21: Organization and properties of nanostructure networks

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Announcements

- Project meetings Thursday, please sign up
- Project presentations next M, 6-9pm, 165 CC
- Project reports due Tues (Apr/20) 5pm; may be submitted as late as Fri (Apr/23) without penalty
- GCC review late next week?
Order = quality, purity, alignment

Quantity = #/volume

Images from many sources including Nanocomp, Dai, Kim, Rinzler groups
Today’s agenda

- Nanostructure networks: concepts and dominant behavior
- Electrical transport: percolation theory
- Thermal transport in networks
- Mechanical properties of networks
- Methods of joining nanostructures
Today’s readings

OPTIONAL: (ctools)

*Electrical*
- Balberg, “Critical behavior of the two-dimensional sticks system”
- Kumar et al., “Percolating conduction in finite nanotube networks”

*Thermal*
- Prasher et al., “Turning carbon nanotubes from exceptional heat conductors into insulators”

*Mechanical*
- Berhan et al., “Mechanical properties of nanotube sheets”
- Koziol et al., “High performance carbon nanotube fiber”
Today’s readings

OPTIONAL: (ctools)

Joining

- Krasheninnikov and Barnhart, “Engineering of nanostructured carbon materials with electron or ion beams”
- Manzo et al., “Heterojunctions between metals and carbon nanotubes as ultimate nanocontacts”
Networks of nanostructures

**GOAL:** Achieve properties of individual nanostructures at large (bulk) scales, by assembling the structures into a 2D or 3D network

**AND/OR**
achieve *combined* properties of different types of nanostructures and host materials by making a network

**Practically, network performance is dominated by:**
- Network architecture and morphology (alignment and interconnection)
- Geometry (shape) of the individual nanostructures
- Intrinsic properties of the individual nanostructures (e.g., defect density)
- **Structure-structure interactions (contact resistance)**
- Structure-matrix interactions (functionalization, bonding)

→ *the complexity of a network also complicates characterization*
Applications of nanostructure networks

- Conductive plastics for electrostatic discharge/shielding
  - vehicle interiors
  - E/M shielding

- Thin-film electronics
  - memory
  - flexible transistors
  - transparent conducting films

- Strain sensors and chemical sensors (resistive or capacitive)

- Energy conversion and storage devices
  - battery and fuel cell electrodes
  - catalyst supports

- Electrical/mechanical/thermal interfaces
Electrical properties of networks

Percolation at low loadings gives large increase in electrical conductivity

- Typically 0.1-1% percolation threshold for high-aspect-ratio structures
- Large conductivity difference between filler and matrix, meaning electron transport is almost entirely through the filler, e.g., $>10^{11}$ conductivity ratio for CNTs/polymer
Thermal properties of networks

- No sharp transition at percolation
- Phonon scattering at structure-structure contacts dominate thermal transport
- Structure-matrix interactions can also significantly affect conductivity by phonon scattering
Mechanical properties of networks

- Largely follow a linear rule of mixtures
- Stiffness can scale to near-theoretical values
- Strength governed by defect isolation and propagation
- Overlap/joining between structures (shear strength) vital for load transfer, especially between strong structures and a weak matrix
- Alignment (waviness) is critical
- Joint morphology is critical
What types of joints are in this network?
Joints: an intrinsic attribute of a network

Entangled (VDW contact)

(a)

Branched (as-grown)

(b)

Welded (irradiated)

(c)

“Soldered” (deposited)

(d)

Coated (e.g., metal or polymer)

(e)

Interface region

Types of contact

**Non-bonding:** van der Waals adhesion
- contact
- thin interlayer (e.g., polymer, functional group)

**Bonding:** covalent linkages
- contact
- thin interlayer (e.g., polymer, functional group)
Relevant separation distances

Electrical: 0 to \(\sim10\) nm
  - tunneling

Thermal: 0 to \(\sim1\) nm
  - phonon propagation

Mechanical: contact only
  - direct load transmission
Network deposition methods

- Direct growth (e.g., CVD) on a substrate

- Dispersion (and purification, separation) then deposition on a substrate by, e.g.,
  - Spin-coating
  - Dip-coating
  - Vacuum filtration
  - Electrophoretic deposition
  - Transfer (e.g., contact printing)
  - Bulk mixing (e.g., polymer composites)
CNT films: tangled vs. aligned

(1) Mo/Fe/Al₂O₃ in CH₄/H₂, 875 °C

Mo mediates CH₄ decomposition to give SWNTs

Fewer active catalyst particles
Low activity carbon source

(2) Fe/Al₂O₃ in C₂H₄/H₂, 750 °C

More active catalyst particles
High activity carbon source

Vacuum filtration

- Büchner funnel
- moistened filter paper
- porous plate (plate with holes in)
- rubber bung
- rubber tubing
- suction from aspirator creates partial vacuum in flask
- filtrate (liquid that passes through filter paper) collects here

large enough particles of solid cannot fit through tiny holes in filter paper, so remain here

