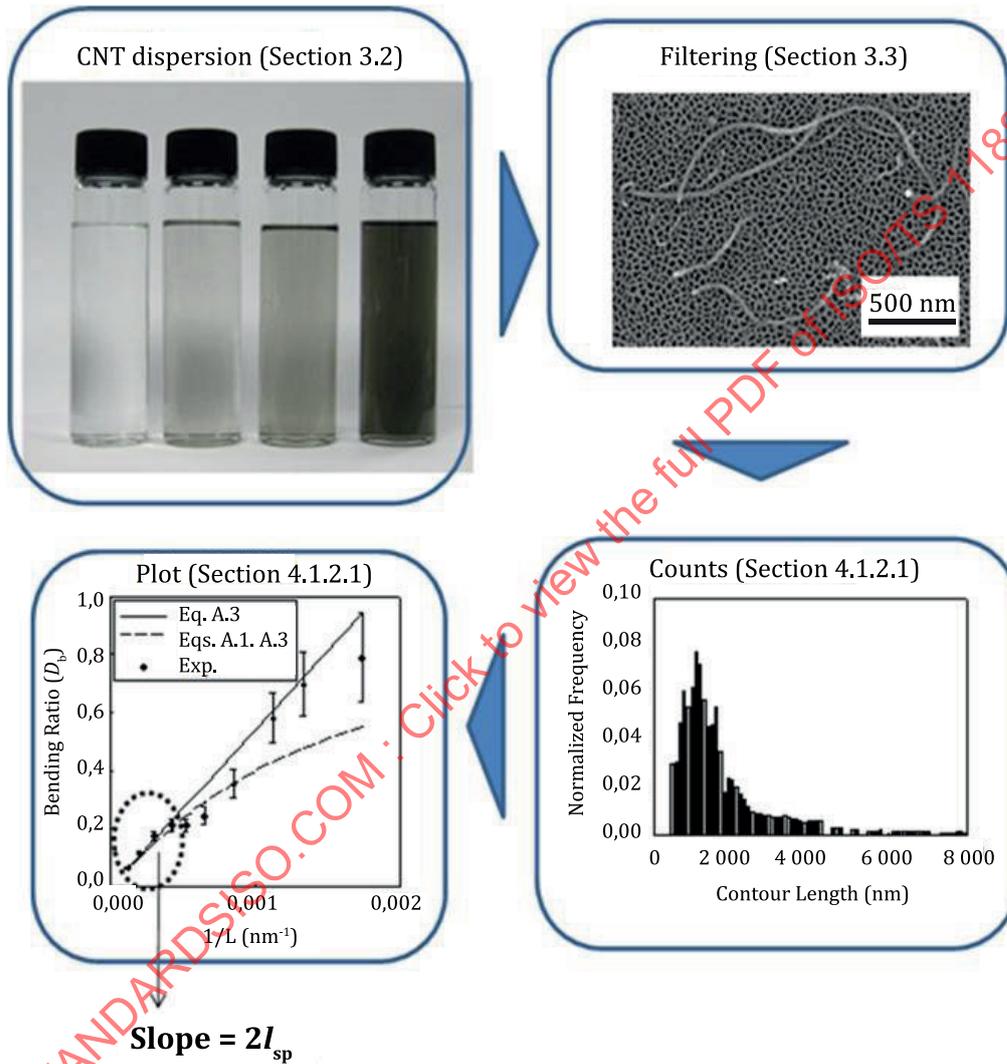
$$D_R = \left(\frac{kT}{\eta_s} \right) \left(\frac{2}{l_{ap} \bar{L}_w^2} \right) \left[0,253 \left(\frac{\bar{L}_w}{4l_{ap}} \right)^{1/2} + 0,59 \ln(2L_{ap}) - 0,227 \right] \quad (C.7)$$

SBPL measured by DLS represents the average shape of MWCNTs in a dispersion.

Annex D (informative)

Case study and reports

A brief summary for the measurement of SBPL using Method 1 is illustrated in [Figure D.1](#).



NOTE SOURCE: 2010 ACS

Figure D.1 — Pictorial process flow for the measurement of SBPL using Method 1

Mesoscopic shape factors of various MWCNTs can be reported as shown in [Table D.1](#). In the report of mesoscopic shape factors, it is recommended that the average outer diameter and SBPL, l_{sp} , be included. The measurement method for evaluating l_{sp} should be reported. Contour length and bending ratio can optionally be included in the report. Because the order of magnitude of l_{sp} has physical significance, it is recommended that the values of l_{sp} are expressed, e.g. $A \times 10^B$, where A and B are integers.