Small Angle Scattering Measurements of Nanotube Dispersion

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Purity and Dispersion Part II

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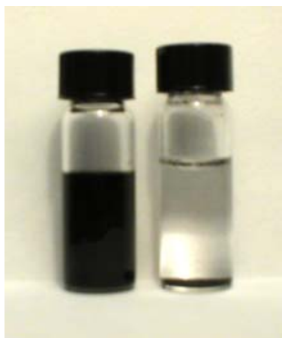
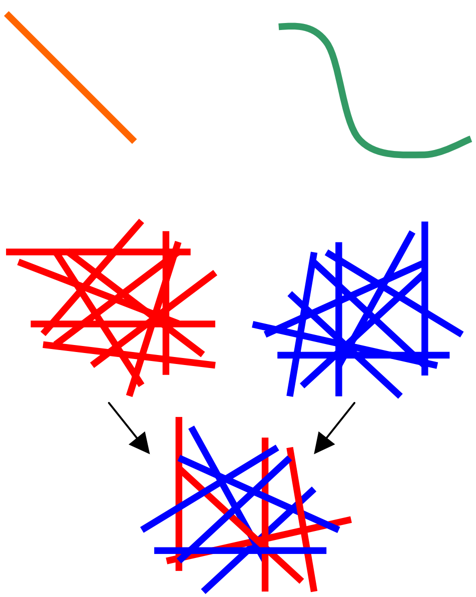
dispersion criteria





- macroscopic dispersion
  - non-settling
  - long term stability
- nanoscopic dispersion
  - individual tubes
    - rigid rods
    - flexible chains
  - clusters of many tubes
    - weak associations
    - permanent branching

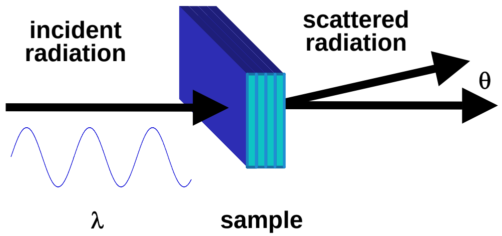
dispersion metrologies

method	sample form	population	strength	weakness
microscopy AFM TEM SEM	generally dried	$< 10^3$	direct visualization specific examples	biasing possible due to small population structure based on non-dispersed
spectroscopy UV-vis-NIR Raman fluorescence	dispersed	$> 10^{15}$	chirality	difficult interpretation
scattering SANS SAXS LS	dispersed	$> 10^{15}$	isotopic labeling sensitive to branching	difficult interpretation incoherent dominates certain sizes

- three major classes of dispersion measurements
  - microscopy, spectroscopy, scattering
- three dispersion techniques:
  - surfactant, polymer wrapping, covalent modification

small angle scattering background

- scattering parameter, $q = 4\pi \sin(\theta/2) / \lambda$
  - λ = wavelength, θ = scattered angle
  - q probes sizes $d = 2\pi/q$
- intensity of scattering
  - contrast factor
    - light – refractive index
    - x-ray – electron density
    - neutron – atomic content
  - isotopic labeling
    - neutron scattering only
    - hydrogen-deuterium substitution
      - change scattering contrast
      - assume thermodynamically and chemically identical



available scattering methods

method	λ	q	$d = 2\pi / q$	strength-weakness
small angle neutron scattering (SANS)	(4 to 20) Å	(10^{-3} to 10^{-1}) $Å^{-1}$ (10^{-5})	(10^{2} to 10^{4}) Å (10^{6})	isotopic labeling incoherent national facility required
small angle x-ray scattering (SAXS)	1.54 Å	(10^{-3} to 10^{-1}) $Å^{-1}$ (10^{-5})	(10^{2} to 10^{4}) Å (10^{6})	short counting time national laboratory or in-house
light scattering (LS)	(3 to 10) μm	(10^{-5} to 10^{-3}) $Å^{-1}$ (10^{-6})	(10^{4} to 10^{6}) Å (10^{7})	large size scale in-house
wide angle neutron and x-ray scattering		(10^{-1} to 10^{1}) $Å^{-1}$	(10^{2} to 10^{0}) Å	tube bundle interior adsorbed molecules

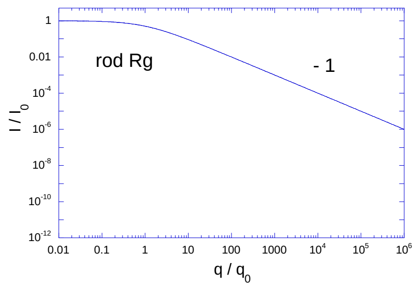
- measurements vary by q range and contrast type
- wide angle scattering probes SWNT diameter sizes

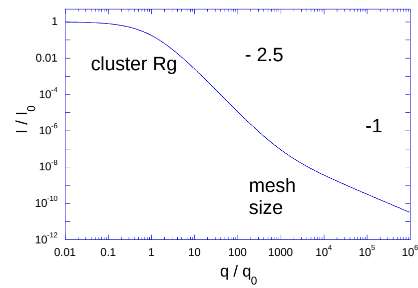
specific SANS factors

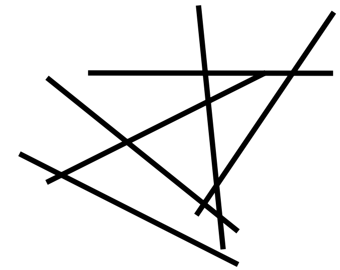
- incoherent scattering
  - flat background – low intensity, high q affected
  - due to hydrogen content – deuterated solvents necessary
- contrast factors
  - SWNT similar to deuterated solvents
  - most scattering is due to dispersant
    - surfactant, polymer, attached groups
    - dispersant that is strongly associated with SWNT is representative of SWNT itself