A. Rinzler
Vacuum-filtered CNT films at different densities

Figure 1. SEM images of the NTNs on alumina substrates, taken at 1.5 kV and 5 μA emission current. (a) Network resulting from filtering 7 mL of NT solution through the membrane. The filter pores are not visible in the scale shown. The network is near the percolation threshold and has few or no percolative paths through the sample. (b) 10 mL of NT solution for this sample. The network is above the percolation threshold and has several parallel pathways, allowing conduction across the film. (c) Film resulting from 400 mL of solution. Film is several layers thick.
MICROELECTRONIC-GRADE CARBON NANOTUBE COATING

Microelectronic-grade carbon nanotubes are now commercially available through Nantero’s licensee Brewer Science. Brewer Science, a trusted, long-term provider of leading edge materials and processes to the semiconductor industry has announced commercial availability of the first microelectronic-grade carbon nanotube coating. A breakthrough in the refinement of the carbon nanotube material enables the removal of metallic and carbonaceous contaminants. The coating is easily applied by spin, spray, micro-dispensing or ink-jet printing.

Qualities

- Industry standard cleanliness for trace metals
- Low carbonaceous impurities
- Individual/unbundled CNTs in surfactant-free benign solvent
- Stable suspension of individual carbon nanotubes
- Trusted semiconductor materials manufacturer
- Processed by CMOS industry fabrication and diagnostic tools

Patternable Coating

![Patternable Coating Image]
Anisotropic networks

(a) SWNTs (transfer printed)

(b) Ag NWs (Langmuir-Blodgett method)

Figure 6. SEMs of four terminal test structures formed on SWNTs with different layouts, including (a) aligned arrays, (b) crossbars, and (c) random networks.
Configuration matters

A single uniaxial rope is $\sim 60 \times$ more conductive than the disordered mat. The compressed mat is $\sim 3 \times$ densified. For all three materials $\rho(T)$ is quite flat.

Geometry determines transport pathway(s) (electrons, phonons, forces)

Square lattice

isotropic filler: high threshold, “orientation” has no meaning

rod-like filler: onset of percolated path determined by concentration and mis-alignment!

Stick count $\rightarrow$ density; 1D concept introduces cluster size

Imaging network connectivity

FIG. 2. A series of voltage contrast SEM micrographs under various bias conditions: (a) both electrodes at −20 V, (b) top electrode at −20 V, bottom electrode at ground, and (c) top electrode at ground, bottom electrode at −20 V. (d) Image generated by subtracting (b) and (c) from (a).
Percolation threshold

The density (volume fraction) of filler above which there is a continuous path across a material

- Typically 0.1-1% for “long” (fiber/wire) conductors
- Typically 1-10% for agglomerates/disk

*Percolation is a random process...*
Percolation is a sudden transition!

N. Grossiord et al, TU/Eindhoven.
A general network conductivity (diffusivity) model (above percolation threshold)

\[ \sigma = \sigma_{\text{max}} \left( \rho - \rho_c \right)^t \]

For a “perfect” 3D network (lattice), \( t = 2 \)

Practically, \( t \) varies a lot (\( t < 2 \)) based on
- Geometry and morphology of conductors (e.g., CNTs)
- Electron hopping between conductors (across gaps)
- Network is often locally agglomerated
Resistor network model

FIG. 1. The transformation of a conducting-sticks system into a resistor network. The sticks are assumed to be conducting and a resistor is assumed to be associated with the intersection of two sticks. Note that the equipotential stick is reduced to a point or a junction in the resistor network.
“Composite” transistor shows size effects and network effects

- Narrow = ballistic
- Wide = diffusive

- Junction resistances
  \( \sim 1000' \) s of ohms
  (tunneling, M/M, M/SC)

Low CNT density: few CNT-CNT contacts

- Density is below percolation threshold
- Vary channel length relative to mean free path: ballistic and diffusive regimes
- $L_C = \text{channel length}, L_S = \text{CNT length}$

![Graph and equation](image)

**Equation (1):**

\[
I_B \propto N_S = \frac{2D_x}{\pi} \int_0^\theta_L (L_S \cos \theta - L_C) d\theta \\
= \left( \frac{2}{\pi} \right) D_x L_S \left[ \sqrt{1 - \left( \frac{L_C}{L_S} \right)^2} - \left( \frac{L_C}{L_S} \right) \cos^{-1} \left( \frac{L_C}{L_S} \right) \right].
\]

**FIG. 2.** Comparison of analytical results and numerical predictions of channel length dependence of ballistic and diffusive currents for densities below the percolation limit.

