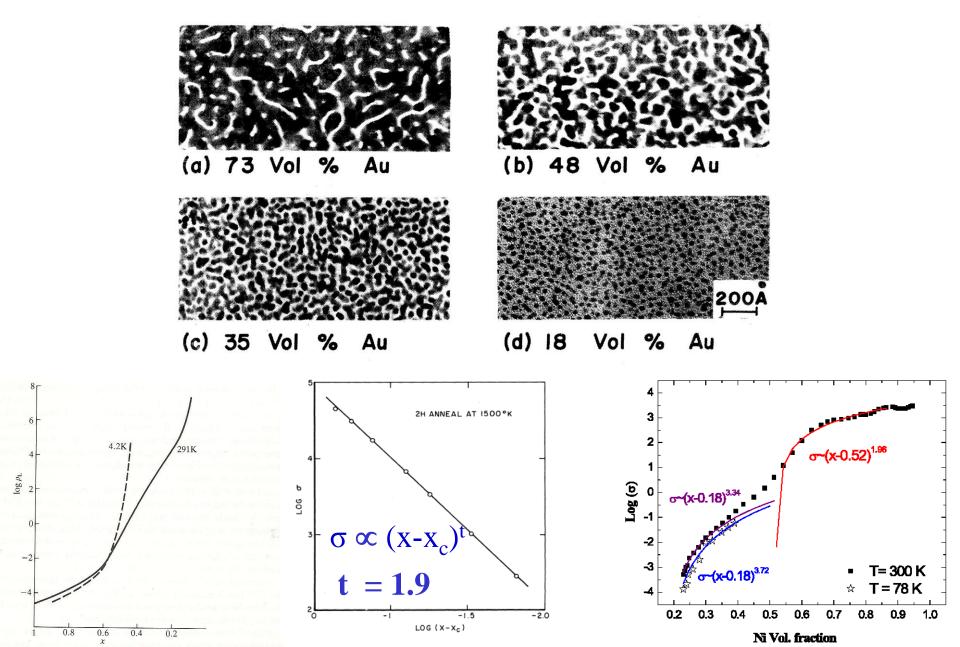
The Tunneling Percolation Staircase

Isaac Balberg

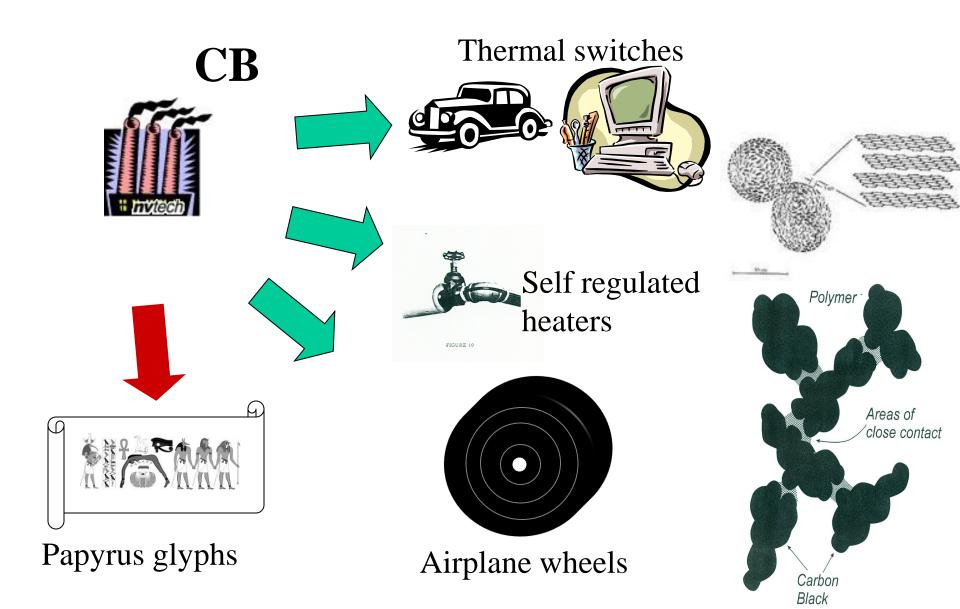
Racah Institute of Physics,

The Hebrew University, Jerusalem, Israel

GRANULAR METAL COMPOSITES

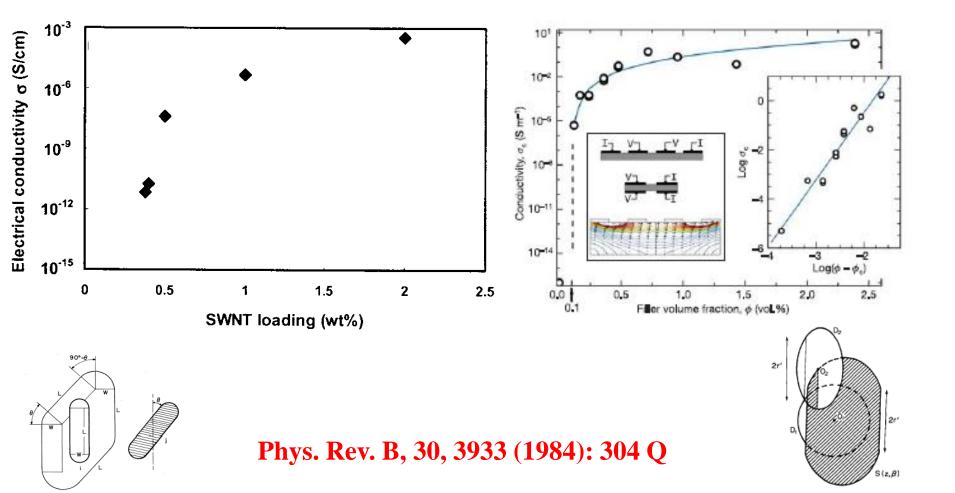


CB polymer composites and applications

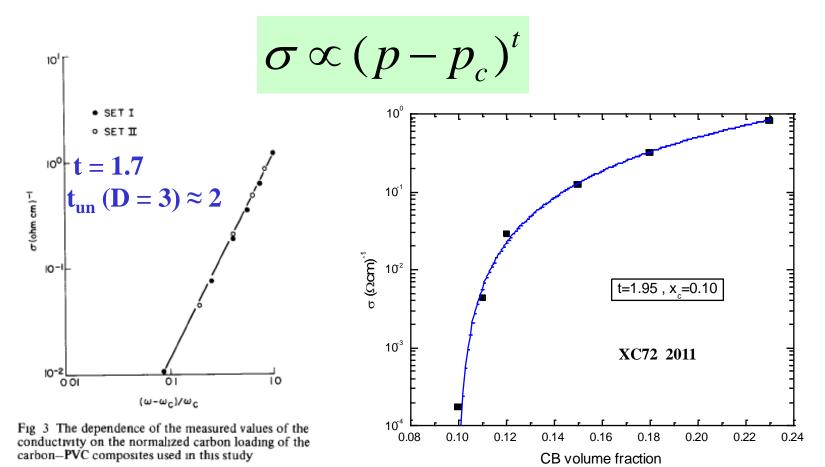


Two fundamental questions

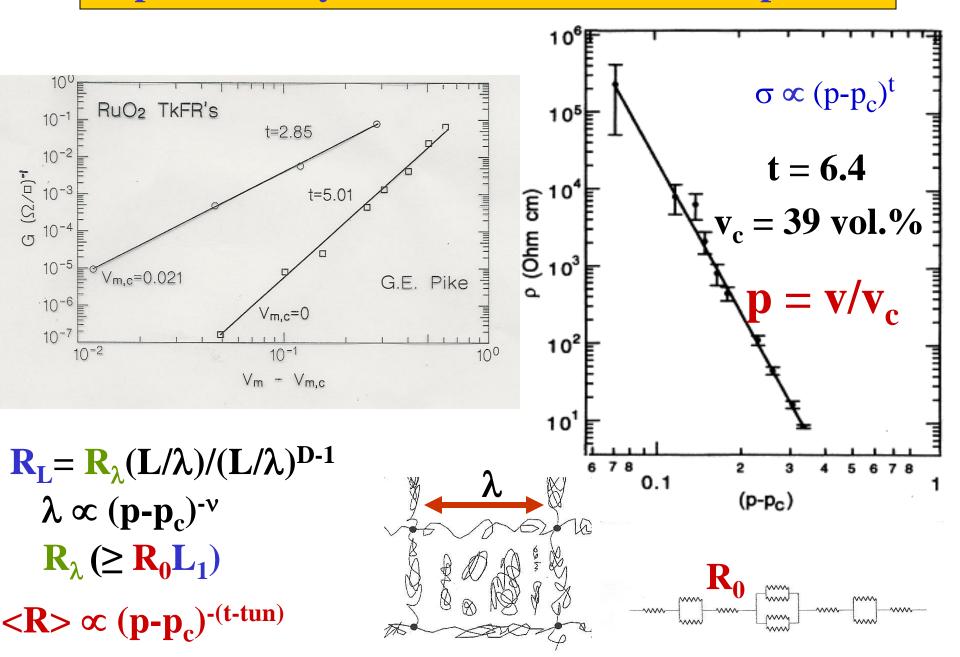
- 1) What determines the conductivity threshold?
- 2) What determines the shape of the $\sigma(\Phi)$ dependence?



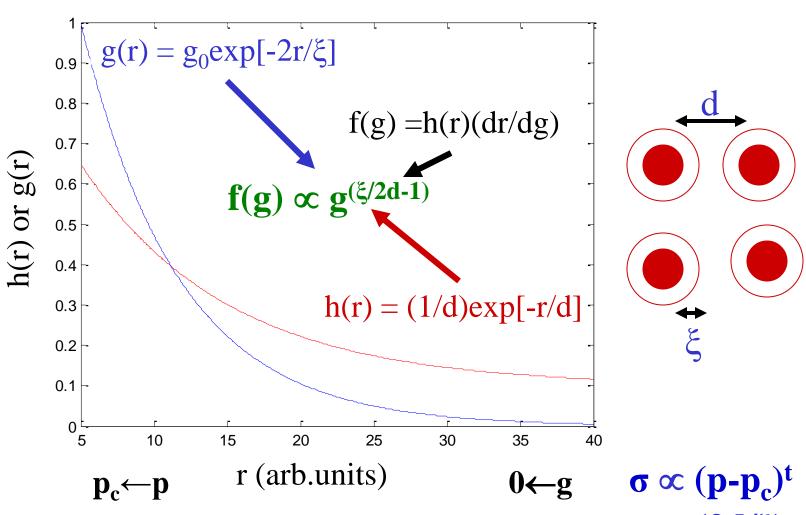
Confirmation of universality



Experimentally observed non universal exponents



The diverging normalized distribution in the tunneling percolation problem

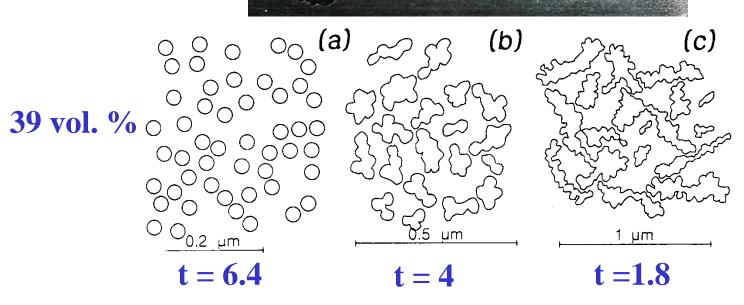


Phys. Rev. Lett, 59, 1305 (1987): 215 Q

 $t = t_{un} + (2d/\xi) - 1$

Various carbon blacks

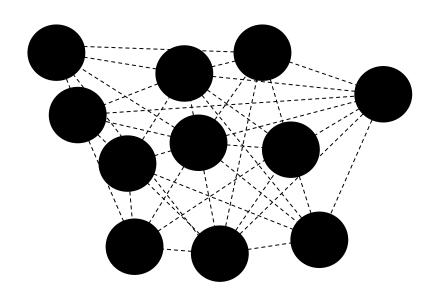


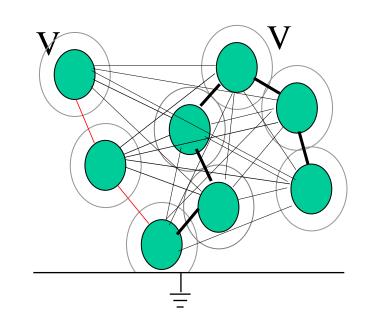


10 wt. %



Percolation and Tunneling?



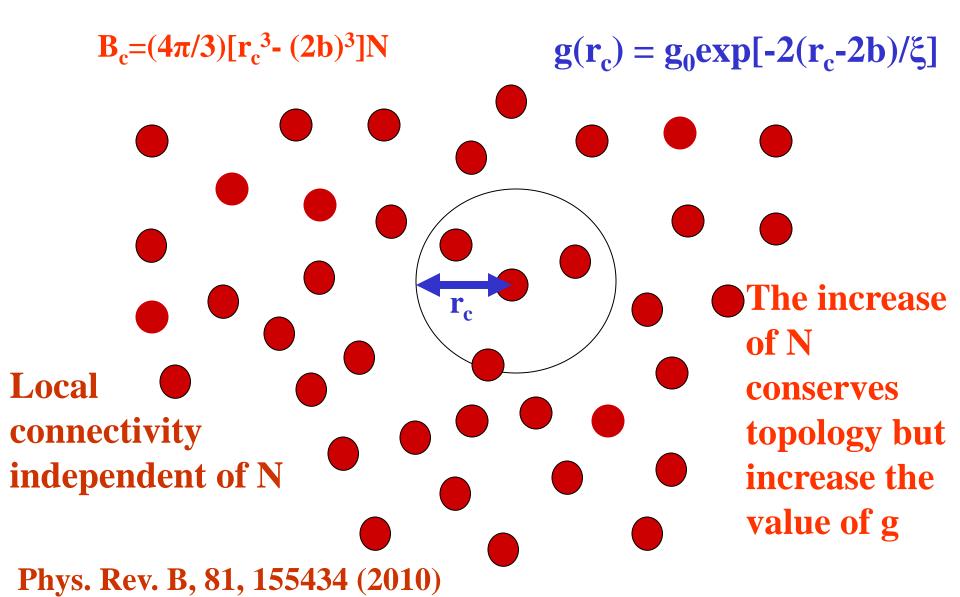


$$g(r_{ij}) = g_0 \exp[-2(r_{ij}-D)/\xi]$$

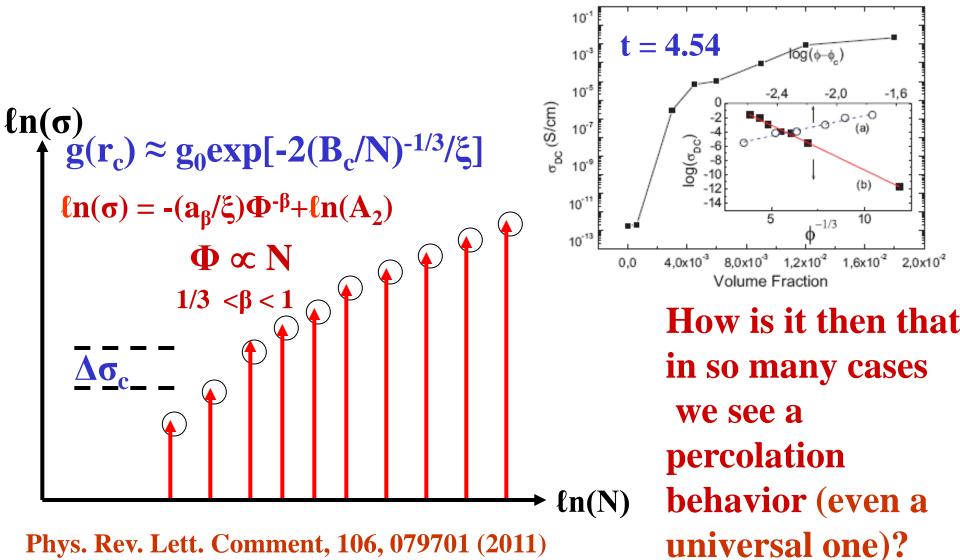
What is the meaning of v_c ?

Carbon, 40, 139 (2002): 100 Q.