scattering from model structures

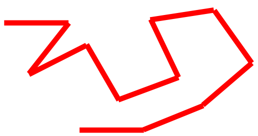
rod



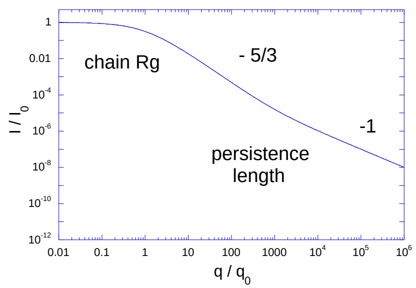


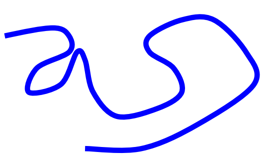


rod cluster

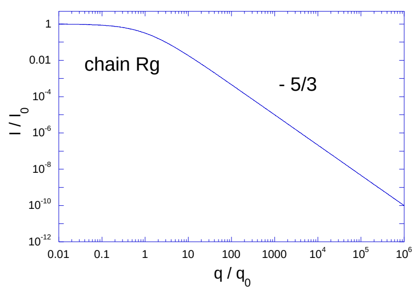


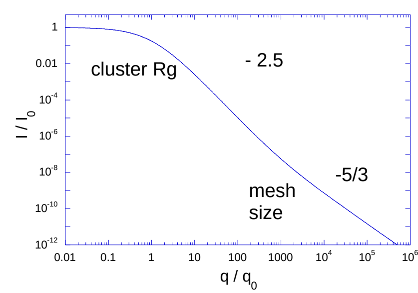
broken rod

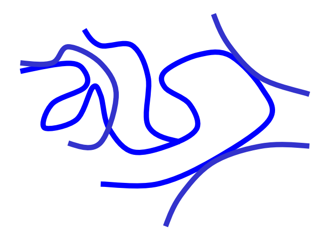




chain







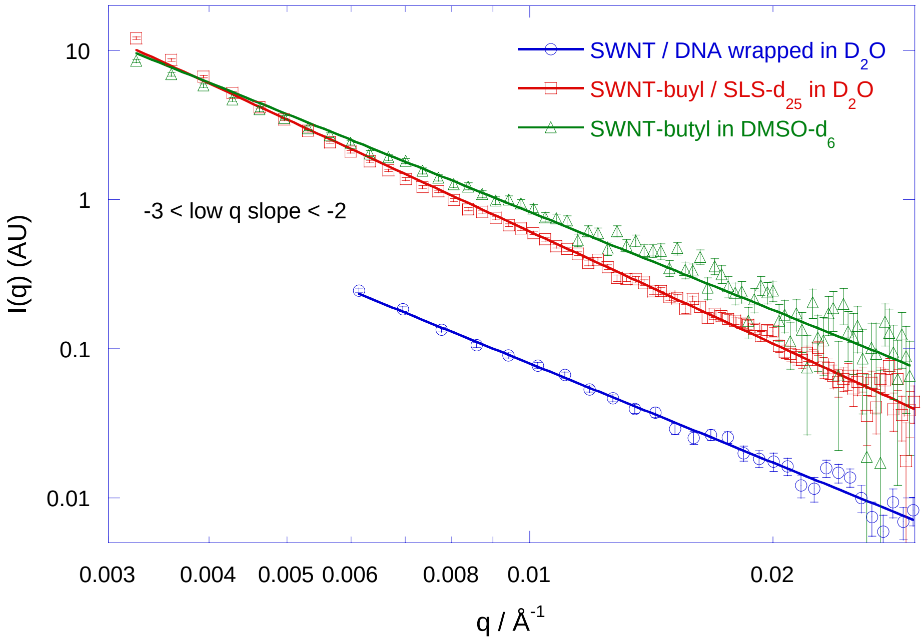
chain cluster

scattering of SWNT dispersions

scattering	author	title	dispersant	quote
SANS	Wang et al	Dispersing single-walled carbon nanotubes with surfactants: A small angle neutron scattering study	Surfactant (Triton)	“depletion interaction between SWNT **bundles** mediated by surfactant micelles.”
SANS	Krishnamoorti et al	Small-angle neutron scattering from surfactant-assisted aqueous dispersions of carbon nanotubes	Surfactant (SLS)	
SANS	Fischer et al	Small angle neutron scattering from single-wall carbon nanotube suspensions: evidence for isolated rigid rods and rod networks	Surfactant (NaDDBS)	“rod **networks**”
SAXS - LS	Schaefer et al	Morphology of dispersed carbon single-walled nanotubes	Polymer (PSSO3, PMAA, PAAHCl)	“Rather, a network structure of **aggregated tubes**, similar to that seen in dry samples, is found.”
SAXS - LS	Schaefer et al	Structure and dispersion of carbon nanotubes	Polymer (PSSO3, PMAA, PAAHCl)	“The single most important conclusion of the study is that even well dispersed both forms of carbon exist in an **aggregated state**.”
SANS	Rols et al	Neutron scattering studies of the structure and dynamics of nanobundles of single-wall carbon nanotubes	Surfactant (SLS)	“assign the SANS signal to **bundles** of some hundreds of tubes”