High CNT density: many contacts

- Channel length is much larger than mean free path for electron scattering with phonons and at tube-tube contacts
- Occurs when:
  - Channel is long
  - Channel is short and density far exceeds percolation threshold

- Conduction strongly depends on tube-tube contact resistance
- I-V characteristics (conductance exponent) depend on $L_C$

FIG. 3. (a) Computed conductance dependence on channel length for different densities ($\rho$) in the strong coupling limit ($g_{ij} = 50$) is compared with experimental results from [15]. $\sigma_0 = 1.0$ (simulation; $\rho = 1.35 - 10 \ \mu m^{-2}$), $\sigma_0 = 1.0$ (experiment; $\rho = 1.0 \ \mu m^{-2}$), and $\sigma_0 = 1.4$ (experiment; $\rho = 10.0 \ \mu m^{-2}$). The number after each curve corresponds to $\rho$ and the number in [ ] corresponds to $\rho$ in experiments from [15]. (b) Dependence of the conductance exponent ($n$) on channel length for different densities ($\rho$) based on Fig. 3(a) (i.e., $\sigma/\sigma_0 \sim L_C^n$). Assumed parameters, chosen to reflect experimental conditions in [15], are: $H = 90 \ \mu m$, $L_S = 2 \ \mu m$, and $L_C = 1 - 25 \ \mu m$. 

Percolation in metal nanowire films

Figure 6. Volume electrical resistivity ($\rho$) of PS nanocomposites for different concentrations of a) Ag and b) Cu nanowires. The lines connect the average values calculated from replicate specimens prepared at each concentration.

Percolation in nanoparticle films

Antimony-doped tin oxide (ATO)

Figure 3. FE-SEM images of the surface of deposited layers prepared with ATO volume fraction $\phi = 0.0083$ observed at low (a), medium (b), and high (c) magnifications.

Figure 4. Surface resistivity as a function of ATO volume fraction for deposited layers. Controlled relative humidity during layer deposition: 54% RH (●), 40% RH (○). Inset: log–log plot of surface resistivity $\rho_s$ versus ATO volume fraction $\phi$. Relative humidity during layer deposition: 54% RH.

Legend:
- Latex particle
- Nanotube
- Surfactant
CNT/PS film

N. Grossiord et al.
MWCNT/PS composites

- Disperse CNTs in SDS surfactant
- Mix with PS; emulsion polymerization

![Graph showing conductivity vs. MWCNT concentration.](image)

**Bounds**
- Individual CNT = $10^5 - 10^8$ S/m (MW→SW)
- Buckypaper (about 50% CNTs) = $10^4 - 10^5$ S/m
- Typical composite (1 wt% CNTs) = $10^0 - 10^3$ S/m

**Figure 6.7.** Four-point conductivity of MWCNT/PS composite as a function of MWCNT content. Each point of the curve is the average of several measurements performed several times on several locations on the two sides of the nanocomposite films. Several types of MWCNTs, viz. VGCNTs (□) and IPCNTs of Nanocyl, batch 060213 (♦), were dispersed in the same PS matrix, namely EP2.

N. Grossiord et al, TU/Eindhoven.
Performance relates to CNT quality

Figure 6.9. Thermograms of crude VGCNTs (plain line) and of IPCNTs (dashed line) performed under air at a flow rate of 25 mL/min and a heating rate of 5 °C/min.

N. Grossiord et al, TU/Eindhoven.
Thin CNT networks are also transparent

A. Rinzler.
Reverse percolation strain sensors

Increasing MWCNT vol%:

- Pristine PEO
- 0.003 vol% MWCNT
- 0.014 vol% MWCNT
- 0.022 vol% MWCNT
- 0.028 vol% MWCNT
- 0.056 vol% MWCNT
- 0.139 vol% MWCNT

Polycarbonate

MWCNT/PEO Composite Film

Reflective Tape

Free End

M. Park et al.
Reverse percolation strain sensors

What is the mechanism of resistance increase in each region?

M. Park et al.
Electrical properties of CNT assemblies: real vs. ideal values

- Conductivity vs. Packing fraction
- SWNTs, OD = 1 nm
- MWNTs, OD = 10 nm
- MWNTs, OD = 100 nm
- Cu: w = 50 nm
- w = 20 nm

Crossover target
40% CNTs = Cu@20nm

Individual CNTs

VA-MWNT vias (Fujitsu)
HA-MWNT ribbons
HA-SWNTs on quartz (UIUC)

MWNT (Gu, 2005)
More applications of percolation theory

- Spread of forest fires
  - predicting rate of forest consumption and extinction
- Distribution of oil/gas inside porous reservoirs
  - predicting needed drilling locations and reservoir size
- Polymer and gel materials
  - predicting kinetics of polymerization and gelation

Thermal properties of networks

- No sharp transition at percolation
- Phonon scattering at structure-structure contacts dominate thermal transport
- Structure-matrix interactions can also significantly affect conductivity by phonon scattering
Individual CNTs have exceptional thermal conductivity