The hopping model (the CPA network)

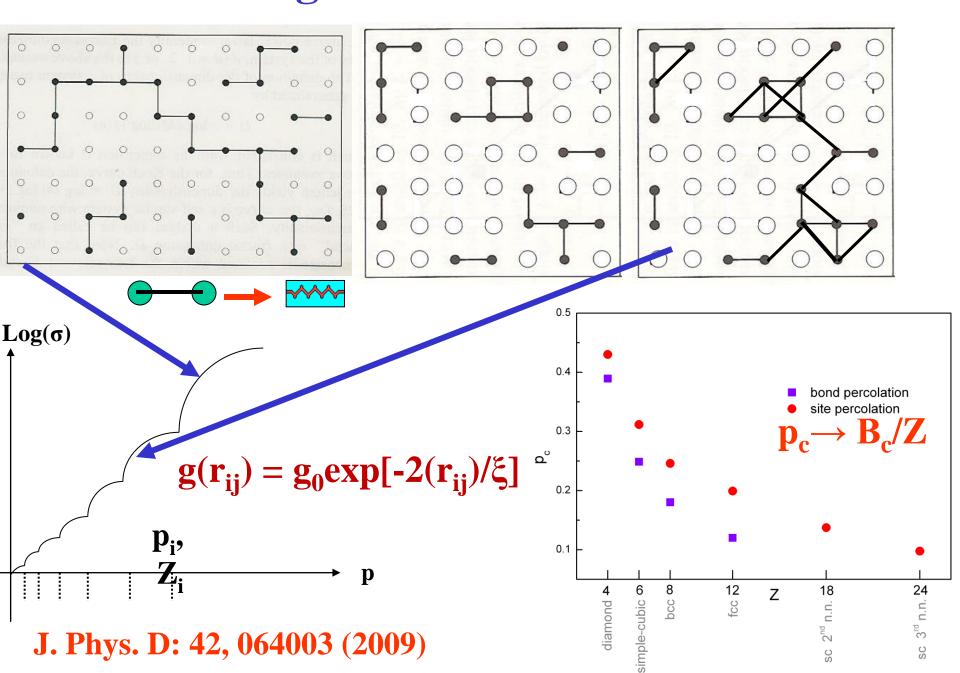


The prediction of the percolation-threshold (criticalresistor, hopping like) model and its relation to the critical-percolation (phase-transition like) model



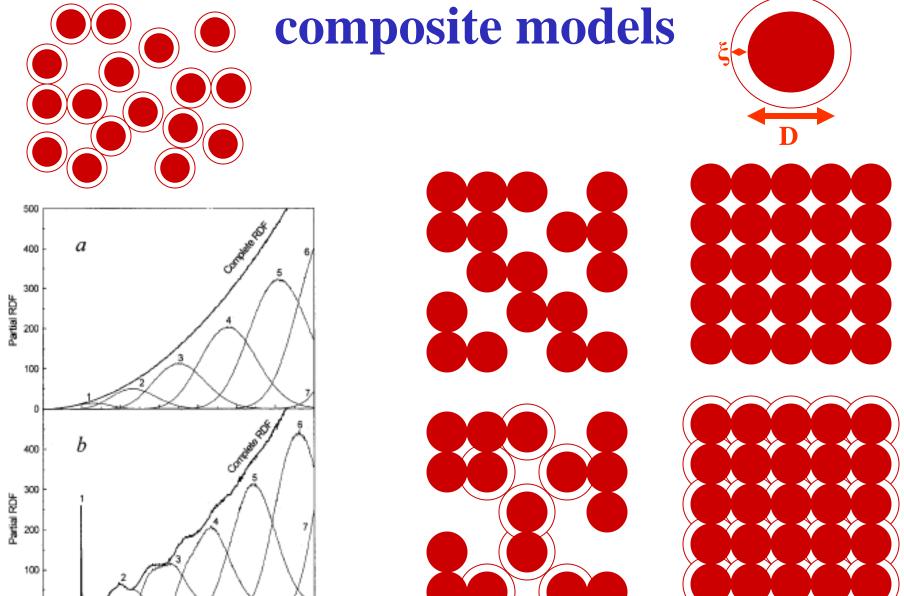
Phys. Rev. Lett. Comment, 106, 079701 (2011)

The origin of the staircase model

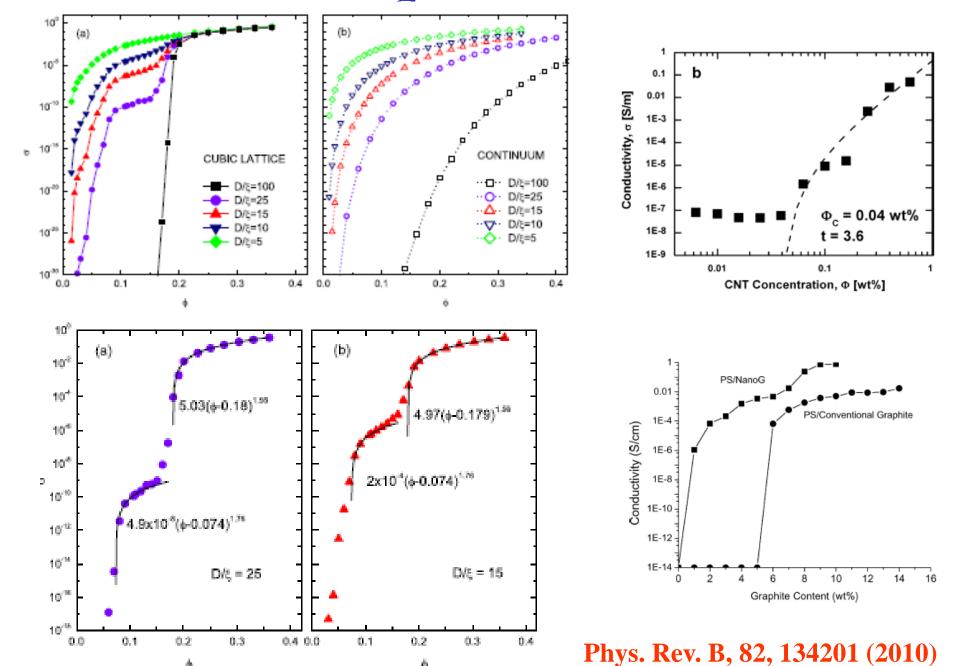


The lattice and continuum

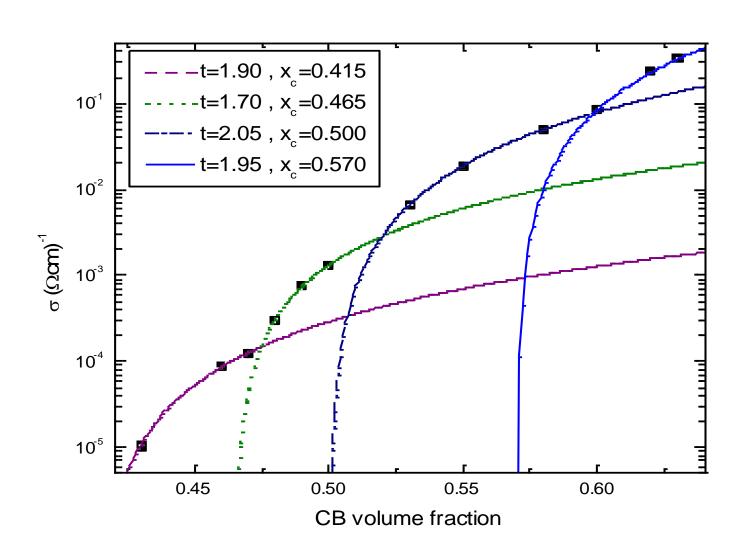




The effect of tunneling in lattices and the continuum



Staircase observed in N990/Polyethylene Composites



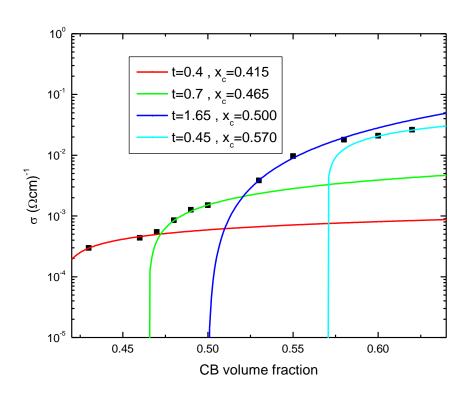
Conclusions

- The observed $\sigma(\Phi)$ behavior is a series of percolation transitions, the stairs.
- In the lattice these have to do with the series of lattice neighbors. In the continuum these have to do with shells of neighbors that result from an RDF with peaks.
- In the continuum the $\sigma(\Phi)$ behavior of each stair is that of a universal behavior while the envelope of the stairs yields a non universal percolation behavior which simply presents hopping.
- The experimentally observed Φ_c is either of a "universal" stair or a result of the fact that the data do not go to $\Phi = 0$. Percolation is well confirmed if both, a universal behavior and a non hopping behavior are exhibited by the data.
- One can get a simple universal percolation behavior if all the resistors are nearly equal (non divergent distribution) and all belong to a random network (as for anisotropic particles).

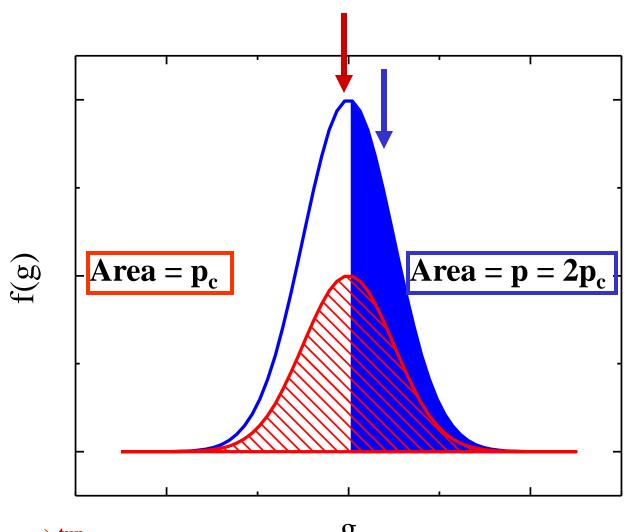
The End



RF transmission ("AC Conductivity") at 80 MHz



What if we have a distribution of (or $r_0 = 1/g$) values?



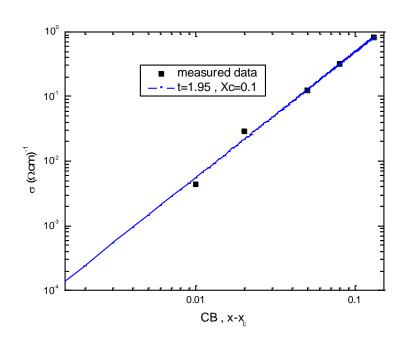
$$R_{L} \propto \langle r \rangle (p-p_{c})^{-tun}$$

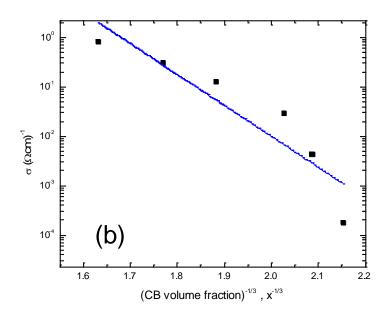
$$\langle r \rangle = \int_{gc}^{1} (1/g)f(g)dg.$$

$$p[_{gc}]^{1}f(g)dg] = p_{c}$$

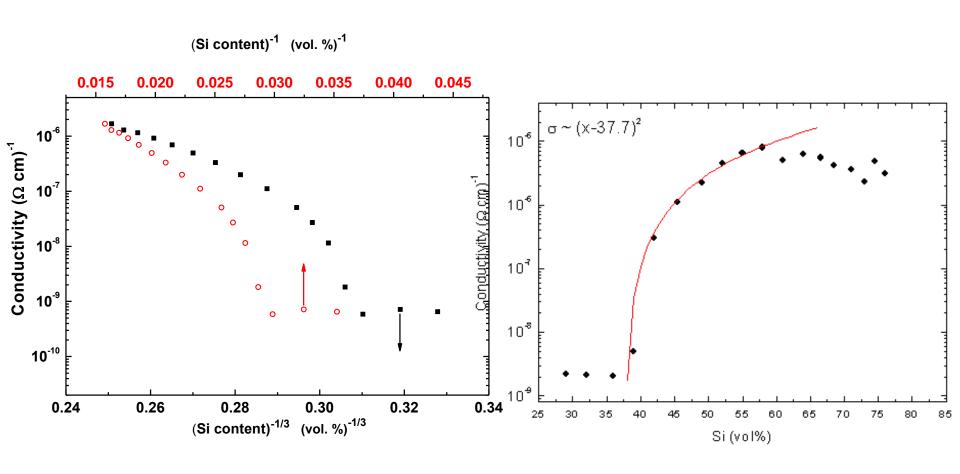
$$\begin{split} f(g) &= (1\text{-}\alpha)g^{\text{-}\alpha} \text{ yields that:} \\ g_c &= [(p\text{-}p_c)/p]^{1/(1\text{-}\alpha)} \\ < r > \infty & (p\text{-}p_c)^{\text{-}\alpha/(1\text{-}\alpha)} \propto (p\text{-}p_c)^{\text{-}(t\text{-tun})} \end{split}$$

Universal and Hopping Interpretations in XC72-Polyethylene Composite



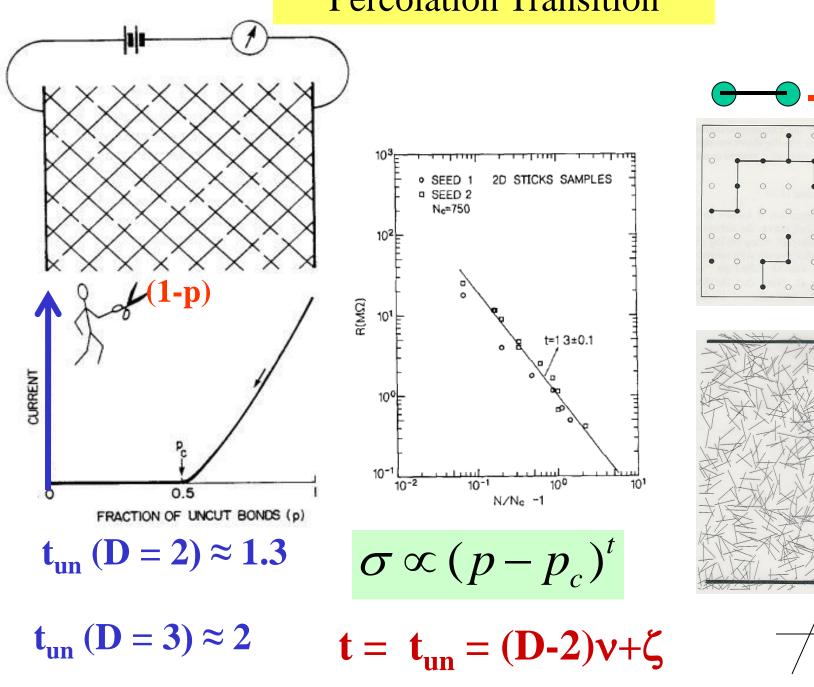


Non-Hopping but Percolation Behavior

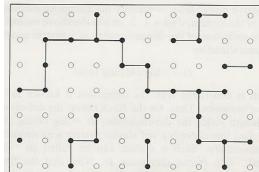


Phys. Rev. B, 83, 035318 (2011)

Percolation Transition

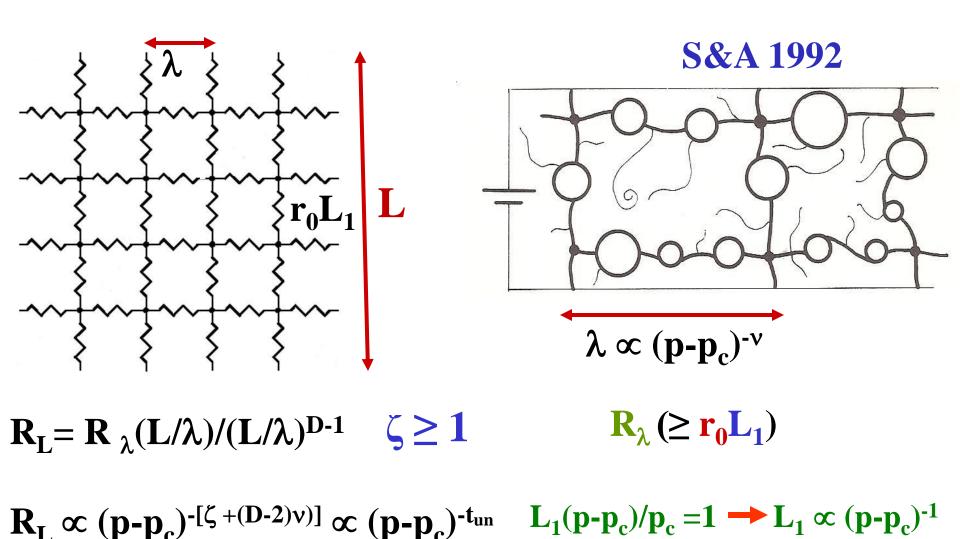




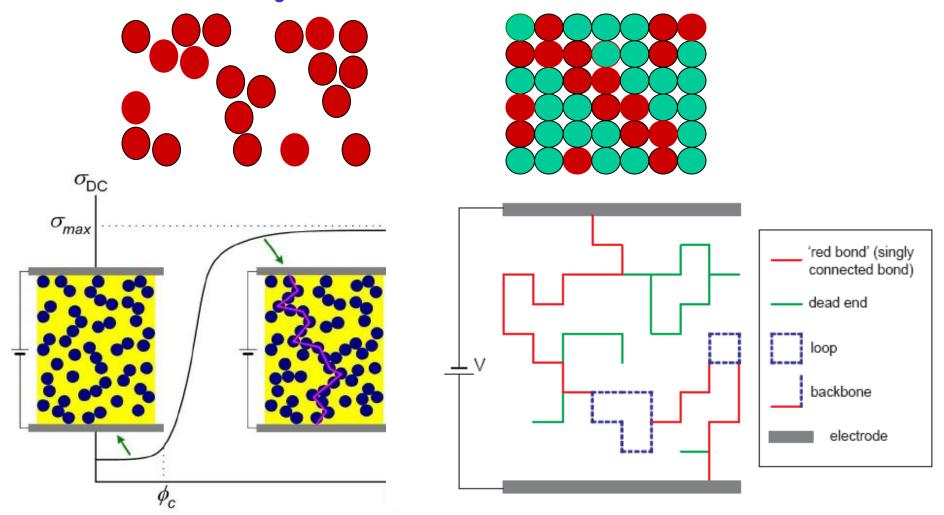




The LNB Model of the backbone



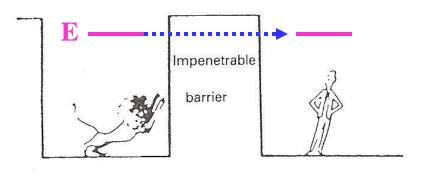
The electrical conductance in composites and the analysis of the conductance network



One expects intuitively and we can show rigorously that $V-V_c = (N-N_c)(v_{HC}) \ (vol.\%) \ in \ the \ continuum, is equivalent \ to \ p^s-p^s_c \ in \ lattices$

TUNNELING (Wiesendanger, 1994)

$$\sigma(r) = \sigma_0 \exp[-2r/L]$$



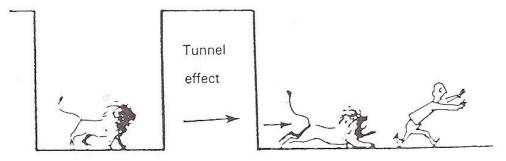
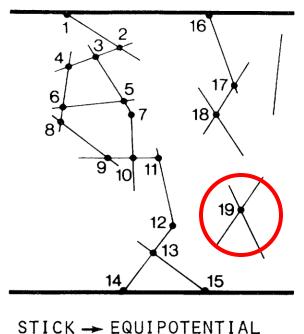


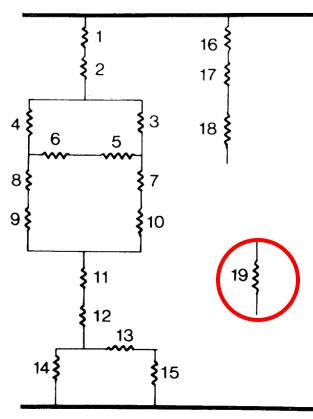
Fig. 1.1. The difference between classical theory and quantum theory, illustrating tunneling through a potential barrier (Bleaney, 1984).