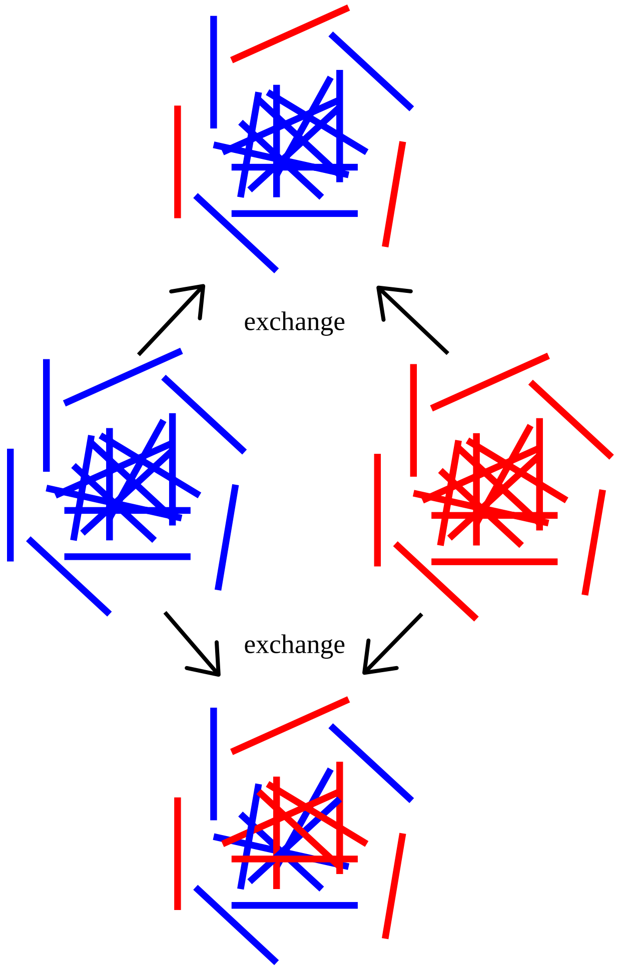
- clustered SWNT structures are commonly seen

typical SANS of SWNT dispersions



- dispersion method
  - surfactant
  - wrapping polymer
  - covalent modification
- low q power law
  - generally between –2 and –3
  - likely due to clustering

stability of clusters



- SANS power laws
  - between –2 and –3
  - branched or clustered
  - individual chains present
- dynamic equilibrium
  - single chains and clusters
  - chains within clusters
- deuterium labeled tubes
  - does exchange occur?
  - what is tube shape?

SANS isotopic labeling

- SWNT needs hydrogen content for labeling, $^{12}C/^{13}C$ not practical
- permanent structure (covalent), surfactants or polymers can exchange
- synthesize two identical samples, SWNT-C_4H_9 and SWNT-C_4D_9 .
- samples are identical except for different for neutron contrast factors, σ_H and σ_D in solvent σ_S. with volume fractions x_H and x_D .
- scattering contributions come from single chain correlations, P(q) and interchain correlations, Q(q).

SANS isotopic labeling

- $I(q) = K\, M_W((x_D(\sigma_D - \sigma_S)^2 + x_H(\sigma_H - \sigma_S)^2)P(q) + (x_D\, \sigma_D + x_H\, \sigma_H - \sigma_S)^2 \phi Q(q))$
- start with 100 % SWNT-C_4H_9 and 100 % SWNT-C_4D_9 in D_2O/SLS-d_{25}
- calculate match point at which Q(q) prefactor goes to zero.
- use appropriate fractions x_H and x_D for SANS sample.
- fit P(q) and Q(q) from three SANS experiments

grafting of butyl groups to SWNT

- free radical grafting
  - Billups et al

$$(\phi COO)_2 \longrightarrow 2\phi COO\bullet$$

- generate radicals thermally

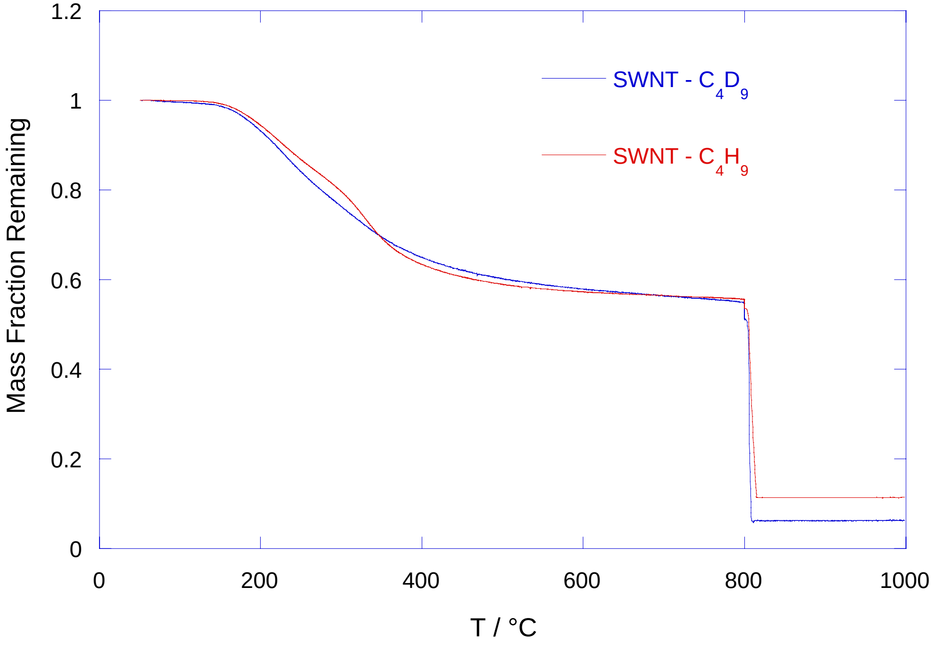
$$+C_4H_9I \longrightarrow C_4H_9\bullet$$