Figure 6. Analytic plot of the intrinsic SWNT thermal conductivity over the 100–800 K temperature range as computed with eq 3. The length dependence is included heuristically with a simple scaling argument, but differences in chirality may lead to variations up to 20% between different tubes.\textsuperscript{11}

\begin{equation}
\kappa(L, T) = \frac{1}{3.7 \times 10^{-7} T + 9.7 \times 10^{-10} T^2 + 9.3(1 + 0.5/L) T^{-2}}
\end{equation}


Figure 1. Scanning electron microscope (SEM) image of a typical SWNT freely suspended across a 2-μm trench and lying on top of the Pt contacts. This sample was coated with 1.5 nm Ti/2.5 nm Au to facilitate SEM imaging.
Thermal contact resistance

"Macroscopic” contact resistance

\[ R_c = \frac{A \Delta T}{q} = \frac{1}{G_c} \]

A = contact area
q = heat flow per unit area
\( \Delta T \) = temperature change across interface
h = heat transfer coefficient

\[ h = \frac{1}{R_c A} = \frac{G_c}{A} \]
Table 2.1  Some typical interfacial conductances for normal surface finishes and moderate contact pressures (about 1 to 10 atm). Air gaps not evacuated unless so indicated.

<table>
<thead>
<tr>
<th>Situation</th>
<th>$h_c$ (W/m²K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron/aluminum (70 atm pressure)</td>
<td>45,000</td>
</tr>
<tr>
<td>Copper/copper</td>
<td>10,000 – 25,000</td>
</tr>
<tr>
<td>Aluminum/aluminum</td>
<td>2,200 – 12,000</td>
</tr>
<tr>
<td>Graphite/metals</td>
<td>3,000 – 6,000</td>
</tr>
<tr>
<td>Ceramic/metals</td>
<td>1,500 – 8,500</td>
</tr>
<tr>
<td>Stainless steel/stainless steel</td>
<td>2,000 – 3,700</td>
</tr>
<tr>
<td>Ceramic/ceramic</td>
<td>500 – 3,000</td>
</tr>
<tr>
<td>Stainless steel/stainless steel (evacuated interstices)</td>
<td>200 – 1,100</td>
</tr>
<tr>
<td>Aluminum/aluminum (low pressure and evacuated interstices)</td>
<td>100 – 400</td>
</tr>
</tbody>
</table>
Case study: CNT-CNT thermal contact (see extra slides for more details)

FIG. 1. (Color online) Correspondence between molecular dynamics (upper figure) and finite difference (lower figure) models. Two nanotubes are configured with a given overlap and spacing, which are varied to see the effect on tube-tube and reservoir-tube resistances. Hot and cold ends of the nanotubes are maintained at temperatures $T_H$ and $T_C$, respectively.

At the boundary

$$-k \frac{\partial T}{\partial x} \bigg|_{0^-} = \frac{T(0^-) - T(0^+)}{R} = -k \frac{\partial T}{\partial x} \bigg|_{0^+}.$$

Thermal contact resistance

*molecular formulation*

Lennard-Jones potential

\[ U(z) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

repulsive - attractive

Heat is transferred by atomic vibrations at the interface; VDW interactions transfer vibrations across a small gap
Thermal conductivity of a CNT mat

Heat suspended film by IR and measure resistance versus temperature

Calibrate absorbed power from absorption spectroscopy measurement at applied IR wavelength (940 nm)

Figure 1. (a) Bolometric configuration for measurement of thermal conductivity of SWNT film suspended between electrical contacts. The heat is provided by IR LED illuminating the SWNT film through the narrow slit diaphragm which generates a triangular temperature profile. (b) Semitransparent film of as-prepared SWNTs film grown in the electric arc discharge chamber and suspended across the opening in a sapphire ring. (c) Semitransparent film of purified SWNTs prepared by vacuum filtration mounted for thermal conductivity measurements. SEM images of fragments of (d) AP-SWNT film, and (e) P-SWNT film. Note that the P-SWNT film is much more densely packed than the AP-SWNT network.
AP- = as-prepared
P- = purified

Lorentz number:
Relative role of phononic versus electronic heat conduction

\[ L = \frac{k}{\sigma T} \]

\( L_e \) = for metal

→ Composites show a lower thermal conductivity (polymer layer is additional thermal barrier)

Measuring thermal conductivity of a packed bed (ASTM standard)

**Top rod:** resistively heated

**Bottom rod:** water-cooled

Stainless steel rods give a measurable temperature drop across the series of mounted TCs.
Can we have “too much” contact?

Effect of two junctions separated by less than the phonon mean free path

FIG. 3 (color online). (a) The running integral of the power auto correlation function converging to the contact conductance between the two (10, 10) SWCNT obtained by MD simulation for a single isolated junction. Atomistic Green’s function simulation independently gives similar value of the contact conductance (see text for details). The error in conductance obtained from MD is ~5 pW/K (b) The lower data show the ratio of the conductance of a double junction and a single junction obtained by AGF simulations. The two junctions in the double junction are separated by a distance much smaller than the mean free path. The conductance of the double junction is ~1 order of magnitude smaller than a single junction (see text for details).