Resistors Equivalent Network



INTERSECTION → RESISTOR



$$(I_i) = (g_{ij})(v_i - v_j)$$
 $(I) = G(v)$

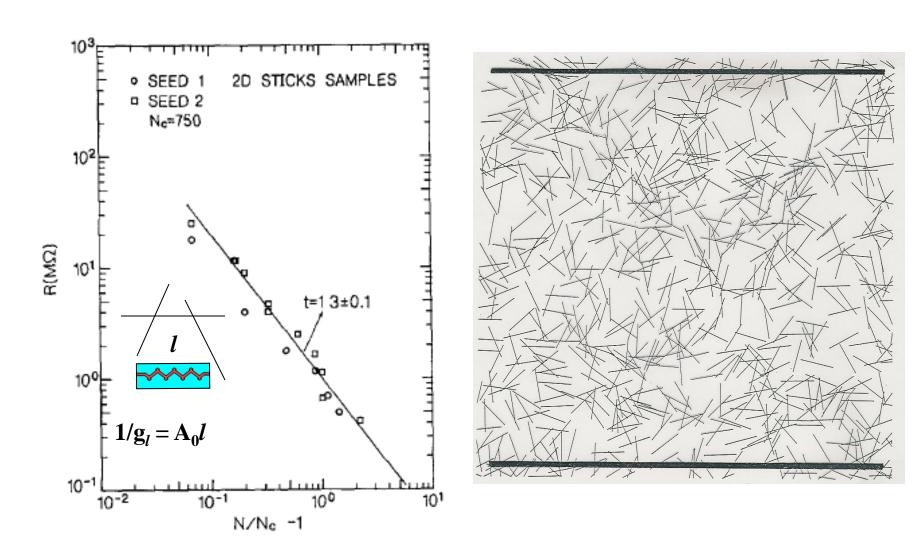
$$R = (v_1 - v_N)/I$$
 $(v) = G^{-1}(I)$

$$I_1 = -I_N = I, I_i (i \# 1,N) = 0$$

 $G_{ii} = \Sigma g_{i,j}, G_{ij} = -g_{ji}$

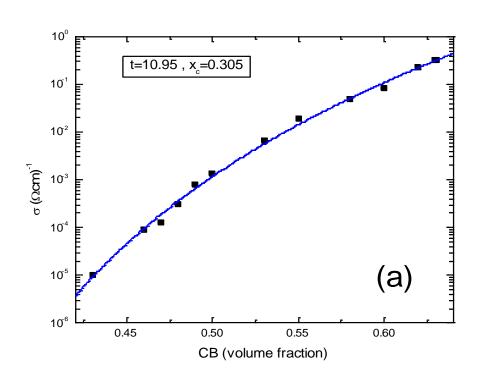
Phys. Rev. B, 28, 3799 (1983): 162 Q

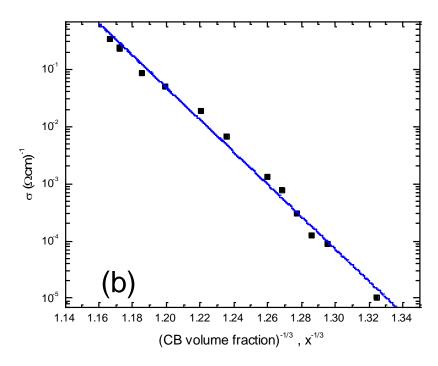
The critical behavior of the resistance of pencil generated line-segments system



J. Water Resources Research 29, 775 (1993): 101 Q

Non Universal and Hopping Interpretations





The model of Kogut and Straley

$$f(g) = (1-\alpha)g^{-\alpha}$$

- $<\mathbf{r}>=_{gc}^{\int 1} [f(g)/g]dg \propto |(g_c^{-\alpha}-1)|, g_c = [(p-p_c)/p]^{1/(1-\alpha)}$
- we have here the three types of $\langle \mathbf{r} \rangle = \mathcal{F}(\mathbf{g_c})$ behaviors; strongly-diverges for $0 < \alpha < 1$, logarithmically diverges for $\alpha = 0$ and it will not diverge for $\alpha < 0$.
- Correspondingly: $\langle r \rangle \propto (p-p_c)^{-\alpha/(1-\alpha)}$,
 - <r> <r> <r> <math><r> <math><r> <math><r $> = [(1-\alpha)/(-\alpha)] = const.$

The basics of non-universal behavior

$$R_{L} \propto \langle r \rangle (p-p_{c})^{-t_{un}}$$

$$\langle r \rangle = \int_{gc}^{1} (1/g)f(g)dg.$$

$$p[g_{c}]^{1}f(g)dg] = p_{c}$$

Example (K&S, 1979): $f(g) = (1-\alpha)g^{-\alpha}$ yields that:

$$\begin{aligned} \mathbf{g}_{c} &= [(\mathbf{p}\text{-}\mathbf{p}_{c})/\mathbf{p}]^{1/(1-\alpha)} \\ <\mathbf{r}> &\propto (\mathbf{p}\text{-}\mathbf{p}_{c})^{-\alpha/(1-\alpha)} \propto (\mathbf{p}\text{-}\mathbf{p}_{c})^{-(t-t_{un})} \\ &(<\mathbf{r}> &= [(1-\alpha)/(-\alpha)]) \end{aligned}$$

"RDF" of the polymer shells

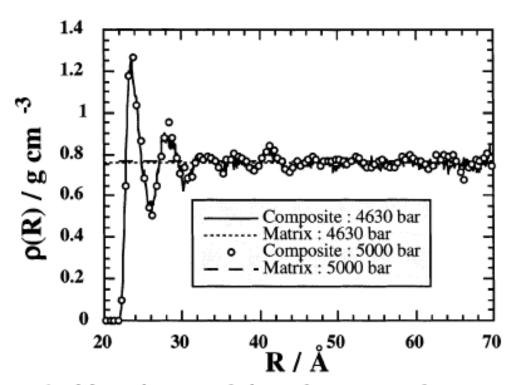


Figure 1. Mass density of the polymer as a function of R, the distance from the center-of-mass of the silica particle. The dotted and dashed lines give the limiting, large R, densities as determined from the pure polymer matrix simulations at the pressures shown.

"RDF" of the polymer shells

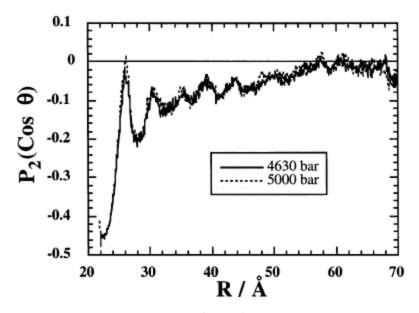


Figure 3. Mean values of $P_2(\cos \theta)$ plotted as a function of R for the composite system at the two pressures shown. θ is the angle between the local polymer chain axis and the outwardly pointing vector normal to the nanoparticle surface. An alignment of the chains parallel to the nanoparticle surface implies a value of -1/2 (small R). A random alignment corresponds to a value of zero (large R).

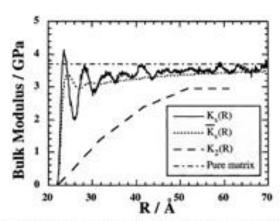


Figure 8. Smooth approximation to the radial dependent bulk modulus $K_*(R)$ for the interphase region of the polymer matrix as determined from eq 14. Also shown is the mass-weighted running average of this function. $K_*(R)$, and the corresponding bulk modulus based on the micromechanical calculations, $K_2(R)$.

Evidence for stairs in MWCNT-polymer composites

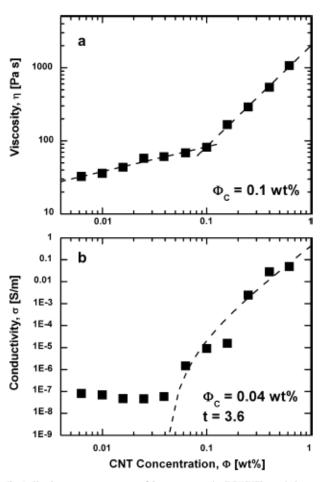


Fig. 4. Simultaneous measurement of the nanocomposite (MWCNT/epoxy) viscosity (a) and electrical conductivity (b) as function of the nanotube weight fraction, performed in the liquid state prior to curing at 0.1 s⁻¹ and 20 °C. The rheological percolation threshold is located at 0.1 wt% and the electrical one at 0.04 wt%.

Some idea about the materials

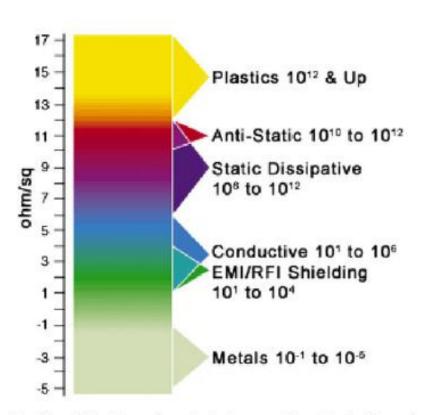
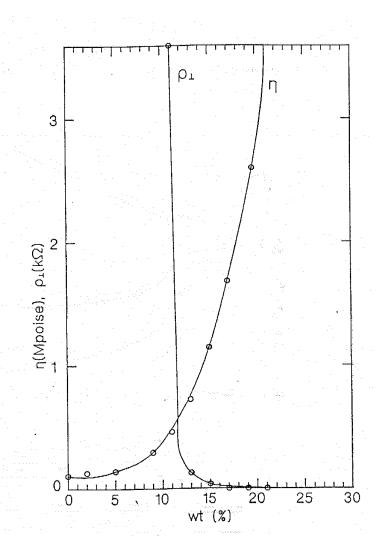


Fig. 1 – Classification of materials according to their surface resistivity and application ranges. (Note: [cited 2007 July]; Available from: http://www.rtpcompany.com/products/conductive/index.htm.)



Evidence for stairs in MWCNT-polymer composites

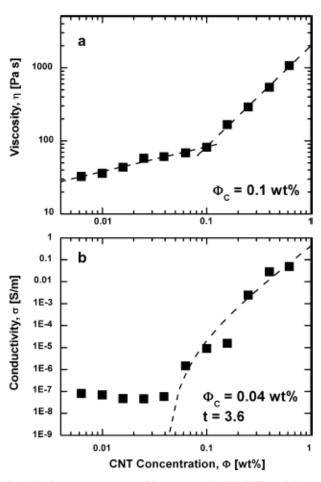


Fig. 4. Simultaneous measurement of the nanocomposite (MWCNT/epoxy) viscosity (a) and electrical conductivity (b) as function of the nanotube weight fraction, performed in the liquid state prior to curing at 0.1 s⁻¹ and 20 °C. The rheological percolation threshold is located at 0.1 wt% and the electrical one at 0.04 wt%.

Conductivity and viscosity

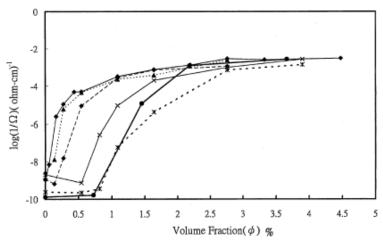


Fig. 1 Dependence of the electrical conductivity on the volume fraction of carbon black dispersed in PDMS liquids with various viscosities. *Diamonds on solid line* 10 cp, *triangles* 100 cp, *diamonds on dotted line* 500 cp, *crosses* 1000 cp, *asterix* 60 000 cp, *circles* silicon rubber

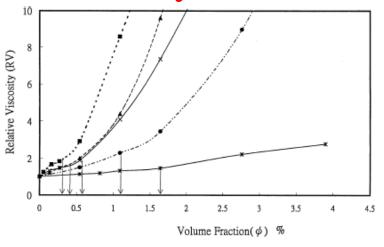


Fig. 3 Dependence of relative viscosity (RV) on the volume fraction of carbon black dispersed in PDMS liquids with various viscosities. Squares 10 cp, triangles 100 cp, crosses 500 cp, circles 1000 cp, asterix 60 000 cp

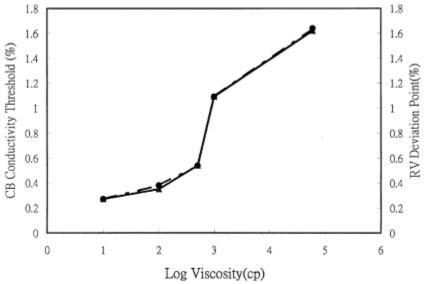


Fig. 5 Dependence of the RV deviation point and threshold conductivity on PDMS viscosity. *Triangles* CB conductivity threshold, *circles* RV deviation point

Conductivity and viscosity

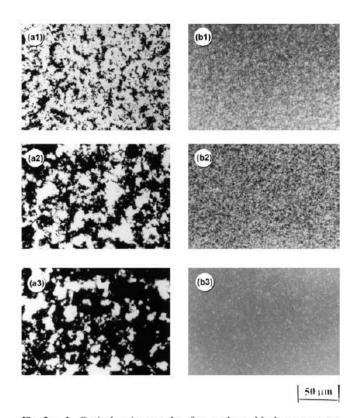


Fig. 2a, b Optical micrographs for carbon black aggregates dispersed in PDMS liquids. Dispersion of 0.13%, 0.27%, and 0.54% carbon black by volume into 500 cp PDMS are shown in a.1 to a.3. The correspondent conductivities are 6.36×10^{-10} , 1.50×10^{-8} , and 9.04×10^{-6} (Ω-cm)⁻¹, respectively. In contrast, dispersion of 0.81%, 1.09%, and 1.64% carbon black by volume into 60 000 cp PDMS are shown in b.1 to b.3. The correspondent conductivities are 3.56×10^{-10} , 5.63×10^{-8} , and 4.21×10^{-6} (Ω-cm)⁻¹, respectively

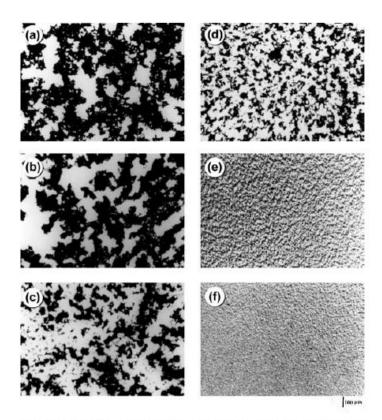
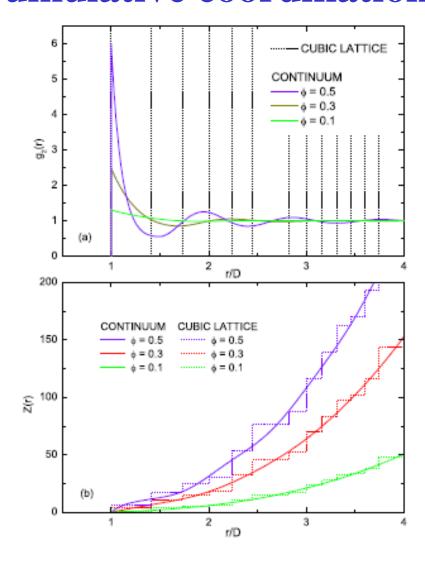
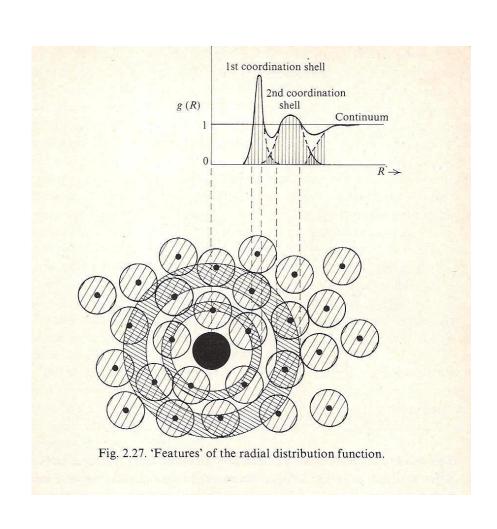


Fig. 4a-f Optical micrographs for 0.43% volume fraction of carbon black dispersed in PDMS liquids with various viscosities: (a) 10 cp (b) 100 cp (c) 500 cp (d) 1000 cp (e) 10 000 cp (f) 60 000 cp

RDF and Cumulative coordination number



RDF in the Continuum



Statistics of the t values in CNT-polymer composites

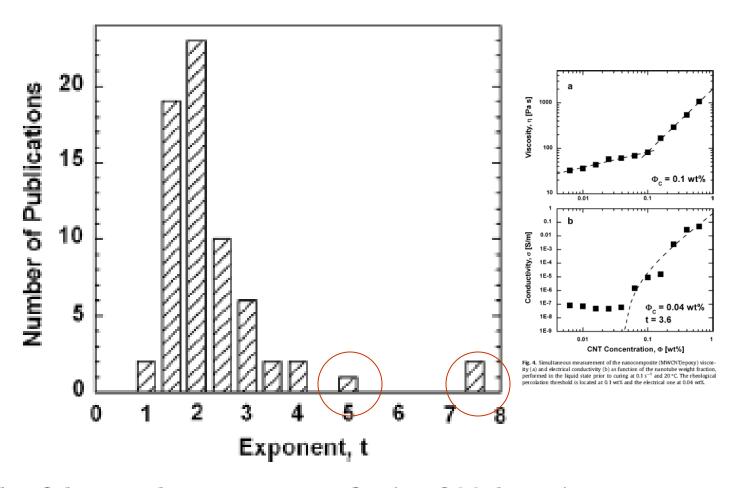


Fig. 7. Plot of the power law exponent t as a function of (a) the maximum conductivity and (b) the percolation threshold for all data in Table 1. The horizontal lines denote t = 1.3 and 4. Fig. 7 (c) shows a histogram of t values.