- abstract iodine from alkyl iodides

$$+SWNT \longrightarrow SWNT - C_4H_9$$

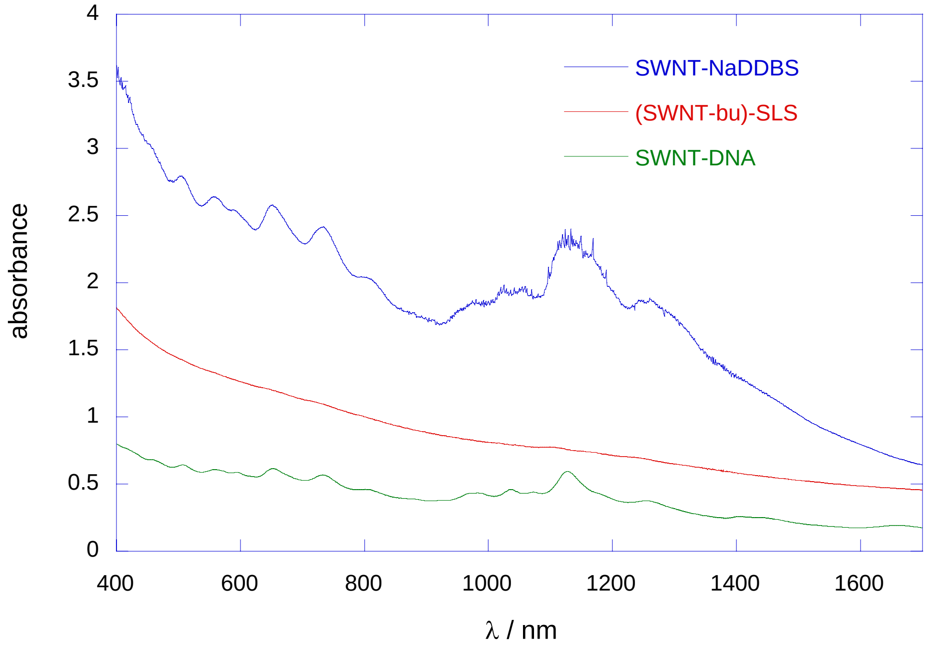
- alkyl radicals attach to tube wall

TGA of SWNT-C_4H_9



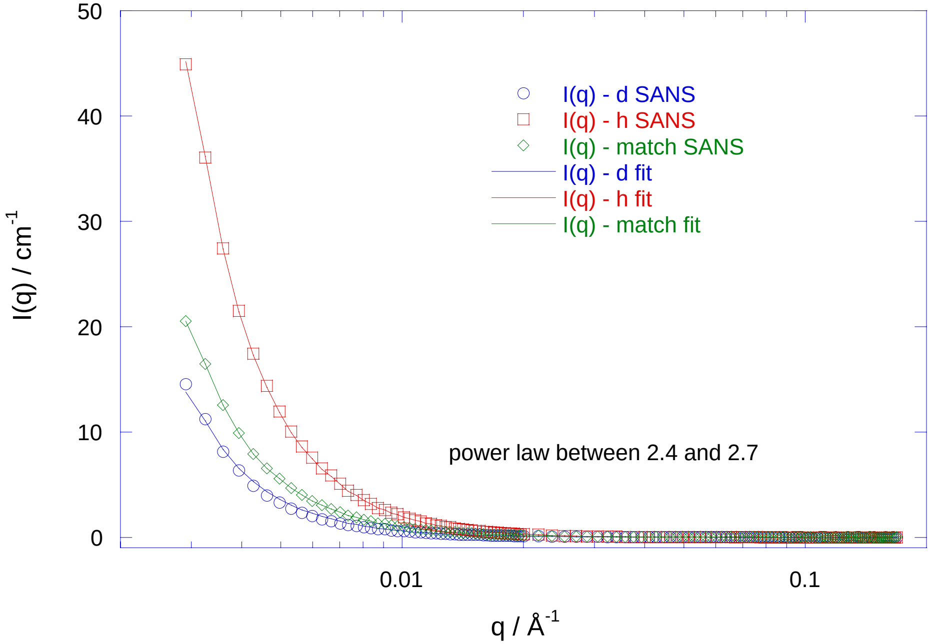
- thermogravimetric analysis (TGA)
  - 10 °C/min in N_2 releases butyl groups
  - anneal at 800 °C in air
  - increase to 1000 °C to burn of carbon
- high mass fraction attachment
- large neutron contrast established