Application of tuning junction behavior: thermoelectrics

Mechanical properties of networks

- Largely follow a linear rule of mixtures
- Stiffness can scale to near-theoretical values
- Strength governed by defect isolation and propagation
- Overlap/joining between structures (shear strength) vital for load transfer, especially between strong structures and a weak matrix
- Alignment (waviness) is critical
- Joint morphology is critical
Paper: a mechanical network

\[ X = \text{fiber fraction along } x \]
\[ Y = \text{fiber fraction along } y \]
\[ Z = (1 - X - Y), \text{ equally along } x \text{ and } y \]

http://aic.stanford.edu/sg/bpg/annual/v15/bp15-17.html

Fig. 1. Effect of fibre orientation on the principal values of Young’s modulus
Mechanical network model: randomly placed beams

- Determine geometry using SEM/TEM

- Randomly lay beams
- Trim unit area
- Trim unconnected segments

Mechanical model of a network

Key parameters (derived from distribution models):

- Total number of crossings per area
  \[ N_c = \frac{(N_f L_f)^2}{A \pi} \]

- Number of crossings per fiber
  \[ c = \frac{2 N_c}{N_f} \]

- Mean fiber length between crossings
  \[ L_s = \frac{L_f}{c} \]

→ Must also consider fiber width

An exemplary joint model

Beam+spring model

\[ R_{\text{fillet}} \]

\[ E_{\text{fillet}} \]

Rigidity parameter

\[ K = \frac{KL_1}{EI + KL_1} \]

Tensile properties of CNT forests


1 N/tex = 1 GPa/[g/cm$^3$]
Mechanical properties of CNT yarns

Mechanical properties of CNT assemblies: real vs. ideal values

![Graph showing specific modulus and specific strength for various materials, including Individual CNTs, Current CNT fibers, Advanced fibers, Metals, Al alloys, Steels, Polymers, Composites, GFRP, CFRP, and Foams. The graph compares real vs. ideal values for these materials.]
How to join structures individually? → *Process using electron/ion beams*

Advantages:
- Small (variable) spot size
- Rapid scanning (vs. probe techniques)

But possible damage mechanisms –remember, we are impinging upon nuclei and electrons
- Knock-on displacements (conductors) –ion beam displaces atom
- Bond breakage (insulators)

→ Balance between damage generation and healing depends on beam energy and temperature; must exceed threshold energy for desired atom displacement
→ See also: radiation damage, ion implantation, doping
Electron-beam induced damage

(a) $t = 10\ s$  
(b) $t = 30\ s$  
(c) $t = 180\ s$
Defect generation and healing

Threshold energy (room temp \( \approx 0.03 \text{ eV} \)):
- \( \text{sp}^2 \) carbon (graphene/CNT) = 15-20 eV
- \( \text{sp}^3 \) carbon (diamond) = 30-50 eV

Cutting and healing of SWNT bundle ends
Welding of CNTs

Very high local temperatures

“Nanopants”
Welding using dopants: Boron crosslinks DWNTs

B is an electron acceptor, lowers Fermi level (highest occupied level)
Crosslinking creates C-B-C and BC$_3$ bridges

Figure 6. (a) Low-frequency and (b) high-frequency Raman spectra of B-DWNTs pristine and heat treated at temperatures ranging from 1300 to 2000 °C. The disappearance of the RBM frequency is a direct indicator of the destruction of the original DWNTs and the formation of diameter-enlarged DWNTs, MWNTs and graphitic material (see text).
Aligning networks by stretching

Figure 3. (a) SEM image of an unstrained film. (b) Typical SEM image of the film after 8–10% strain before broken. (c) SEM image at the breaking point. (d) Macroscopic SEM image near the breaking point. The film is going to be split. (e) Schematic diagram of the structure deformation process during extension. (f) Schematic diagram of one simplified mesh and its morphology after 33% extension. (g) Drawing a (10,10) SWNT from a (10,10) bundle (upper two images), and the interbundle slipping within a 17 nm wide (10, 10) shared bundle. It is easy to count out that the area of the slipping surface is about 10% of the total outer surface for the SWNTs in a semibundle. (h) Low-magnification TEM image for some typical stretched SWNT meshes.

Extras
2D resistor model used to predict critical exponent

- Place sticks randomly in 2D field
- Percolation occurs when both contact electrodes are in the same cluster
- Create geometric model and then reduce lengths to find threshold length

![Graph showing resistance as a function of stick length](image)

**FIG. 2.** The longitudinal and transverse resistance of a two-dimensional system of 1000 sticks as a function of the stick-length variable parameter \((L/L_c)^2 - 1\). These results have been found for one of the seeds. The horizontal “error bars” indicate the regions of the graph to which the results of three other seed (samples) are confined.