Two presentations of the same data

Percolation interpretation

10⁰ 10-2 10-1 10-4 σ [S/cm] 10-2 σ [S/cm] 10⁻³ 10-6 10⁻⁵ 10-8 10-4 10-3 10-2 10-1 10-10 .02 .04 .06 .08 .10 0.00

FIG. 1. Plot of σ as a function of carbon black volume content, p of composites; the critical concentration p_c has been determined using Eq. (1) (p_c =1.1%); inset: log-log plot of σ as a function of $p-p_c$; (t=2.17).

"hopping" interpretation

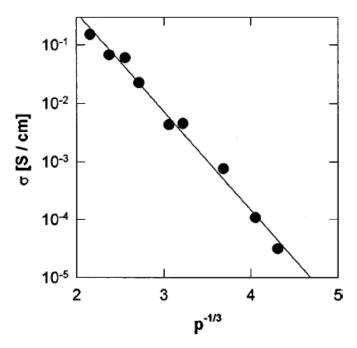
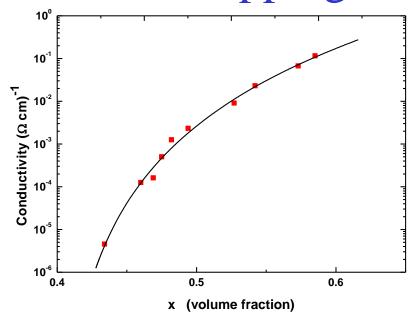
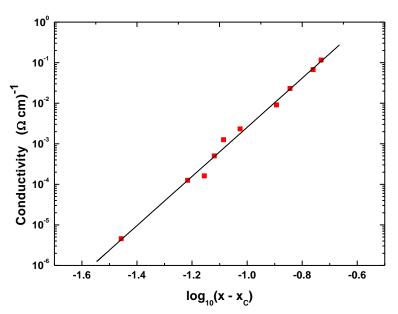
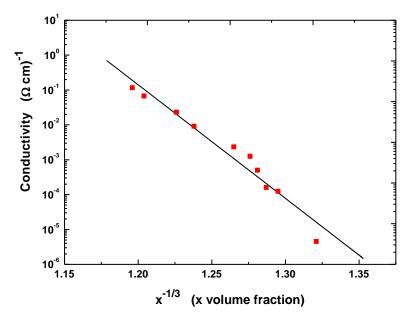


FIG. 2. Linear variation of $\ln \sigma$ vs $p^{-1/3}$.

Non Universal and Hopping Interpretations







The physical and mathematical resemblance of the percolation and (CPA) hopping behaviors:

In the classical hopping (CPA) model : $\log \sigma = -\delta_c/\xi + \log A_1 = -(a_\beta/\xi)x^{-\beta} + \log A_1 \qquad 1/3 \le \beta \le 1$

In our percolation model: $\log \sigma = t \log(x - x_c) + \log A_2$ and we saw (from the Excluded volume argument) that $t = t_{un} + d/\xi$ -1 so that for $t >> t_{un}$ we have that $t \approx -(x^{-\beta})/\xi$ where $1/3 \leq \beta \leq 1$ and $\log (x - x_c) < 0$.

• The two models yield then quite a similar dependence on x. Experimentally; since usually $x >> x_c$ these two are usually non distinguishable. Can we still distinguish between them?

Presentation of the CPA results in the case of spheres

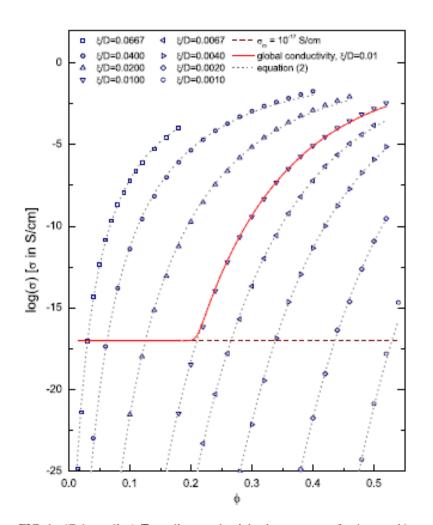
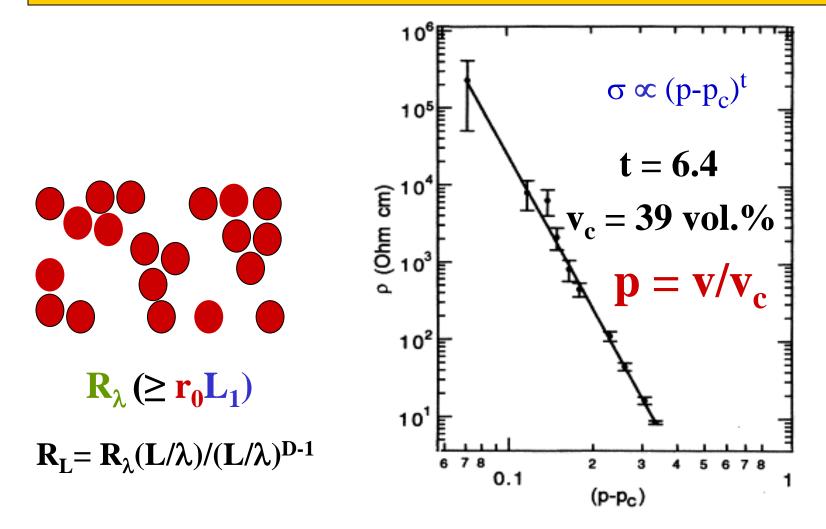


FIG. 1. (Color online) Tunneling conductivity in a system of spheres with different characteristic tunneling distance to spheres diameters ratio ξ/D as a function of the volume fraction ϕ . The matrix intrinsic conductivity for $\sigma_m = 10^{-17}$ S/cm and the overall conductivity for the $\xi/D = 0.01$ case are shown. Results from Eq. (2) with $\sigma_0 = 0.115$ S/cm are displayed by dotted lines

CB-polymer composites



•Non universal value of $t \approx 6$ for low structured CB composites

Phil. Mag. B, 56, 991 (1987): 142Q

Non Spherical Fillers

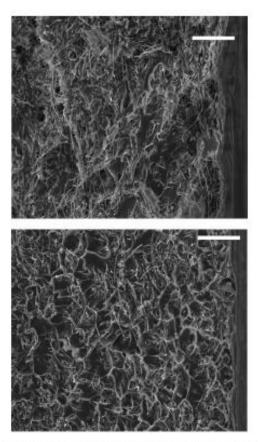
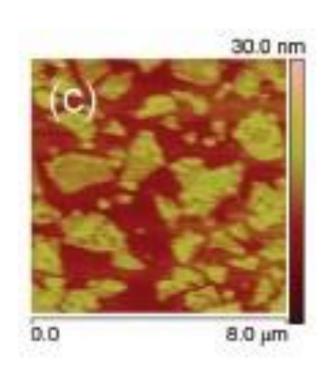
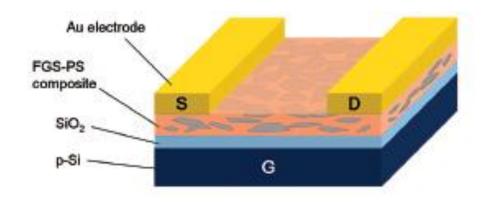


Figure 1. Scanning electron micrographs of the freeze-fractured surfaces of 5PCNF (top) and 5PCNF (bottom) systems, displaying the CNF dispersion throughout the film thickness. The scale bar is 10 μ m.

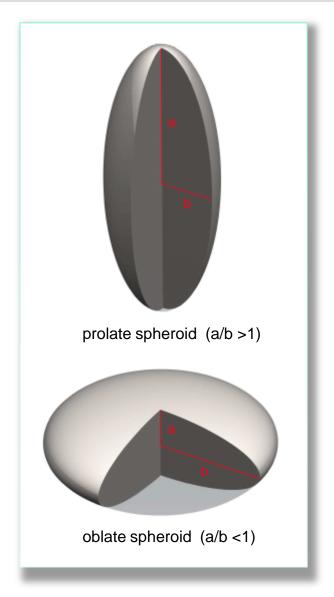
Graphene composites

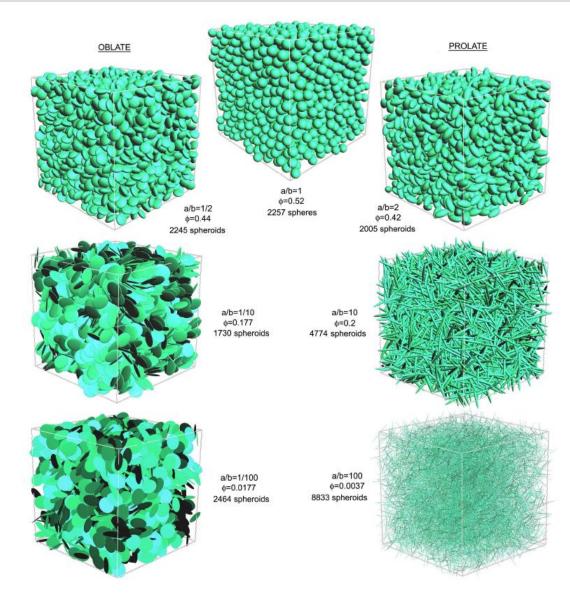




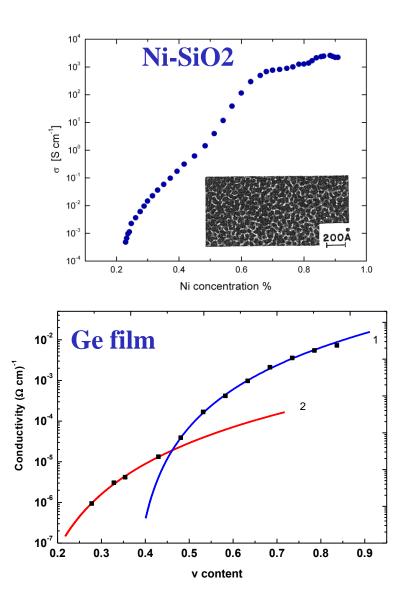
GTN for colloidal conductor-insulator composites

effects of particle shape asymmetry: spheroids (ellipsoids of revolution)

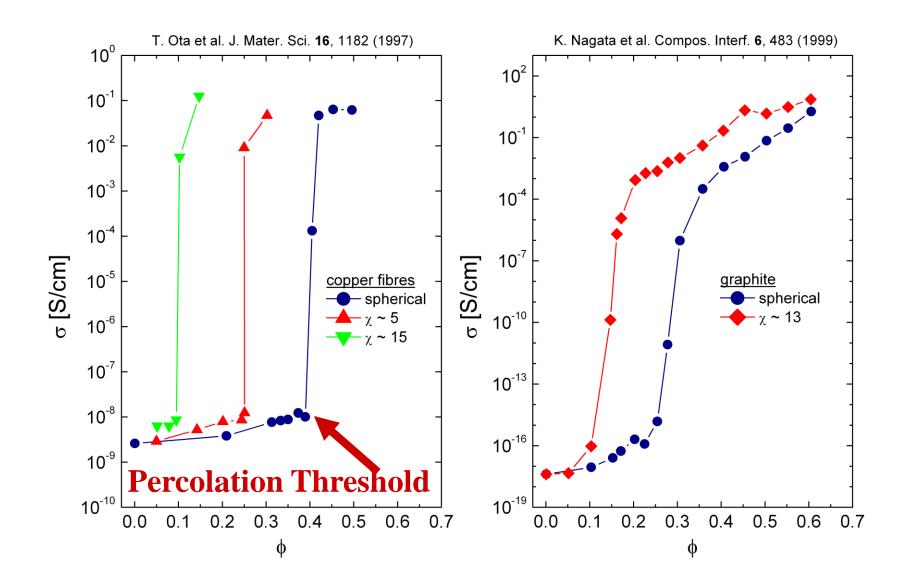




σ(v) behaviors

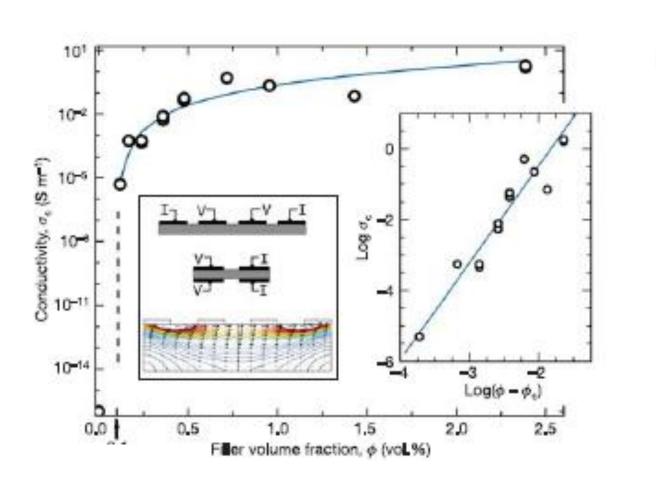


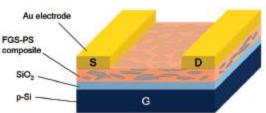
Typical behavior of all composites

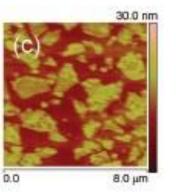


Graphene-based composite materials

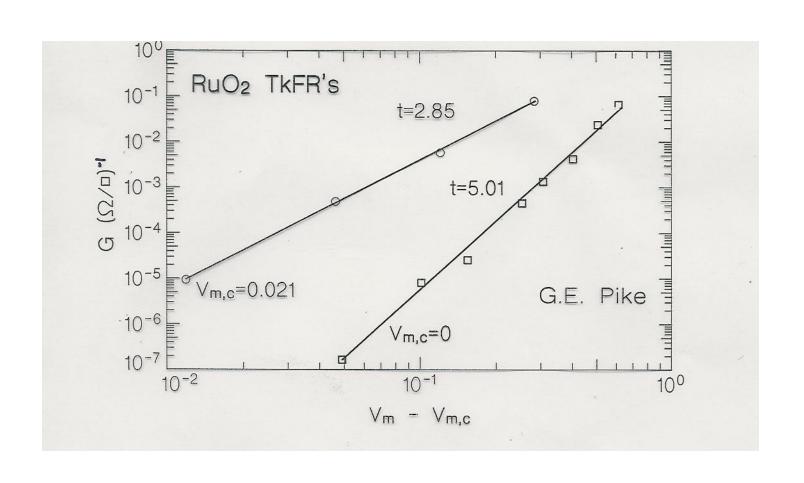
Sasha Stankovich¹*, Dmitriy A. Dikin¹*, Geoffrey H. B. Dommett¹, Kevin M. Kohlhaas¹, Eric J. Zimney¹, Eric A. Stach³, Richard D. Piner¹, SonBinh T. Nguyen² & Rodney S. Ruoff¹



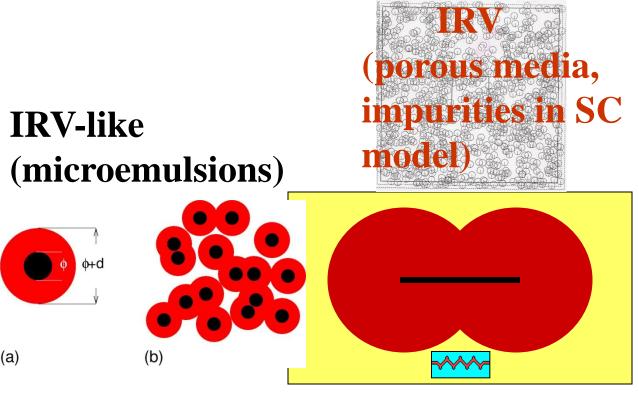


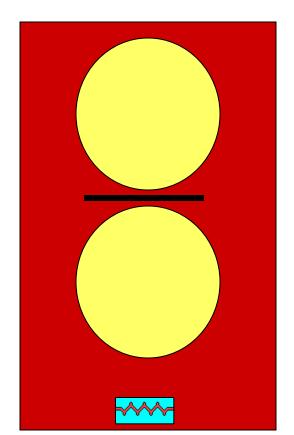


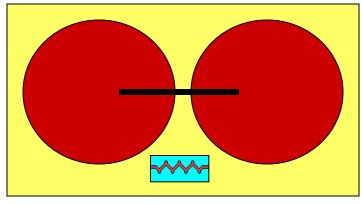
Non Universal behavior

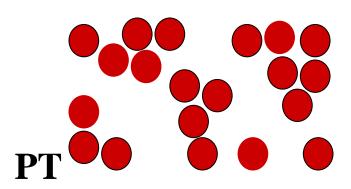


Geometry of Local Resistors





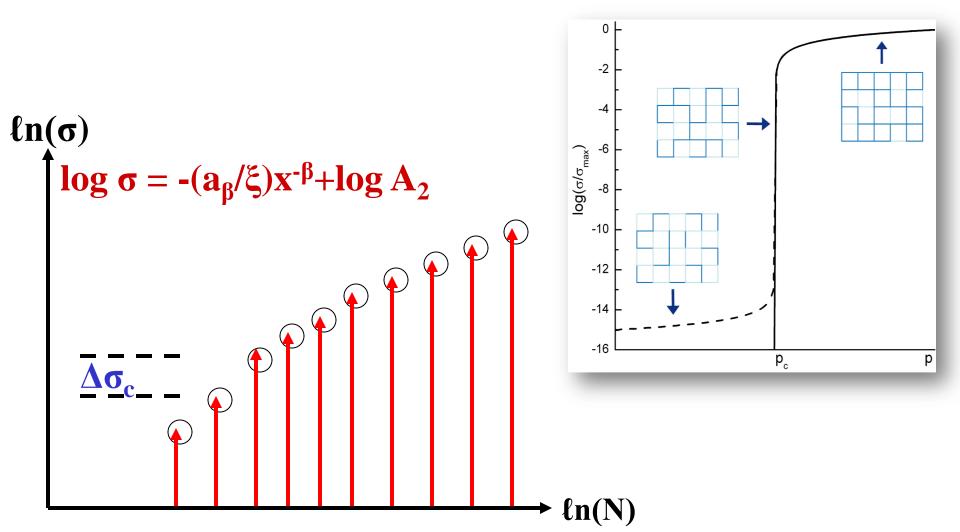




Local connectivity criterion?