UV-Vis-NIR of SWNT- C_4H_9



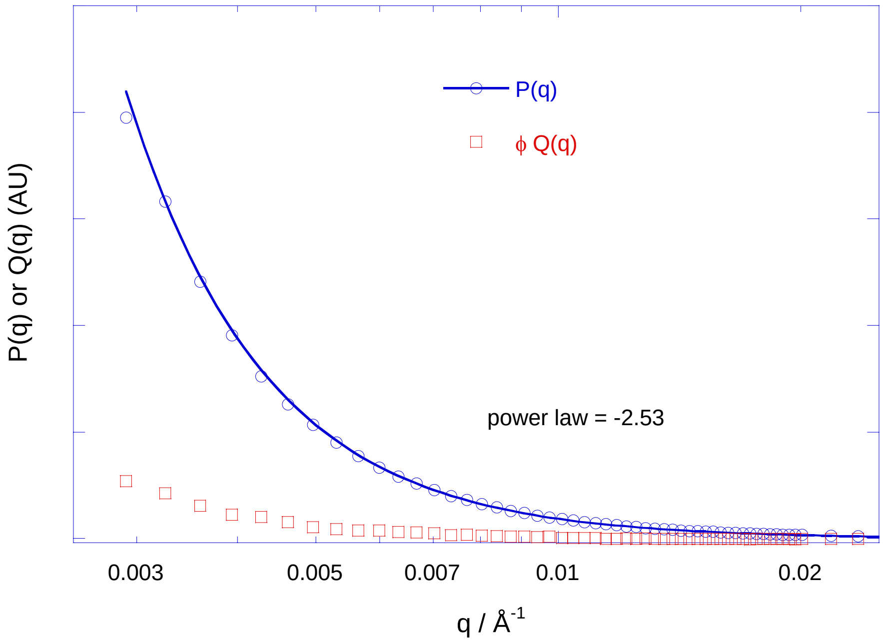
- ultraviolet-visible-near infrared spectroscopy
- van Hove transitions disappear
- sp^2 carbons become sp^3 indicating high conversion
- results consistent with literature

SANS of SWNT- C_4H_9



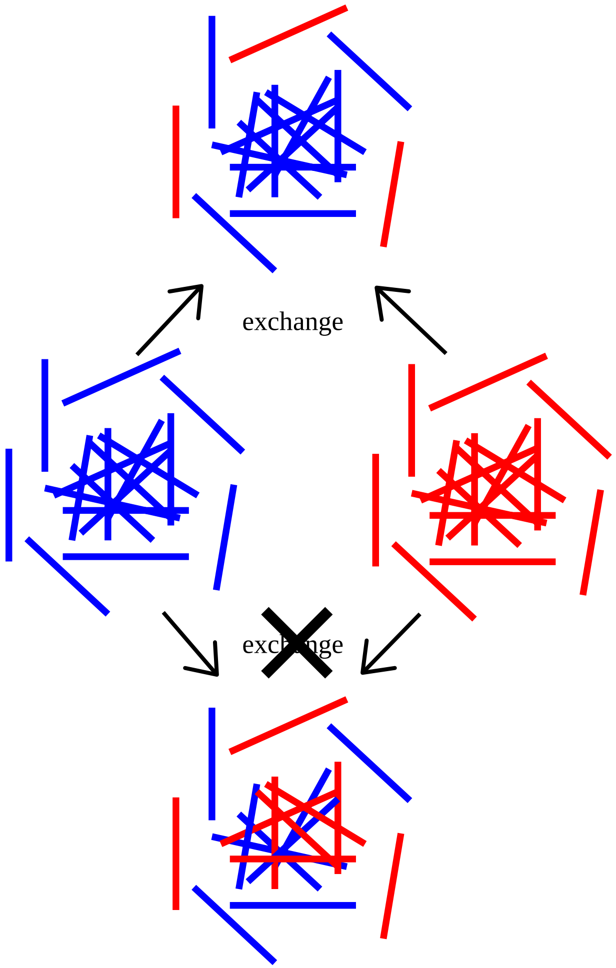
- SANS of all three samples have high power laws
- fits of P(q) and Q(q) accurately represent raw data
- SANS intensity of “match” is high

P(q) and S(Q) of SWNT- C_4H_9



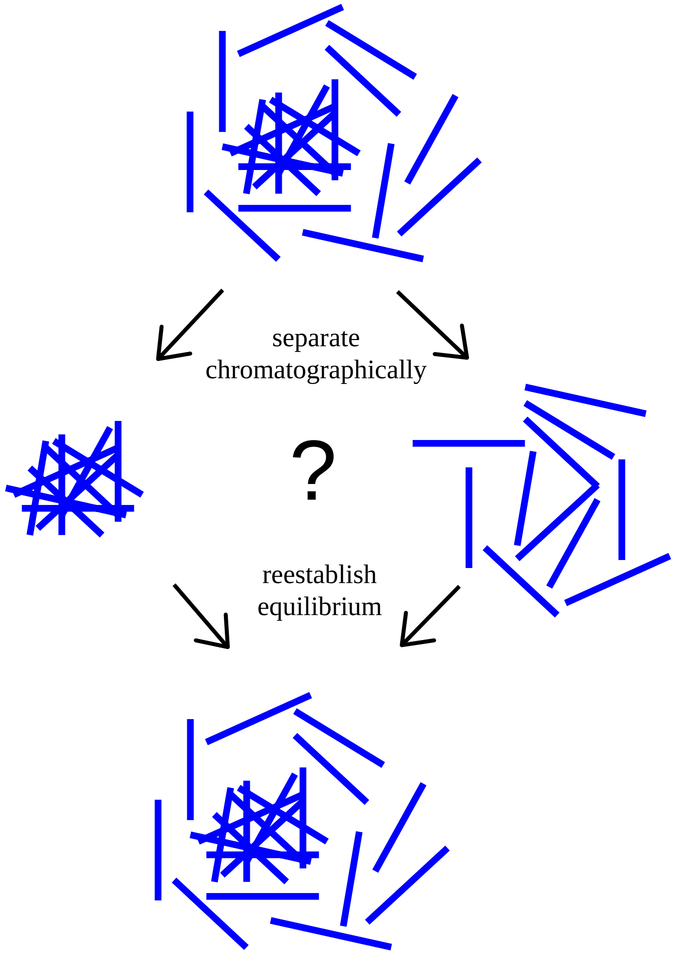
- fit of P(q) shows power law representative of cluster
- fit of Q(q) is positive characteristic of unstable mixture
- raw SANS data is representative of single “entity”