Excluded volume method of calculating the percolation threshold

- **Excluded volume:** Area that another object cannot enter if overlapping of objects is avoided

- “Universal” percolation for circles and spheres
  
  \[ N_c a = const \]
  
  What are values for circles

  \[ N_c v = const \]
  
  and spheres?

...but orientation effects must be considered for non-round (high aspect ratio) objects

\begin{equation}
\langle V \rangle = (4\pi/3)W^3 + 2\pi W^2L + 2WL^2 \langle \sin \gamma \rangle_{\mu}, \quad (24)
\end{equation}

- Average over angular distribution
- If aligned, behave like spheres
- For random orientation,
\[ \langle \sin \gamma \rangle_{\mu} = \pi/4 \]
Comparison of excluded volume theory to experiments

Exfoliated graphite in polymer matrix; model as discs; oriented

Critical concentration \( \phi_c \propto \frac{t}{r} \).

Carbon fibers (long cylinders) in polymer matrix

### TABLE III. Critical concentrations for indicated particles dispersed in a polymer matrix determined experimentally (indicated reference) and calculated here based on concept of excluded volume.

<table>
<thead>
<tr>
<th>Case</th>
<th>Particles</th>
<th>Diameter</th>
<th>Length</th>
<th>$\phi_c$ (vol %)</th>
<th>Calculated $\phi_c$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Elongated carbon black aggregates</td>
<td>$\approx 800$ Å</td>
<td>$\approx 5000$ Å</td>
<td>7.2</td>
<td>$7.00 \leq \phi_c \leq 13.51$</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>Carbon fibers</td>
<td>10 $\mu$m</td>
<td>1 mm</td>
<td>0.52; 0.69; 0.72; 0.71; 0.86; 0.93; 1.1</td>
<td>0.67 $\leq \phi_c \leq 1.35$</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>Carbon fibers</td>
<td>10 $\mu$m</td>
<td>1.15 mm</td>
<td>1.4; 1.47; 1.55</td>
<td>0.59 $\leq \phi_c \leq 1.18$</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Carbon fibers</td>
<td>10 $\mu$m</td>
<td>2.85 mm</td>
<td>0.24; 0.25; 0.265</td>
<td>0.24 $\leq \phi_c \leq 0.48$</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>Carbon fibers</td>
<td>8 $\mu$m</td>
<td>1 mm</td>
<td>0.98</td>
<td>0.54 $\leq \phi_c \leq 1.08$</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>Carbon fibers</td>
<td>10 $\mu$m</td>
<td>1.1 mm</td>
<td>3</td>
<td>0.62 $\leq \phi_c \leq 1.23$</td>
<td>21</td>
</tr>
<tr>
<td>7</td>
<td>Carbon fibers</td>
<td>8 $\mu$m</td>
<td>1 mm</td>
<td>0.90</td>
<td>0.54 $\leq \phi_c \leq 1.08$</td>
<td>22</td>
</tr>
</tbody>
</table>

Vacuum-filtered CNT films at different densities

Figure 1. SEM images of the NTNs on alumina substrates, taken at 1.5 kV and 5 μA emission current. (a) Network resulting from filtering 7 mL of NT solution through the membrane. The filter pores are not visible in the scale shown. The network is near the percolation threshold and has few or no percolative paths through the sample. (b) 10 mL of NT solution for this sample. The network is above the percolation threshold and has several parallel pathways, allowing conduction across the film. (c) Film resulting from 400 mL of solution. Film is several layers thick.

Dimensionality and nature of contacts within network (M/M vs. M/SC \(\rightarrow\) schottky barrier) determine how fast conductivity increases with density ("critical exponent").

Figure 2. Sheet conductance vs volume of NT in chloroform solution. Notice the onset of conduction when the first percolative path across the sample is formed, indicated by \(V_c = 6\) mL on the lower right inset. This inset shows the power fit in the percolation region, where the critical exponent \(\alpha = 1.5\). Outside of the percolation region one starts to enter a linear regime. The inset in the upper left is the measured network resistance versus the source-drain distance, for networks of the same density.

Hu et al., Nano Letters 4(12);2513, 2004.

Subsequently *remove* sacrificial nano-particles.
Nano-sphere removal is easy.

Polystyrene dissolves in acetone, the same solvent used to dissolve the MCE filtration membrane.

Nano-sphere dissolution occurs during film transfer to substrate.
CNT-based memory (Nantero, Inc.)

The concept (1998)

Reversible electromechanical junction

Rueckes et al, Science 289, 2000; http://www.nantero.com
Percolation in dye-sensitized solar cells

Figure 1. Plain-view SEM micrographs of (a) 52% and (b) 71% porous TiO$_2$ films.