RV

A percolation threshold (critical resistor) system vs. a critical percolation (phase transition like) system



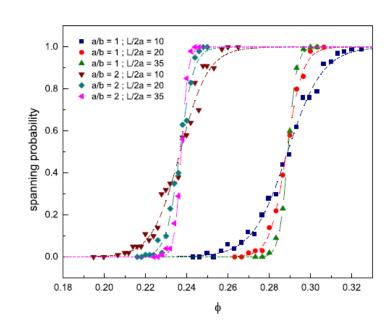
Critical Path Analysis

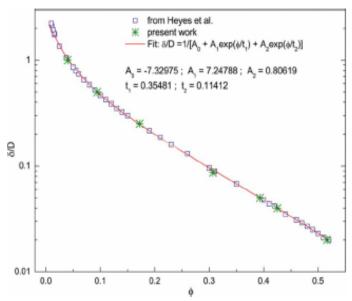
One labels the conductances (the interparticle distances) in the system in descending order until one gets percolation i.e., one finds the thinnest soft shell $\delta/2$ that still provides percolation for a given Φ .

Actually, we implant hard core particles and then attach to each a shell of thickness $\delta/2$. We check then how many particles, or how high a Φ is needed in order to get a percolation path.

The agreement of the CPA with simulation of the resistors network suggests that one finds the largest $\sigma(\Phi)$ without having to calculate the entire resistor networks.

 $\sigma \simeq \sigma_0 e^{-2\delta(\phi)/\xi}$. This works because of the very wide resistor distribution values





The effect of tunneling in lattices and the continuum

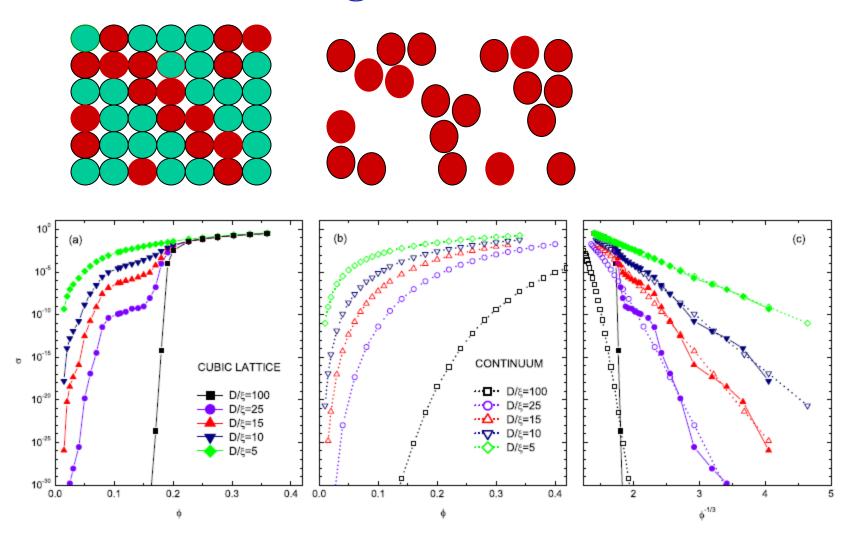
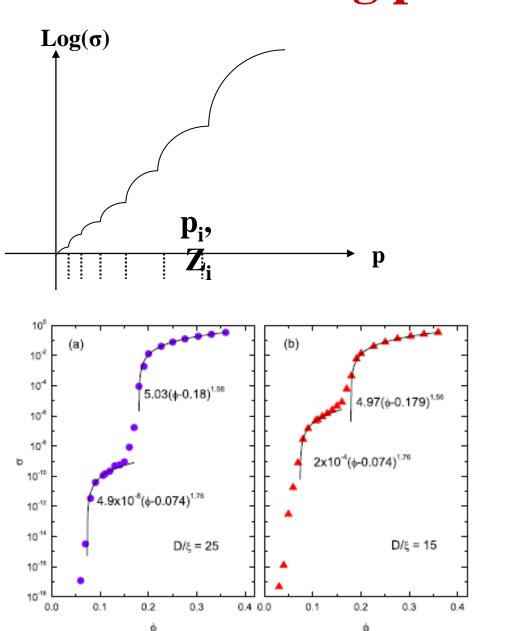
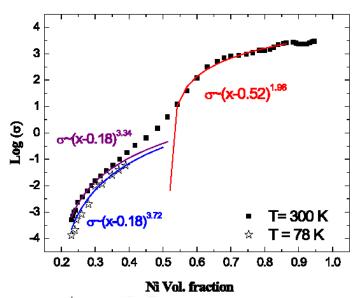


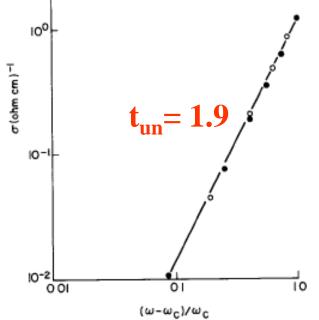
FIG. 3. (Color online) Monte Carlo conductance for (a) the cubic lattice model and (b) the continuum model for different values of D/ξ . (c) The same results of (a) and (b) plotted as a function of $\phi^{-1/3}$.

The tunneling percolation staircase

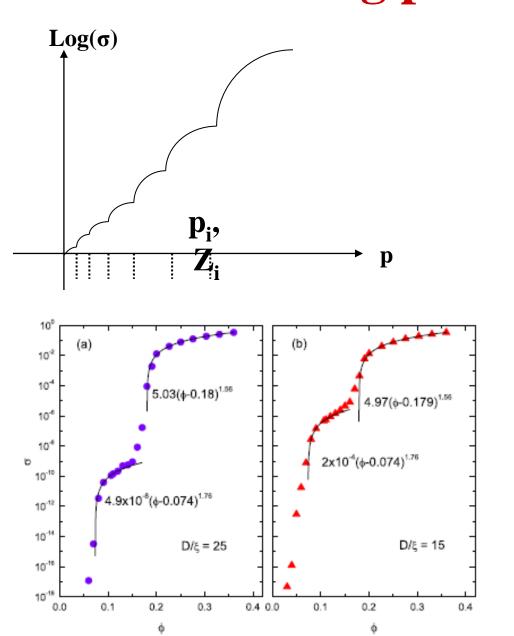


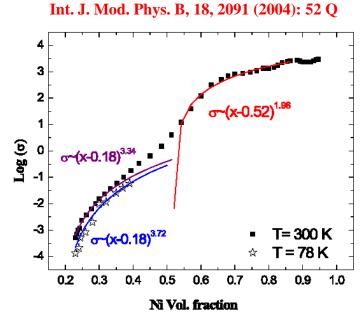


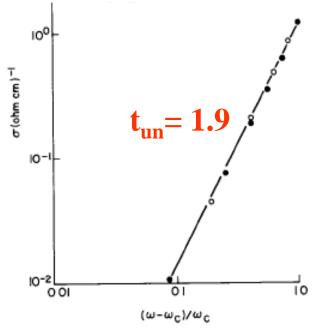
J. Mod. Phys. B, 18, 2091 (2004): 52 Q



The tunneling percolation staircase







Two interpretations of the full set of data points

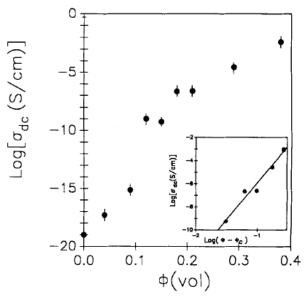


Fig. 1. DC conductivity as a function of the volume concentration of graphite. The insert represents Log σ vs. Log $(\Phi - \Phi_o)$. The slope has a value of 6.27.

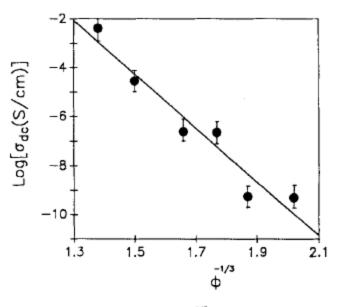
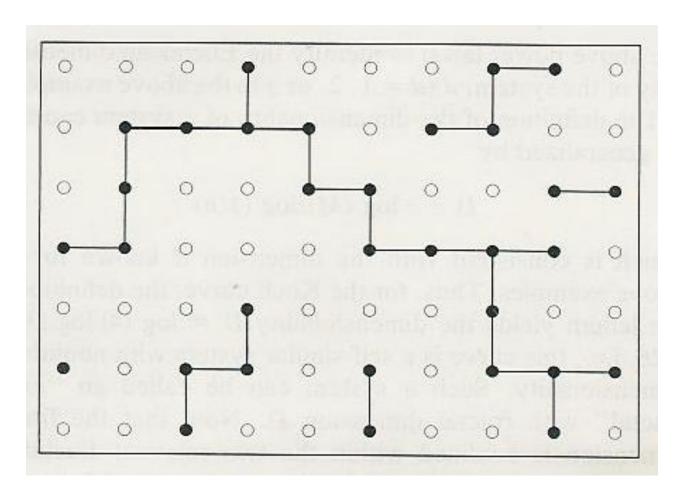


Fig. 3. Variation of Log σ_{dc} vs. $\Phi^{-1/3}$ (see text).

LATTICE PERCOLATION

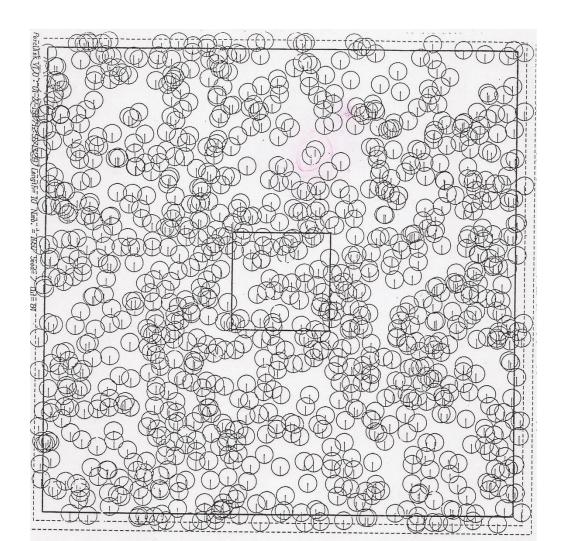


 $\mathbf{p^s}$ $\mathbf{p^b}$ \mathbf{S} $\mathbf{p_c}$



J. Water Resources Research 29, 775 (1993): 101 Q

A typical continuum system



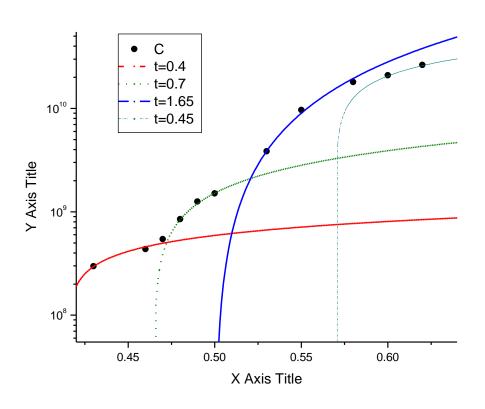
Local connectivity by partial overlap

No p here

The End



The Staircase in the AC measurements



Fluctuations in "experimental" data

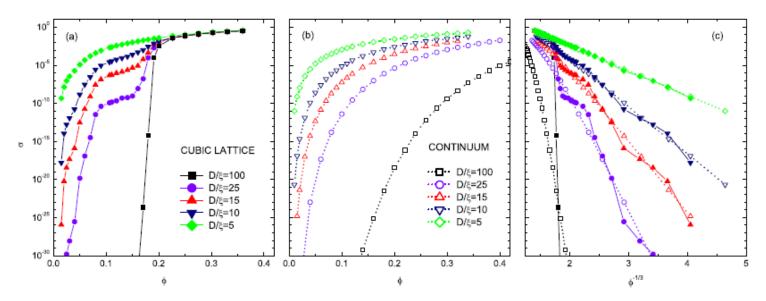
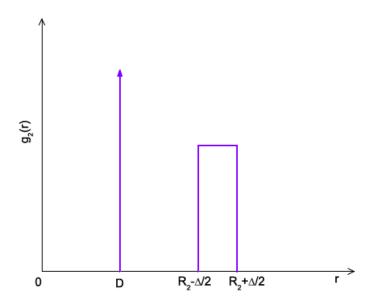
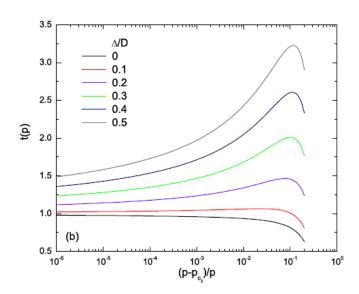
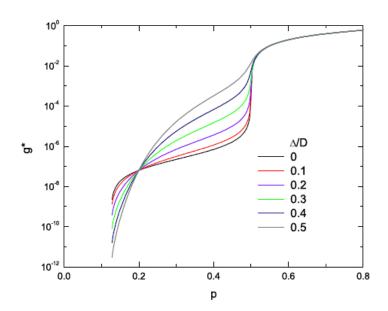


FIG. 3. (Color online) Monte Carlo conductance for (a) the cubic lattice model and (b) the continuum model for different values of D/ξ . (c) The same results of (a) and (b) plotted as a function of $\phi^{-1/3}$.







Two presentations of the same data

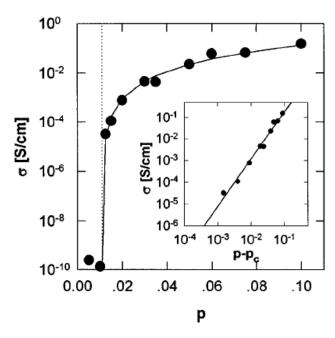


FIG. 1. Plot of σ as a function of carbon black volume content, p of composites; the critical concentration p_c has been determined using Eq. (1) (p_c =1.1%); inset: log-log plot of σ as a function of $p-p_c$; (t=2.17).

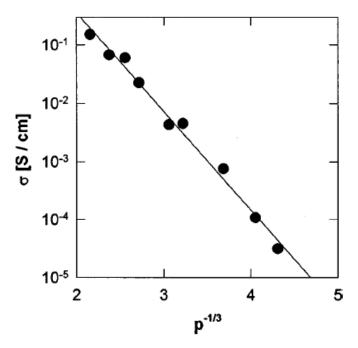


FIG. 2. Linear variation of $\ln \sigma$ vs $p^{-1/3}$.

Two presentations of the same data

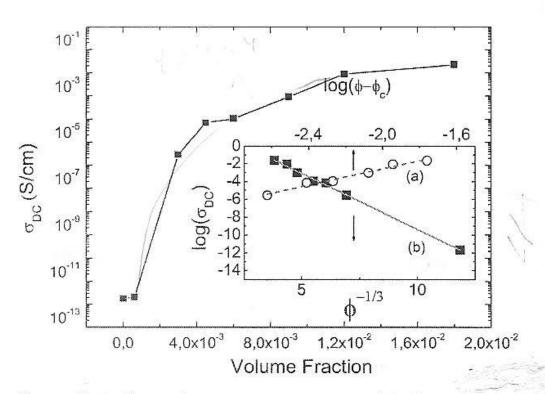
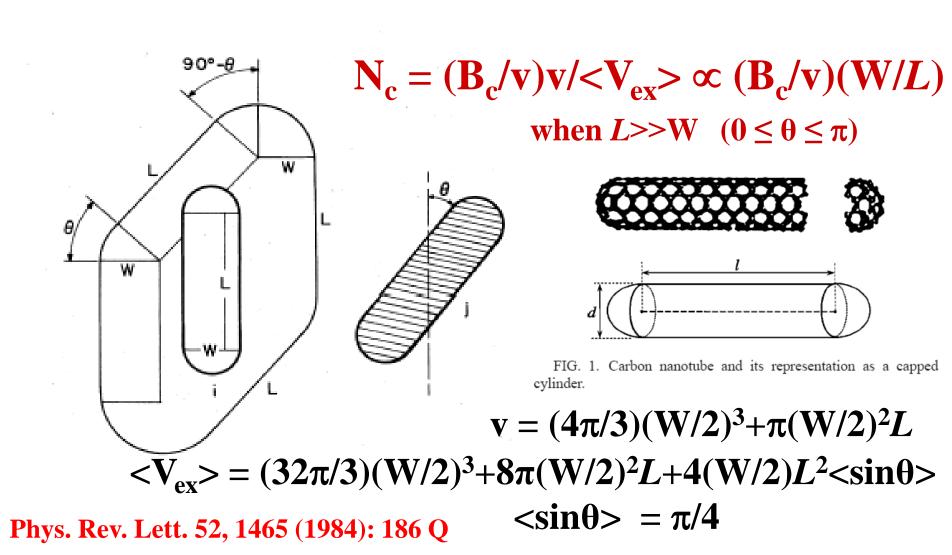


Figure 3 (online colour at: www.pss-a.com) DC conductivity versus volume fraction displayed in a log-linear scale. Inset (a): fit of the percolation law $\sigma_{\rm eff} = \sigma_{\rm conductor}(\Phi - \Phi_c)'$. Inset (b): fit of a single tunneling junction expression in a log-linear plot.