cluster stability in SWNT- C_4H_9



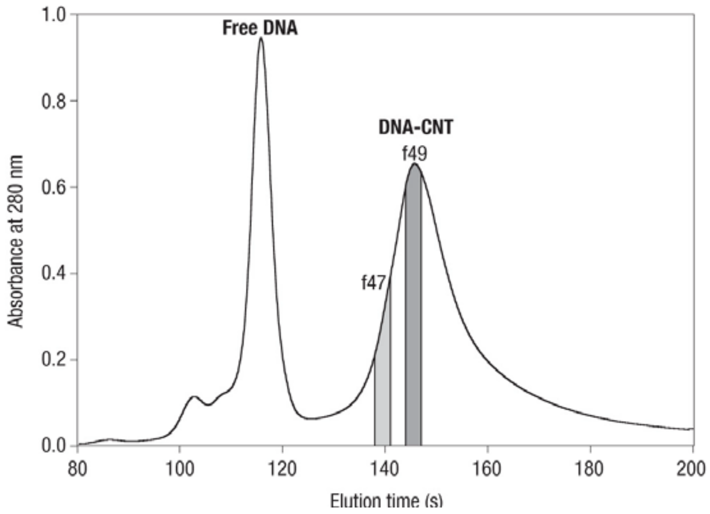
- individual SWNT within clusters do not exchange
- additional sonification does not break up clusters
- the high energy grafting reaction may make this atypical
- other covalent attachment schemes can use this method

chromatographic separation of components



- can clusters be separated from individually dispersed SWNT?
- chromatographic types
  - ion chromatography (IC), size exclusion chromatography (SEC)
- scattering methods
  - SANS, SAXS, LS
- dispersant types
  - surfactant, polymer, covalent
- do clusters reform?

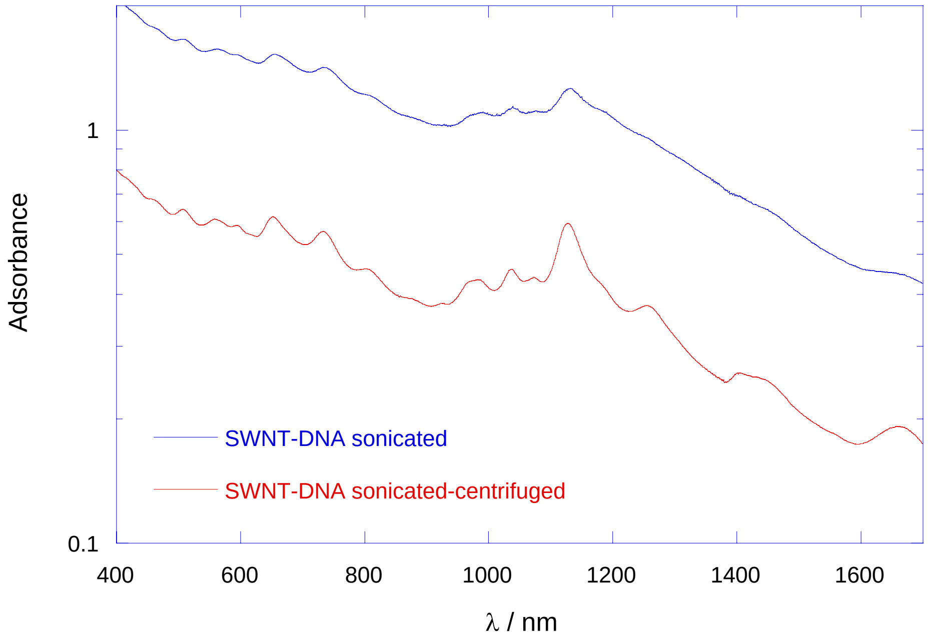
DNA wrapping



from "**DNA-assisted dispersion and separation of carbon nanotubes", Zheng M, Jagota A, Semke ED, Diner BA, Mclean RS, Lustig SR, Richardson RE, Tassi NG, NATURE MATERIALS 2 (5): 338-342 MAY 2003**

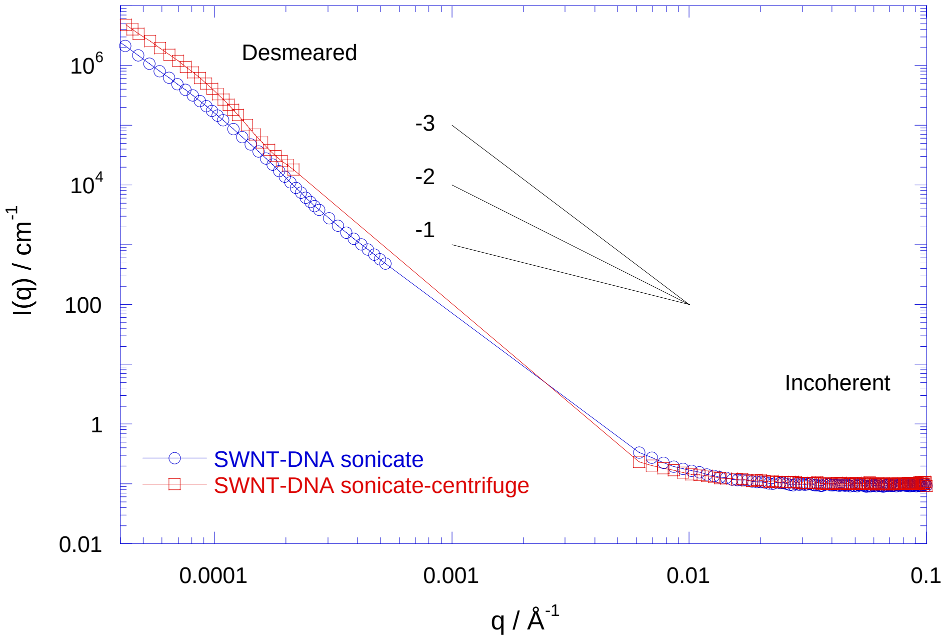
- Zheng et al
- dispersant
  - single strand DNA
  - d(GT)20
- ion chromatography
  - removes free DNA
  - fractionates by chirality
  - removes clusters?