Percolation in dye-sensitized solar cells

Simulation

Figure 2. Dependence of the distribution of particle coordination numbers of simulated TiO$_2$ films on porosity. The dashed line represents a Gaussian fit of the data at $P = 0.5$. The inset shows the average coordination number as a function of film porosity. The dashed line in the inset depicts the predicted plot for a homogeneous distribution of particles based on the relation: $\text{CN} = A(1 - P)^y$. The solid line is a fit to a power-law variation of this relation: $\text{CN} = A(1 - P)^y$, where the values of the fit parameters are $A = 8.16$ and $y = 0.839$.

Simulation vs. experiment

Figure 5. Comparison of the porosity dependence of the diffusion coefficient between the simulations and the measurements for a photocharge density of $10^{17}$ cm$^{-3}$ for two redox electrolytes in methoxypropionitrile: $\bullet$ 0.8 M tetrabutylammonium iodide (TBAI) and 0.05 M I$_2$ and $\circ$ 0.8 M 1-hexyl-2,3-dimethylimidazolium iodide (C6DMII) and 0.05 M I$_2$. $P_c$ was taken equal to the value obtained from the fits of eq 5 to the simulation data (Figure 3). Solid lines are fits to eq 5 for fixed values of $P_c = 0.76$ and $y = 0.81$ as determined from Figure 3 but with different prefactors for the redox electrolytes.
Percolation in dye-sensitized solar cells

Statistical spread of cluster radii

The cluster size refers to the number of particles in a cluster. Percolation theory predicts that $R_s$ scales with $s$ according to the relation

$$R_s \propto s^{1/D_f}$$

(7)

$D_f = 3$ for 3D network with no fractal characteristics

Figure 7. Dependence of cluster radius $R_s$ on cluster size $s$ for a simulated film of porosity $P = 0.775$ and $l = 200$. The solid line is a fit to eq 7. The dashed line shows eq 7 for $D_f = 3$. 

Thermal contact resistance

*molecular formulation*

Relate interatomic potential to thermal contact resistance

\( k = \) thermal conductivity
\( k^* = \) nondimensional thermal conductivity
\( k_{\text{char}} = \) characteristic thermal conductivity
\( d = \) separation distance

\[
\begin{align*}
  k^* &= \frac{k}{k_{\text{char}}} & k_{\text{char}} &= \frac{k_b}{\sigma^2} \sqrt{\frac{\varepsilon}{m}} \\
  \frac{R_c}{A} &= \frac{d}{k} = \frac{d}{k_{\text{char}} k^*} = \frac{d \sigma^2}{k_{\text{char}} k_b} \sqrt{\frac{m}{\varepsilon}} & R &= \left[ \frac{\sigma^2}{\sigma_o^2} \sqrt{\frac{\varepsilon_o}{\varepsilon}} \right] R_o 
\end{align*}
\]

→Now we can generalize results from a molecular dynamics simulation to a continuum finite difference model, with varying separation and LJ parameters

FIG. 5. (Color online) Tube-tube thermal resistance vs spacing and length for 5, 10, 20, and 40 nm nanotubes with 2.5 nm overlap. Asterisks are from steady-state MD simulations for 5 nm tubes; filled symbols are from finite difference fit to transient MD simulations. A four order of magnitude decrease in $R$ is found as nanotube spacing decreases.

Effect of contact length

![Graph showing tube-tube thermal resistance vs tube length for 5, 10, 20, and 40 nm tubes with 2.5 nm overlap and 6 Å spacing. Resistance decreases as tube length increases.]

FIG. 7. (Color online) Tube-tube thermal resistance vs tube length for 5, 10, 20, and 40 nm tubes with 2.5 nm overlap and 6 Å spacing. Resistance decreases as tube length increases.

Thermal contact resistance dominates over CNT thermal resistance

Beyond contact: near-field heat transfer (between NPs)

Fluctuating dipoles transfer heat by electromagnetic radiation and induce vibrations

FIG. 2. Explanation schemes of the calculation of the power dissipated in the NP2 due to the field emitted by the NP1. In the MD computation (above), the power is computed as the work produced by the atomic motions of the NP2 atoms in the potential field generated by the NP1. In the electrostatic calculation (below), each NP is assimilated to one dipole (vectors $p_1$ and $p_2$) situated at the NP centers.

FIG. 3. Thermal conductance $G_{12}$ vs distance $d$ between the centers of mass. $R$ corresponds to the nanoparticle radius and $N$ is the number of atoms in each particle. While the MD (data points) and the analytical (thick lines) predictions agree very well when the interparticle distance is larger than the nanoparticle diameter, a deviation appears when $d < 4R$. The far-field conductance due to emission and absorption is reported for comparison. The inset highlights the conductance values when the NPs are in contact (gray data points). Their abscissa correspond to $2R$. The contact conductance is 2 to 3 orders of magnitude lower than the conductance just before contact.