The volume and excluded volume of the capped cylinders



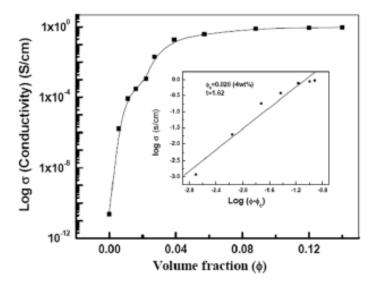


Fig. 2. Electrical conductivity (σ) of SAN-GS composites as a function of GS volume fraction (ϕ) .

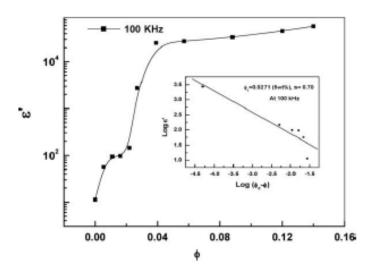


Fig. 3. Dielectric constant (ε') of SAN–GS composites as a function of ϕ at 100 kHz.

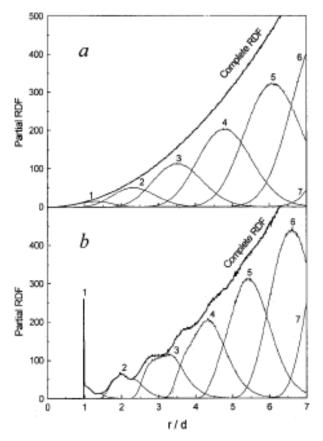


FIG. 2. Radial distribution function. (a) Points, (b) hard spheres $\eta=0.5$, (1-7) partial densities of the probability of distribution of neighbors, respectively, for neighbors 1, 2, etc.

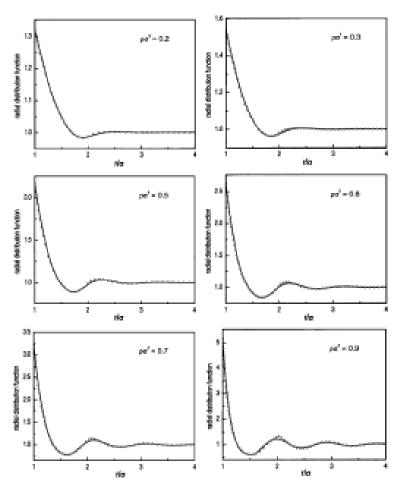
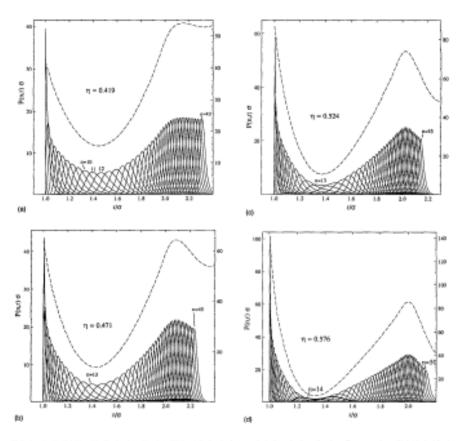
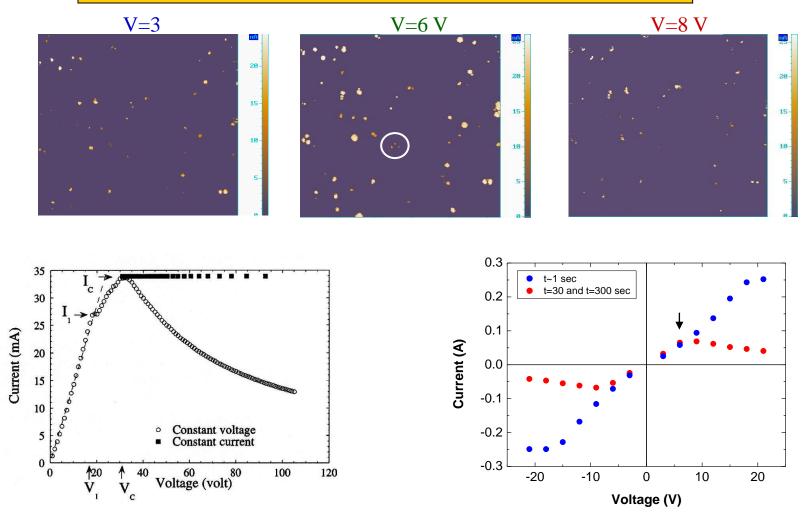


FIG. 4. The hard-sphere RDF evaluated using Eqs. (14)–(16) (this solid line) and the corresponding MC data (symbols) at different desertion.



F1G. 4. (a)-(d) Neighborship distributions P(n,r) (solid lines) for hard spheres at the indicated values fractions. For comparison, G(r) (dashed line) is plotted on the right-hand scale.

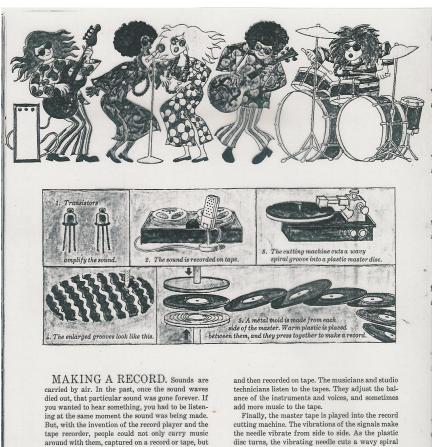
Electro-Thermal Switching: the 'global' effect



- an increase of the *macroscopic* resistance above a threshold bias
- a stationary "switched" state is reached within 30 sec

Phys. Rev. Lett. 90, 236601 (2003): 20 Q.

Making the Audio Disc



they could hear it over and over again, when and where they wanted.

In the recording studio, the microphone changes the music to electrical signals which are amplified, groove into it from the outside in. This groove is a physical "record" of the music.

Metal molds made from the master disc press out the plastic record that you buy in a store.

HISTORY

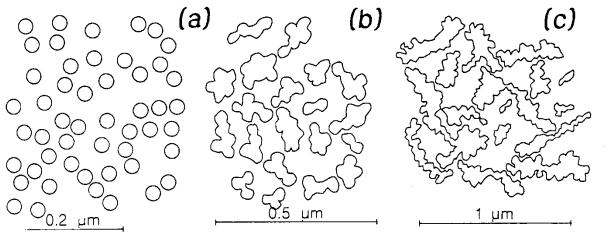


- 1982 RCA Laboratories, Princeton, USA
- Request: High conductivity, High elasticity.
- Question: Carbon Black supplier?
- A) Cabot Corporation, Boston USA
- B) Akzo Chemicals, Amersfoort, The Netherlands

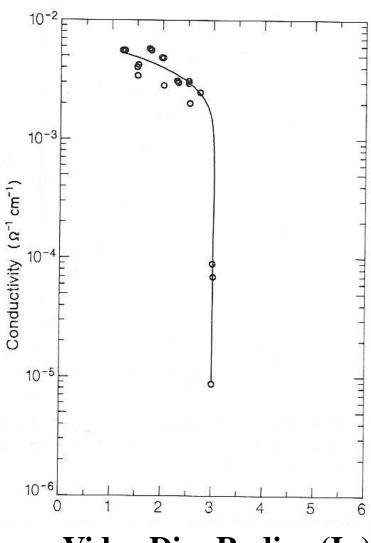


Low structure or high structure?



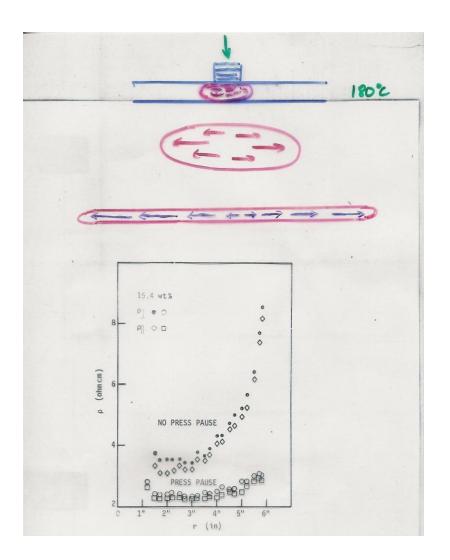


The "lost" signal (Percolation Threshold and Anisotropy)



Video Disc Radius (In)

Overcoming the "Anisotropy"



The Question is:

How to express conceptually and mathematically the feeling that elongated, not parallel, particles will yield a higher conductivity (i.e. connectivity) for the same CB content?

Cylinder like objects

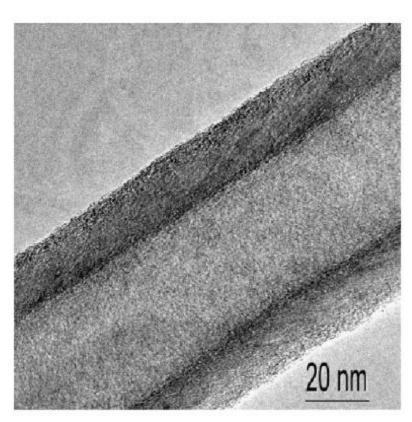


Fig. 2 - TEM micrograph of VGCNF [20].



Phys. Rev. B, 28, 3799 (1983): 156 Q

Behavior of three types of composites that are based on elongated carbon particles

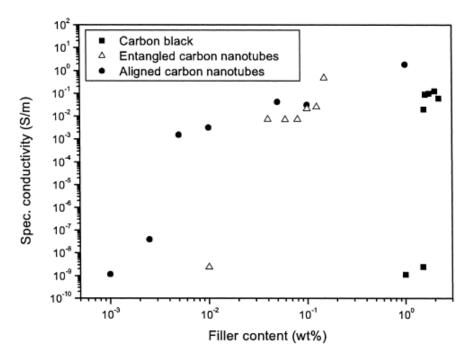
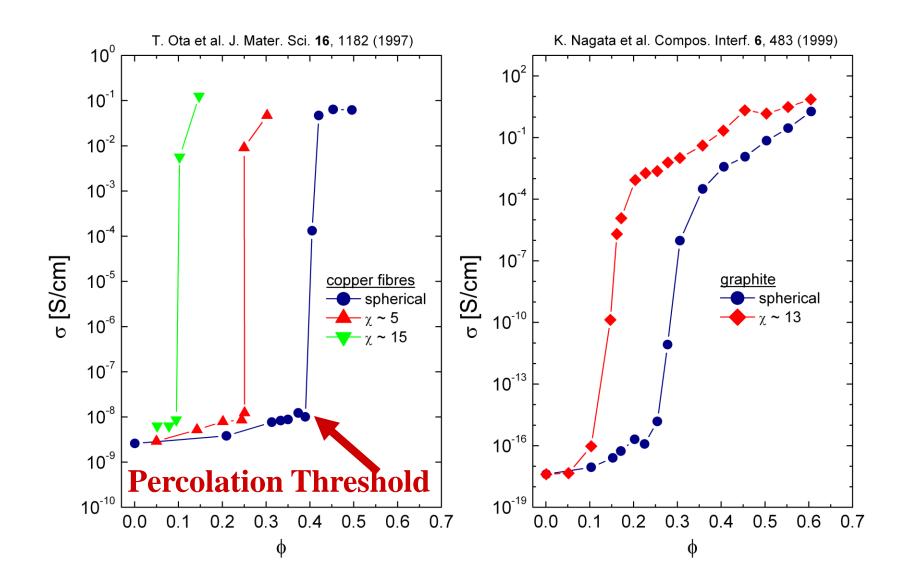


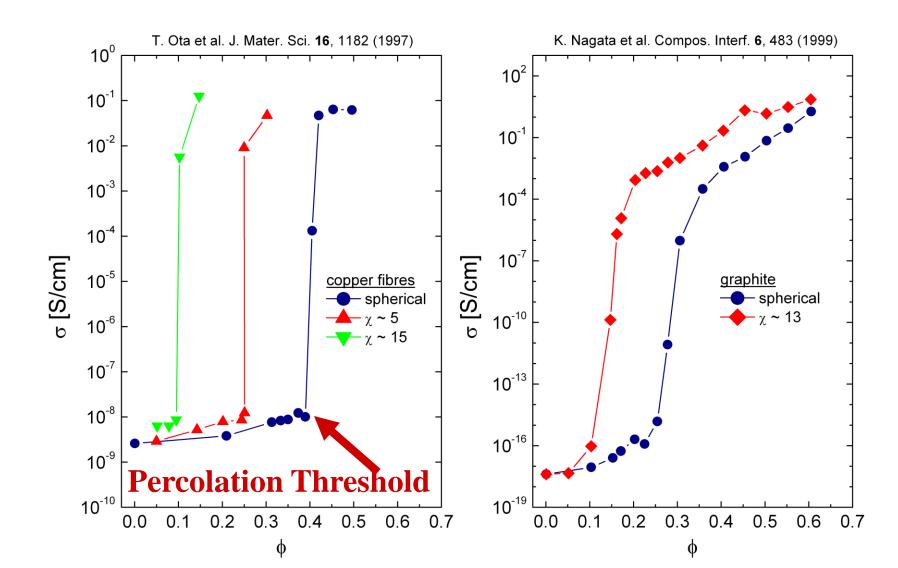
Fig. 6. Epoxy composite conductivity as a function of filler weight fraction for the aligned CVD-grown multi-wall carbon nanotubes compared to results previously achieved with entangled nanotubes and carbon black particles [4].

Table 1 – Typical properties of VGCNF, SWNT, MWNT and CF					
Property	VGCNF ^a	SWNT ^b	MWNT ^b	CF°	
Diameter (nm)	50-200	0.6-1.8	5-50	7300	
Length (µm)	50-100			3200	
Aspect ratio	250-2000	100-10,000	100-10000	440	

Typical behavior of all composites

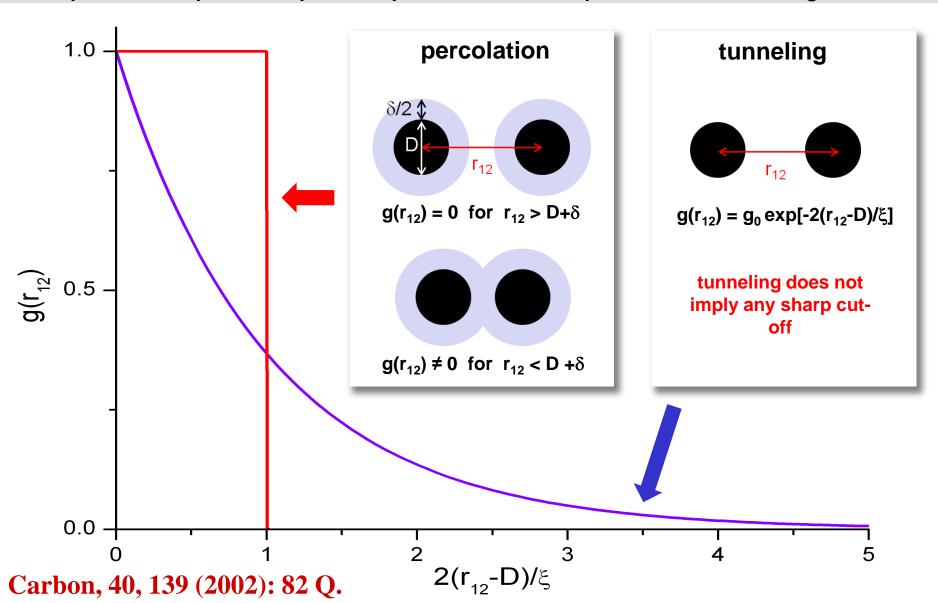


Typical behavior of all composites



percolation versus tunneling

the percolation picture implies the presence of a sharp cut-off, but tunneling does not



The concept of "excluded volume"

We generalized v2^D to other objects calling it "Excluded Volume"

 $NV_{ex} = B$: the average number of overlapping objects, i.e. the average number of bonds per object. B_c is expected then to be a topological invariant. $V_{ex} = v2^{D}$ $\mathbf{v}\mathbf{N}_{\mathbf{c}} = (\mathbf{v}/\mathbf{V}_{\mathbf{e}\mathbf{v}})(\mathbf{V}_{\mathbf{e}\mathbf{v}}\mathbf{N}_{\mathbf{c}}) = (\mathbf{v}/\mathbf{V}_{\mathbf{e}\mathbf{v}})\mathbf{B}_{\mathbf{c}}$

The Excluded Volume is the volume in which the center of the "other object" has to be in order for the two objects to, at least partially, overlap