UV-vis-NIR of SWNT-DNA



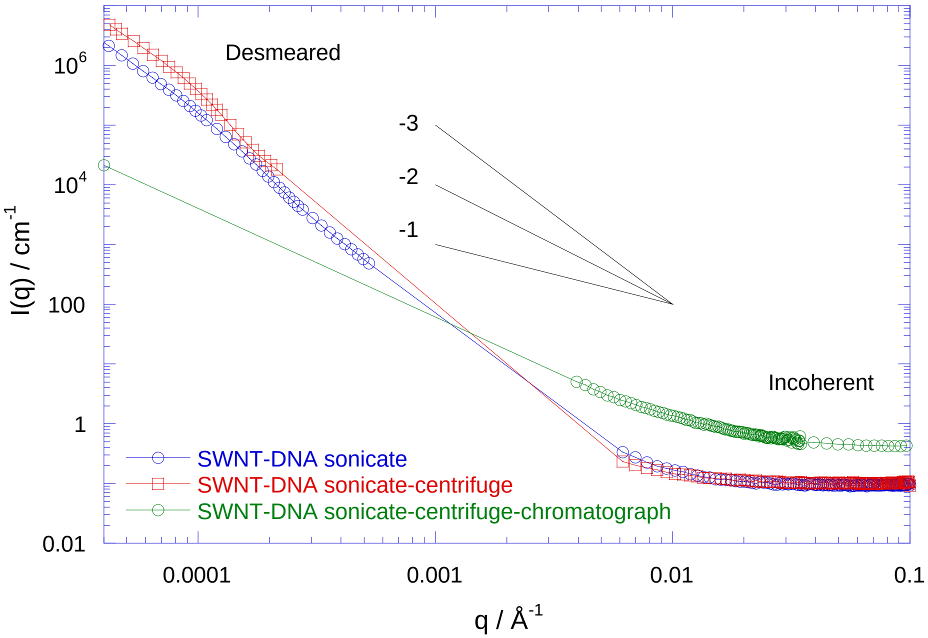
- sonication to disperse 1 mg/mL SWNT
- centrifugation lowers concentration but strengthens van Hove transitions
- improved dispersion?

SANS and USANS at progressive stages



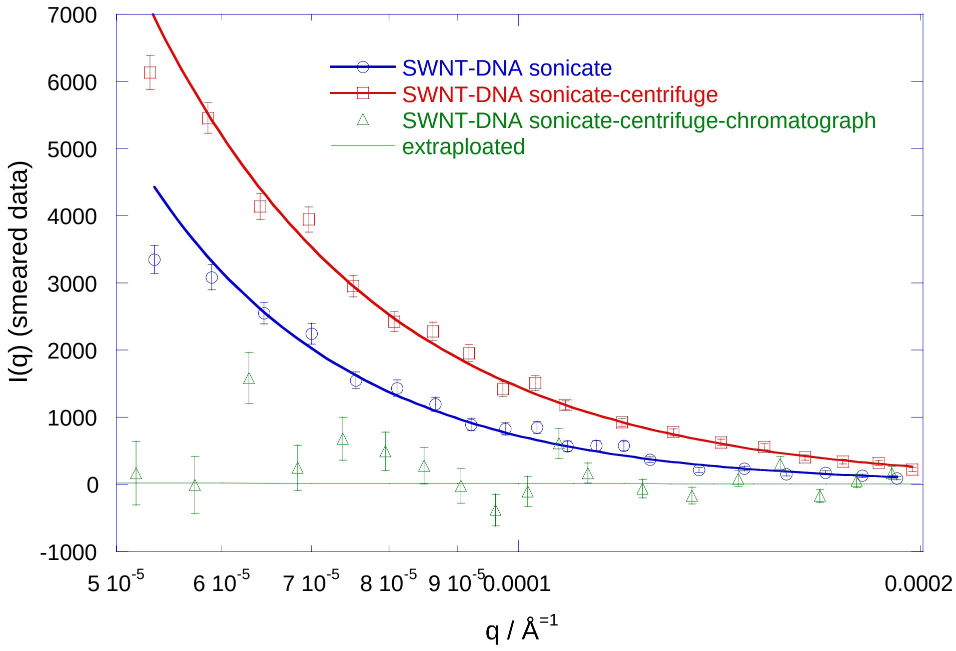
- SANS and USANS of samples
- stages of purification
  - sonication(1)
  - centrifugation (2)
- power laws
  - clusters after stage 2