→ Nanofluids

Mechanical network model

Segment length decreases as network “density” increases

“Waviness” affects interconnect density

Shell models should be used at smaller aspect ratios

\[ y = a \sin(\omega x) \]

Mechanical stiffness of CNT mats

FIG. 12. Stress vs strain results of mechanical tests on nanotube sheet samples.

→ Add polymer to stiffen/strengthen


FIG. 13. Comparison of experimental and simulation results for normalized effective modulus, for nanotube sheets containing nanotubes synthesized by the (a) HiPco and (b) laser ablation processes. Simulation results derived using both Miles (see Ref. 15) and Corte (see Ref. 23) are shown. An average rope diameter 10 nm was assumed in all cases.
Figure 2. SEM images showing covalent carbon junctions of 1D blocks, illustrating branching geometries obtained experimentally with the geometry necessary for complex networks. (Even when the 1D blocks are thicker than CNTs, they show evidence of specific branching geometries as a starting point to the theoretical design of models.) The material was produced using a CVD approach involving the thermolysis of nickelocene (NiCp2) powder in conjunction with thiophene (C4H4S) in an argon atmosphere at 1000 °C. From these images, we observe that the junctions are covalently connected in a variety of stable ways, such as (b) a junction with the geometry of 3D cubic network node, (c and d) a T-junction and a cross-junction, with the correct geometry needed in a 2D square network, (e) a 3-terminal junction with the necessary angles in a 2D hexagonal network, and (f) a 4-terminal junction with a tetrahedral-like architecture.
Figure 3. Electronic properties of four different network building units. The architecture plays a determinant role in dictating the DOS spectra and conductance properties. Preferred conductance paths are observed to cross the node. In each panel is shown the geometry, inequivalent defects (red sites), and terminal labels; conductance spectra for the inequivalent electronic paths through terminals; and electronic DOS for each node presented, based on extended tight-binding Hamiltonian. In part a, the SS block presents only one conducting path along the armchair channel. The SG block presented in part b shows how, even without a band gap in the DOS spectra, the architecture restricts to zero conductance around the Fermi energy. Part c reveals an increase in conductance for the $A \leftrightarrow B$ electronic path around the Fermi level, making it the most favorable one to cross this SC block. Finally, part d presents the SD block, which presents zero conductance for all of its equivalent paths, even with the existence of states in the DOS spectra.

Strain Energy Vs. Strain
Volumetric Compression of 3D ON-CNTs

Videos

http://pubs.acs.org/subscribe/journals/nalefd/suppinfo/nl0622202/nl0622202si20060920_063532.mpg

http://pubs.acs.org/subscribe/journals/nalefd/suppinfo/nl0622202/nl0622202si20060920_065202.mpg

Joints dominate flexibility
Interfacial toughening using a monolayer

Interconnect structure tested in 4-point bending

Quick calculation based on bond breakage confirms measured result

Figure 4 | Calculated system energy as a function of molecular stretching for different combinations of siloxane and hydrogen bonds at the MPTMS/SiO₂ interface. System energy was determined by first-principles density functional theory calculations. Inset, schematic depiction of an MPTMS molecule bonded to the silica underlayer by one siloxane bridge ($i = 1, 33\%$ irreversible dehydration) and two hydrogen bonds ($j = 2$). The arrow indicates the direction of stretching. The graph shows system energy plotted as a function of Cu overlayer/SiO₂ underlayer separation for three different interface bonding chemistries; each curve is plotted up to the fracture point.

XPS reveals Cu-S still bonded post-fracture

Annealing creates Si-O bonds (strong) Cu layer prevents detachment

Welding CNT-metal junctions

- Metal-filled CNTs made by floating catalyst method
- Focused electron beam gives $10^3$-$10^5$ A/cm$^2$
- 11 minutes to form junction shown below
Fig. 2.  High-resolution images from metal–MWNT junctions. (A) Bright-field STEM image (C$_s$-corrected) of a MWNT–Co interface. The Co particle has an fcc structure (the image shows an alignment close to the [110] zone axis projection of the Co fcc lattice). Strain is introduced at the interface as can be seen by the local bending of the graphitic layers at the interface. The *Inset* shows a detail of the interface (white square) after noise filtering, where the bending of the nanotube layers to match the metal lattice is visible. (B) HRTEM image of a MWNT–Ni interface. The Ni particle has an fcc structure.
Fig. 3. Representative I–V curves taken from a Co-filled MWNT (black dots) and from the same tube subjected to e-beam irradiation and with a MWNT–Co–MWNT joint (red triangles) measured by using the STM-TEM "Nanofactory" setup. The current range was limited <1 μA to avoid overheating of the structure. The insets display the corresponding TEM images. (Upper Left) A Co-filled MWNT attached to a gold wire (biased far to the left) connected to the Au STM tip inside the electron microscope. (Lower Center) the appearance of the starting nanotube in the "filled" state. (Upper Right) The same tube after biasing (to induce Joule heating) and irradiation resulted in the Co-joint formation.