Note: 2^D = smallest V_{ex}/v for permeable objects

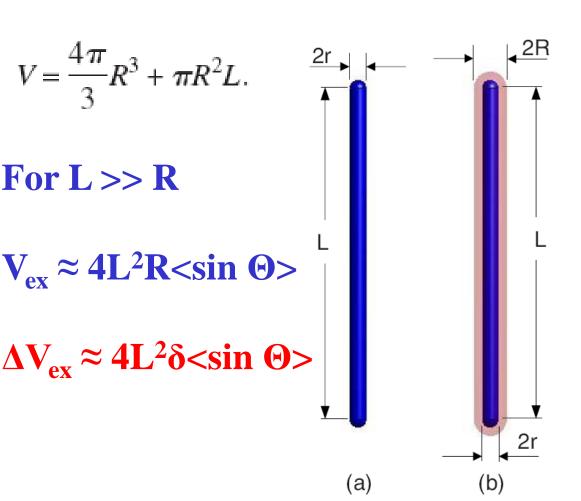
Phys. Rev. B, 30, 3933 (1984): 290 Q

History of percolation Thresholds in the Continuum (Sastry, PRE 2007)

Table 2. Key percolation studies in three dimensional random fibrous materials

Authors	Year	Reference	Arrangement	Objects	Contribution	Approach
Balberg, Binenbaum and Wagner	1984	27	isotropic	capped cylinders	First study of percolation of random objects in three dimensions	Monte Carlo simulations
Balberg, Anderson, Alexander et al.	1984	26	isotropic	capped cylinders	Presented the conjecture that percolation threshold for a system of identical objects in three dimensions is inversely proportional to excluded volume of one object	Monte Carlo simulations
Bug, Safran and Webman	1985	28	isotropic	capped cylinders	Confirmed excluded volume rule and showed constant of proportionality equals one in slender rod limit	cluster expansion
Neda, Florian and Brechet	1999	29	isotropic	capped cylinders	Performed Monte Carlo simulations of 3D stick systems using correct isotropic distribution and confirmed excluded volume theory	Monte Carlo simulations
Yi and Sastry	2004	30	isotropic	ellipsoids	Presented analytical approximation for the percolation threshold of two- and three- dimensional arrays of overlapping ellipsoids	series expansion
Yi, Wang, and Sastry	2004	31	Uniform distribution in x-y plane. Range of distributions from parallel to random in z-direction	ellipsoids	Provided comparisons of cluster sizes, densities, and percolation points for two- and three-dimensional systems of overlapping ellipsoids to investigate the range of applicability of a 2D model for predicting percolation in thin three-dimensional systems	Monte Carlo simulations

The generalization to the hard core case



In considering tunneling, the tunneling range is $R-r = \delta$

The important observation is that:

$$\Phi_{c} = N_{c}v \propto (B_{c}/\Delta V_{ex})v \propto r^{2}L/[L^{2}(R-r)] \propto [r/(R-r)](r/L)$$

If $\delta = (R-r)$ we have that $\Phi_c \propto (r/\delta)(r/L)$

For discs of For Oblate Particles

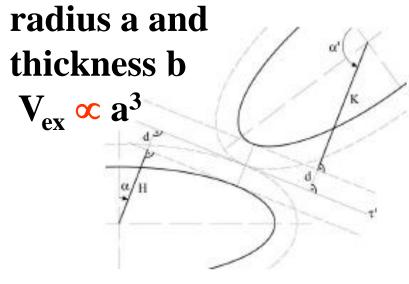


FIG. 8. Two oblate spheroids surrounded with shells of constant thickness which are in contact (2D representation).

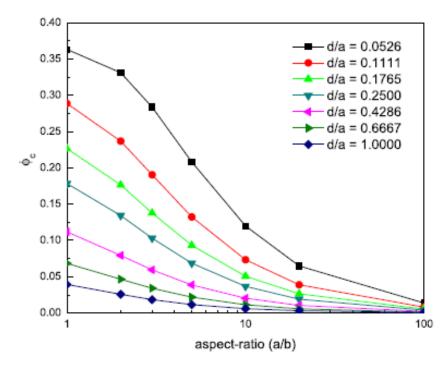


FIG. 3. (Color online) Percolation threshold ϕ_c variation as a function of the aspect ratio for different shell thicknesses.

Asymptotically for a >> b, d and isotropic distribution:

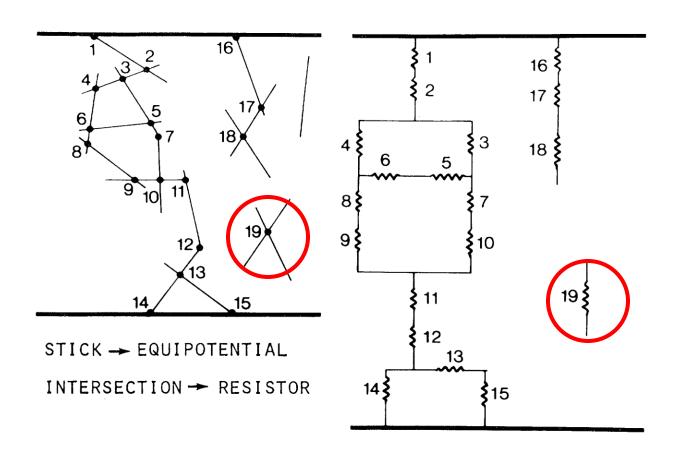
$$\Delta V_{ex} \propto [(a+d)3 - a3] \approx (a^2d), v = \pi a^2b, \Phi_c \propto b/d = (a/d)(b/a)$$

From the simulations:

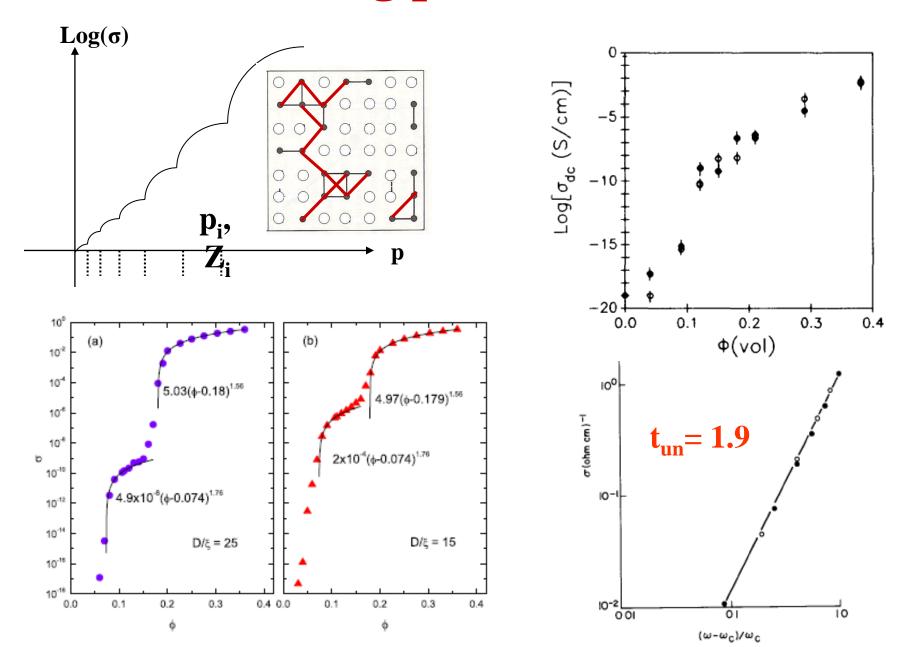
$$\Phi_{\rm c} \propto {\rm v/V_{\rm ex}} \propto \approx ({\rm a/d})({\rm b/a})^{1/2}$$

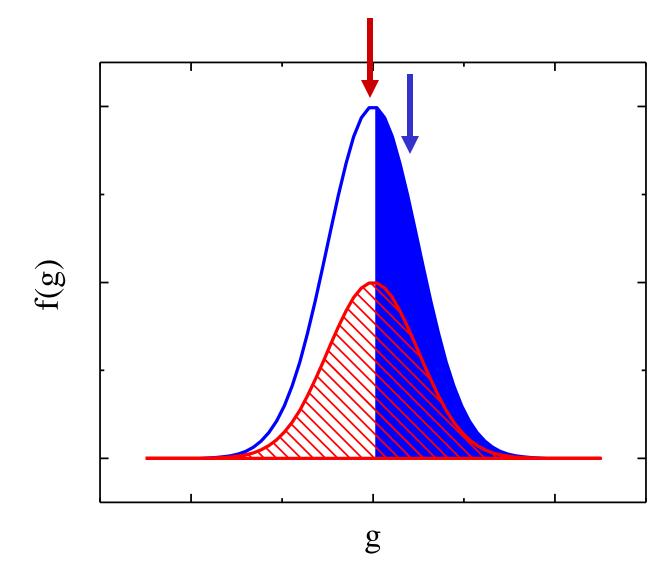
Phys. Rev. B, 81,155434 (2010).

Resistors Equivalent Network



The tunneling percolation staircase





The RDF

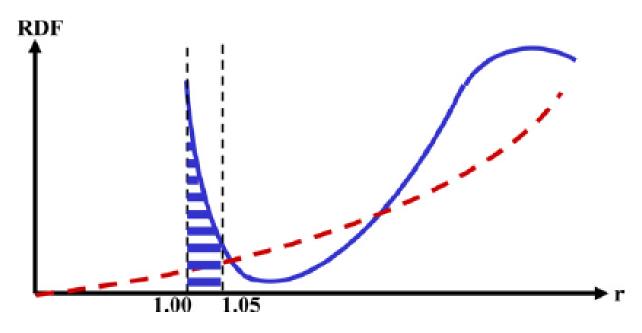
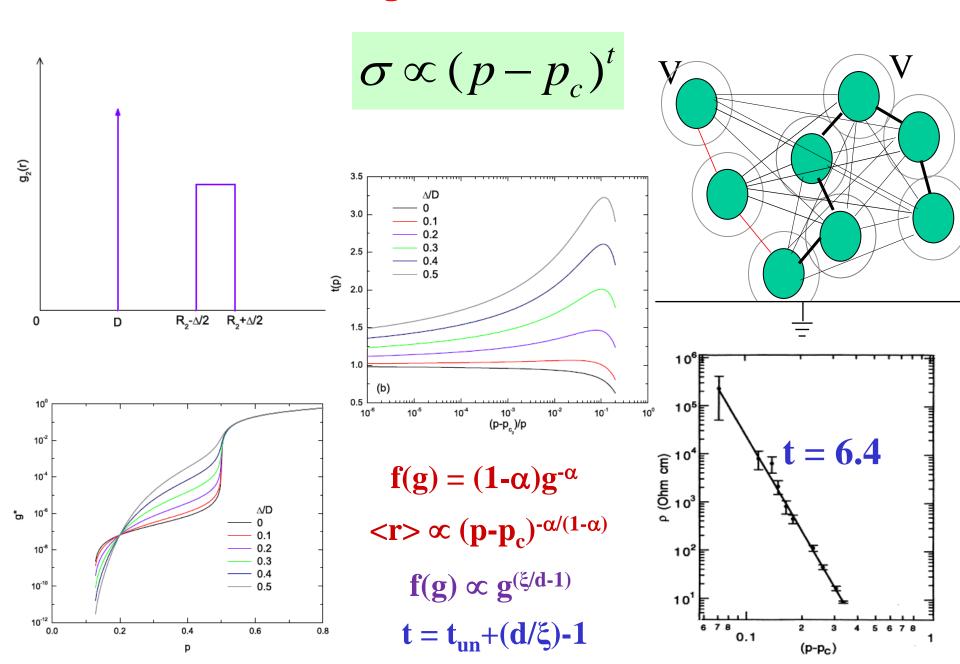
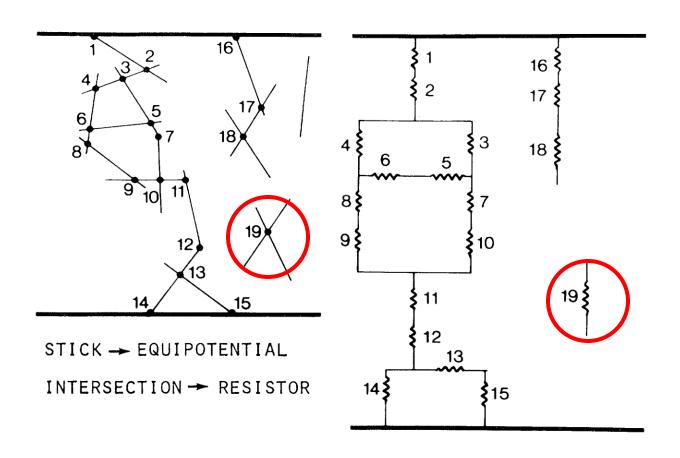


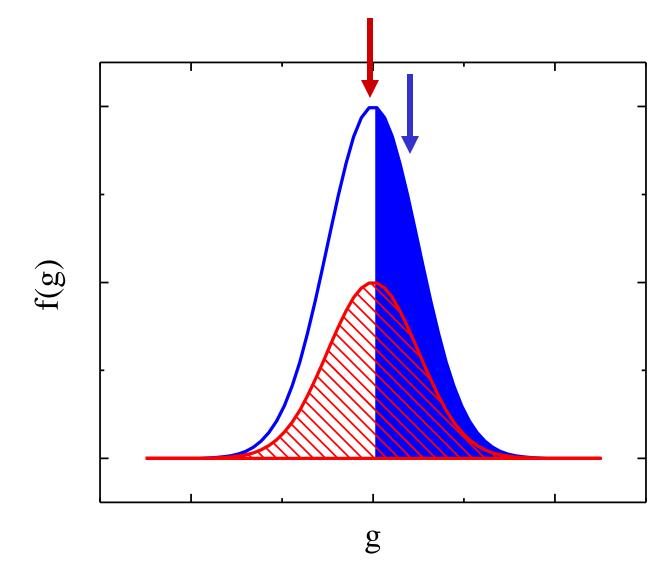
Figure 7. The main features of the RDF of non-interacting hard spheres (see figure 6) for a typical critical density of x = 0.4 (see [59, 60]). The solid curve represents the envelope of the contribution of the various nearest neighbours. In particular note that the integrated area between 1 and 1.05 sphere diameters (that has contributions up to the third nearest neighbours) provides, on the average, the critical two 'needed' near neighbours for a given particle. Also illustrated (by the dashed curve) is the parabolic RDF for the uniform concentration distribution (see figure 3) that is applicable to spheres with a diameter 2b that is negligible in comparison with the average nearest neighbours distance 2a.

The effect of a tunneling like distribution of conductances



Resistors Equivalent Network





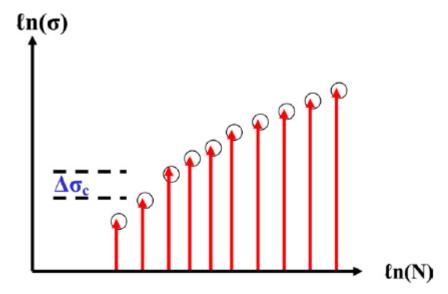
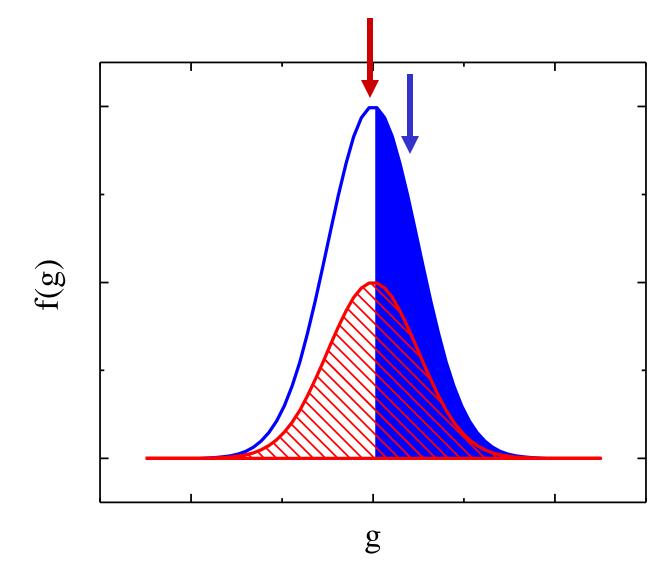
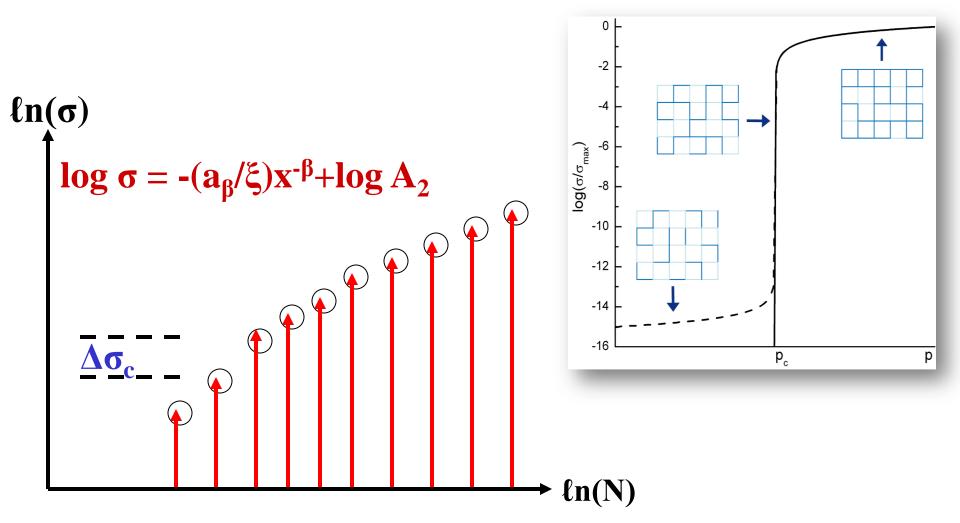


Figure 4. The dependence of the conductivity on the particle concentration in the critical sub-network of the (nearest neighbour) hopping model for a system such as the one that is shown in figure 3. The curve that is described by the open circles indicates primarily the change in the values of the critical resistors in the network. The jump in the critical conductance $\Delta \sigma_c$, with an increase in the density by ΔN is indicated in the figure.