SANS and USANS at progressive stages



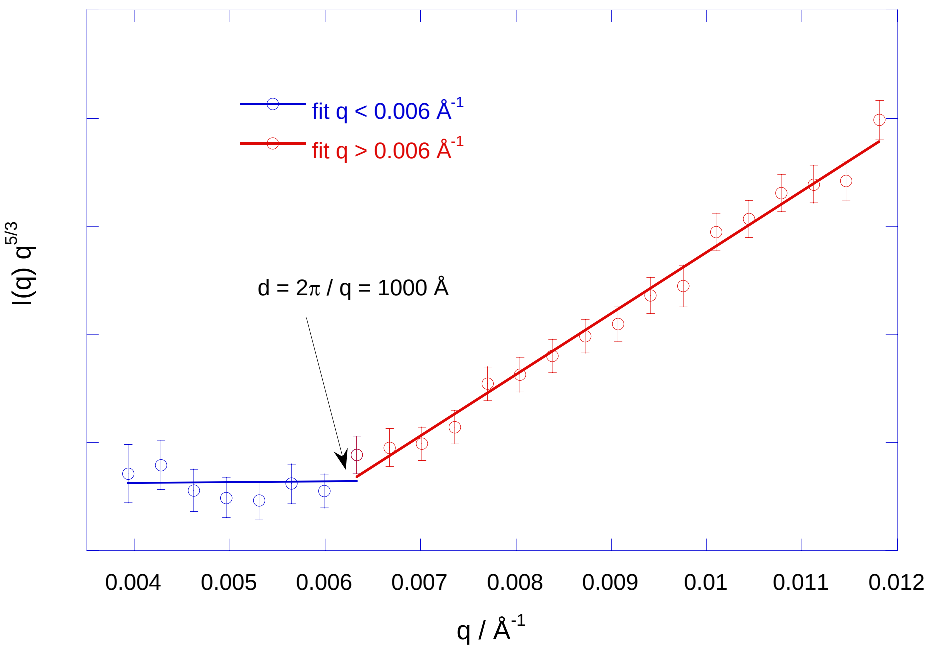
- chromatographed (SEC) from DuPont
- stages of purification
  - sonication(1)
  - centrifugation (2)
  - chromatography (3)
- power laws
  - clusters after stage 2
  - clusters largely removed after stage 3

USANS detail



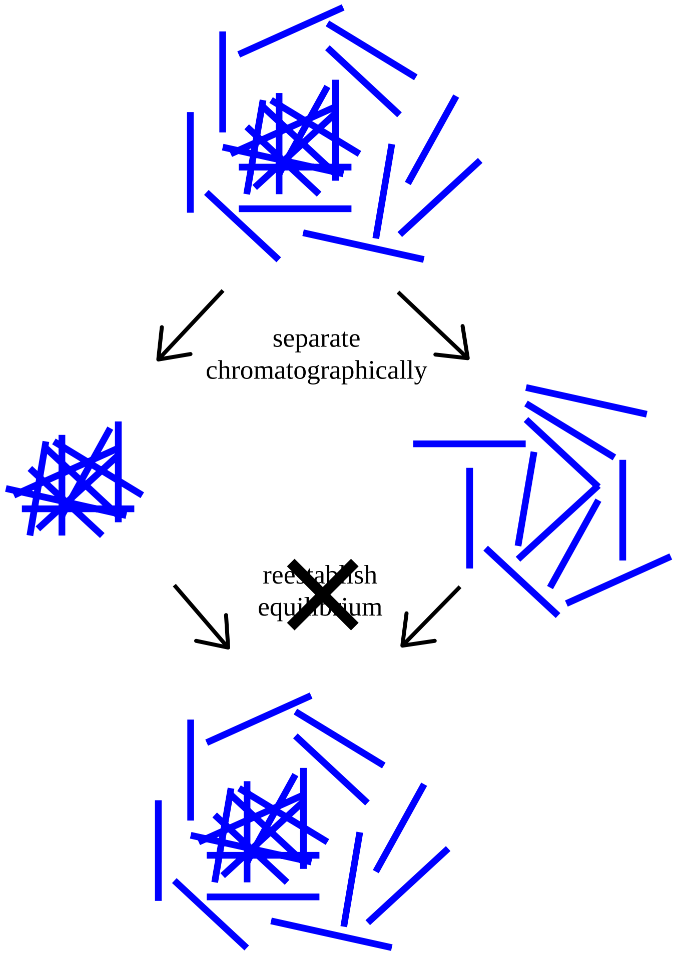
- chromatographed (SEC) sample
  - baseline scattering
  - good dispersion
- other samples
  - strong scattering
  - high power law
  - poor dispersion

Kratky plot of SEC sample



- power law
  - -5/3 for q < 0.006 Å^{-1} (self avoiding walk)
  - transition to stiffer chain
- persistence length
  - $d = 2\pi/q = 1000$ Å
  - incoherent scattering

DNA conclusions



- SANS power law
  - before chromatography
    - -2 to -3
    - clusters present
  - after chromatography
    - -1 to –5/3
    - good dispersion
- clusters do not reform
- separation of clusters
  - chromatography
  - bulk fractionation
  - may provide a route to good dispersion

summary of SWNT small angle scattering metrology

- small angle scattering is a sensitive probe of SWNT dispersion
- many macroscopically dispersed SWNT systems contain large clusters of tubes
- butyl grafted SWNT dispersions contain clusters that do not exchange individual SWNTs
- SWNT/DNA dispersions purified by chromatography do not re-cluster significantly
- LS and SAXS may provide necessary dispersion information for general screening

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