A percolation threshold (critical resistor) system vs. a critical percolation (phase transition like) system



Critical Path Analysis

One labels the conductances in the system in descending order until one gets percolation i.e., one finds the largest soft shell δ that is needed to get percolation for a given Φ .

Actually, one implants hard core particles and then attaches with a shell $\delta/2$. One checks then how many particles, or how high a Φ is needed in order to get percolation.

The agreement of the CPA with simulation of the resistors network suggests that one finds the largest $\sigma(\Phi)$ without having to calculate resistor networks.

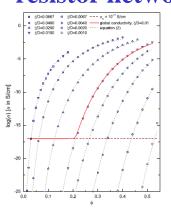
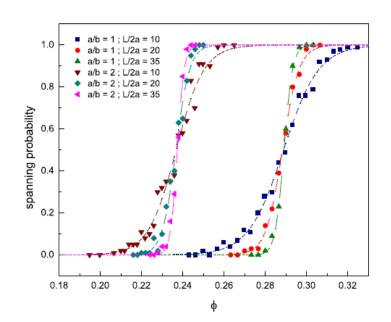
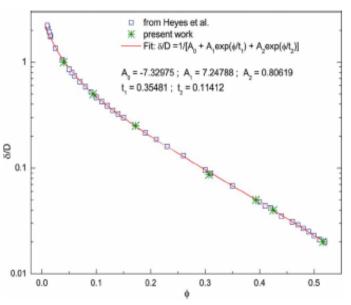


FIG. 1. (Color online) Tunneling conductivity in a system of spheres with different characteristic tunneling distance to spheres dismeters ratio ξ/D as a function of the volume fraction ϕ . The matrix intrinsic conductivity for $\sigma_{\sigma =} 10^{10}$ "S/cm and the overall conductivity for the $\xi/D = 0.01$ case are shown. Results from Eq. (2) with $\alpha_{\sigma} = 0.115$ S/cm are displayed by dotted

This works
because of the
very wide
distribution of
resistor values

$$\sigma \simeq \sigma_0 e^{-2\delta(\phi)/\xi}$$





Presentation of the CPA results in terms of percolation

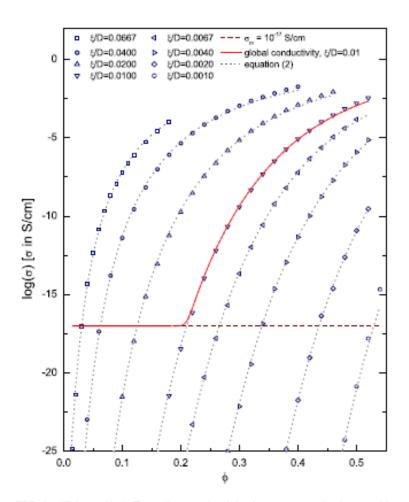
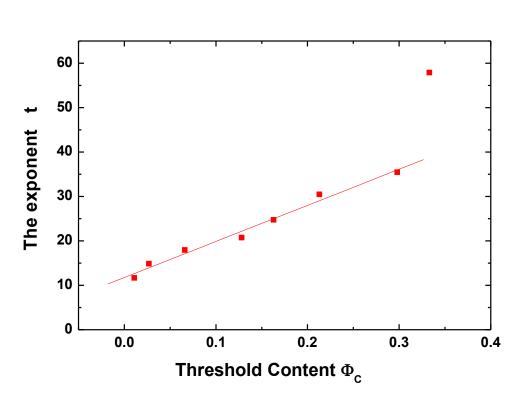


FIG. 1. (Color online) Tunneling conductivity in a system of spheres with different characteristic tunneling distance to spheres diameters ratio ξ/D as a function of the volume fraction ϕ . The matrix intrinsic conductivity for $\sigma_m = 10^{-17}$ S/cm and the overall conductivity for the $\xi/D = 0.01$ case are shown. Results from Eq. (2) with $\sigma_0 = 0.115$ S/cm are displayed by dotted lines

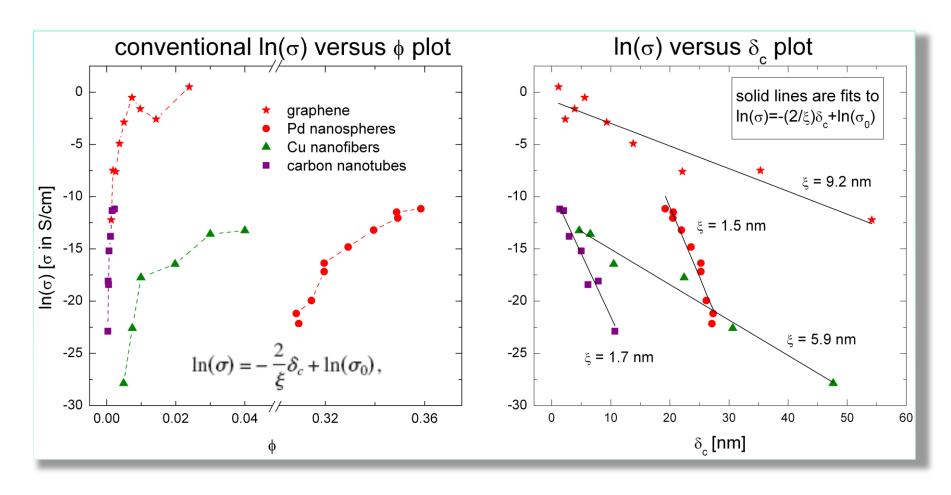


GTN for colloidal conductor-insulator composites

application of CPA formulas to real conductor-polymer nanocomposites

$$\sigma \simeq \sigma_0 \exp\left[-\frac{2\delta_c(\phi)}{\xi}\right]$$

from the knowledge of σ vs ϕ and from the filler geometry [a/b and D=2max(a,b)] one can estimate the value of the tunneling factor ξ



The physical and mathematical resemblance of the percolation and (CPA) hopping behaviors:

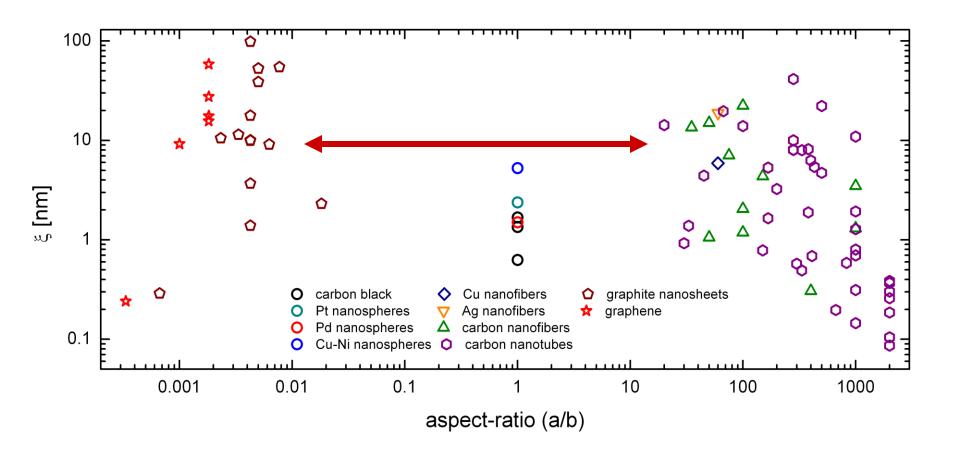
In the classical hopping (CPA) model : $\log \sigma = -d/\xi = -(a_\beta/\xi)x^{-\beta} + \log A_1 \quad 1/3 \le \beta \le 1$

In our percolation model: log σ = t log(x-x_c) +log A₂ we saw (from the Excluded volume argument) that $t = t_{un} + d/\xi$ -1 so that for $t >> t_{un}$ we have that $t \approx -x^{-\beta}/\xi$ where $1/3 \leq \beta \leq 1$ and log (x-x_c) < 0.

• The two dependence yield then quite a similar dependence on x. Experimentally; since usually $x >> x_c$ these two are usually non distinguishable. Can we still distinguish between them?

GTN for colloidal conductor-insulator composites

application of CPA formulas to real conductor-polymer nanocomposites



even if a/b changes over 6 orders of magnitude, the tunneling factor is found to be within the expected range $0.1 \text{ nm} < \xi < 10 \text{ nm}$ [G. Ambrosetti et al. Phys. Rev. B 81, 155434 (2010)]

The effect of tunneling in lattices and the continuum

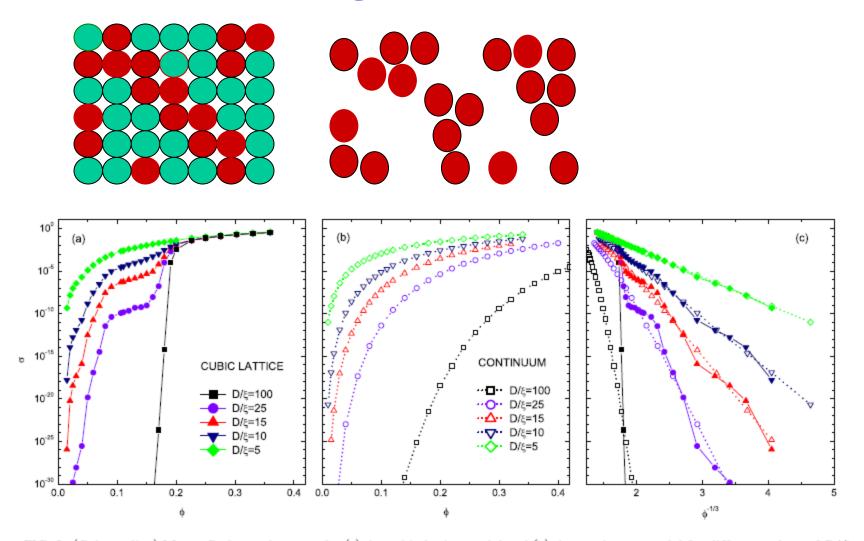
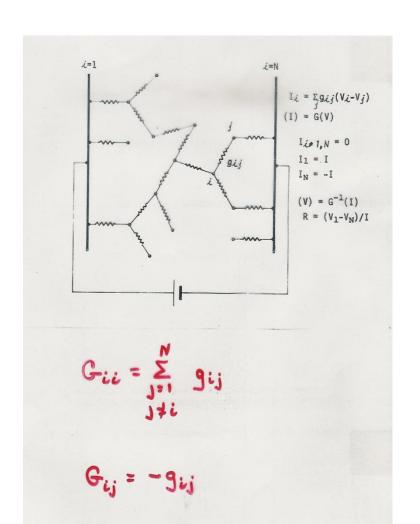


FIG. 3. (Color online) Monte Carlo conductance for (a) the cubic lattice model and (b) the continuum model for different values of D/ξ . (c) The same results of (a) and (b) plotted as a function of $\phi^{-1/3}$.

Analysis of a resistors network



Critical Path Analysis

One labels the conductances in the system in descending order until one gets percolation.

One takes then the smallest conductance thus found and determines its $\delta(\Phi)$ value. The agreement with simulation suggests that:

One can simply arrange the $\delta(\Phi)$ values and find directly the largest needed $\delta(\Phi)$ without having to calculate resistor networks.

This works because of the very wide distribution of resistor values

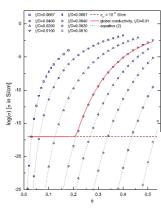
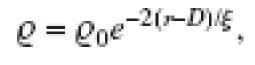


FIG. 1. (Color online) Tunneling conductivity in a system of spheres w
different characteristic tunneling distance to spheres diameters ratio
$$\xi/D$$

a function of the volume fraction θ . The matrix intrinsic conductivity ...
 $\sigma_{\mu}=10^{-15}$ S/cm and the overall conductivity for the $\xi/D=0.01$ case are
shown. Results from Eq. (2) with $\sigma_{\mu}=0.115$ S/cm are displayed by dotted



$$\sigma \simeq \sigma_0 e^{-2\delta(\phi)/\xi}$$
,

$$\frac{\delta(\phi_c)}{\xi} = \frac{1}{2} \ln \left(\frac{\sigma_0}{\sigma_m} \right),$$

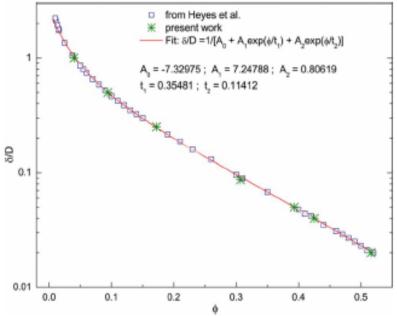


FIG. 2. (Color online) Geometrical percolation threshold of the hard-coresoft-shell model from algorithm of present work and from results of Ref. 16. Shown is the critical interaction distance to sphere diameter ratio δ/D as a function of the hard spheres volume fraction ϕ .

The excluded volume approach

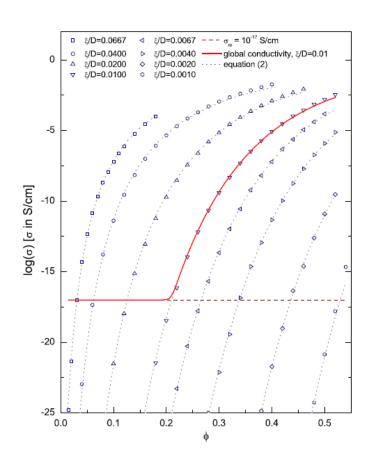
- The parameter that is known experimentally is the critical volume % of the "filler" Φ_c , so the prediction to be made is how does Φc depend on the microscopic parameters.
- For spheres these parameters are D and ξ so:
- $v = (4\pi/3)(D/2)^3$, $\Phi = Nv$, $\Phi_c = N_c v$,
- $B_c = (4\pi/3)(r_c^3 D^3)N$ and $\delta_c = r_c D$
- Case 1: $r_c >> D \rightarrow B_c = (4\pi/3)(\delta_c^3)N = (4\pi/3)(\delta_c^3)\Phi/v$
- $\rightarrow \delta_{\rm c} \propto (\Phi/{\rm V})^{-1/3} \rightarrow$
- Log $\rho = \alpha_1 + \beta_1 \Phi^{-1/3}$.
- Case 2: $r_c \approx D \rightarrow B_c \approx (4\pi/3)(3\delta_c D^2)N = (4\pi/3)(3\delta_c D^3)N/D = (3\delta_c 8)\Phi/D$
- $\Phi/V \rightarrow B_c = 24 \delta_c \Phi/D \rightarrow \delta_c = B_c D/24\Phi$
- $\delta_c \propto D\Phi^{-1}$
- Log $\rho = \alpha_1 + \beta_1 \Phi^{-1}$.

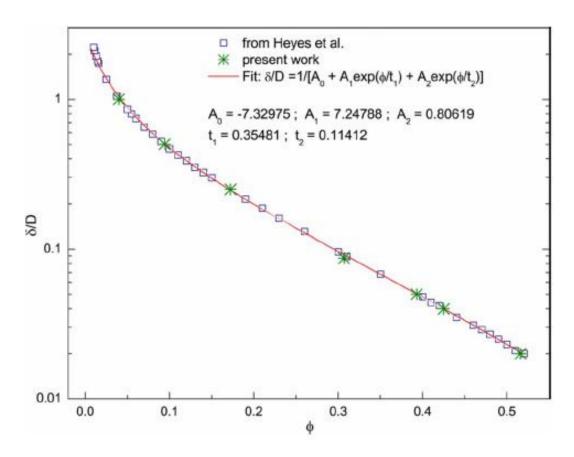
The predicted CPA conductivity dependence on Φ

- For capped cylinders:
- $v \approx \pi R^2 L$, $\Phi = Nv = \pi R^2 LN$
- $\Delta V_{\rm ex} \approx \pi L^2 \delta_{\rm c} < \sin \theta >$, $N \Delta V_{\rm ex} = B_{\rm c}$

- $\delta_c \approx B_c R[(R/L) < \sin\theta >] \Phi^{-1} \propto \Phi^{-1}$
- In general then, $\delta_c \propto \Phi^{-\beta}$ where in 3D: $1/3 \le \beta \le 1$

CPA for spheres





The RDF

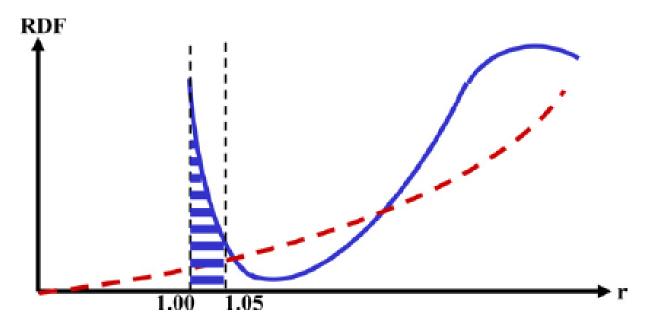
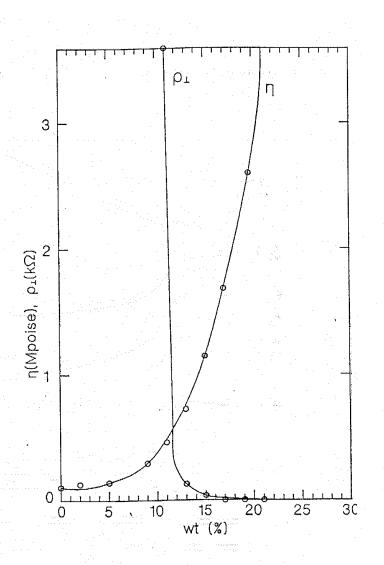


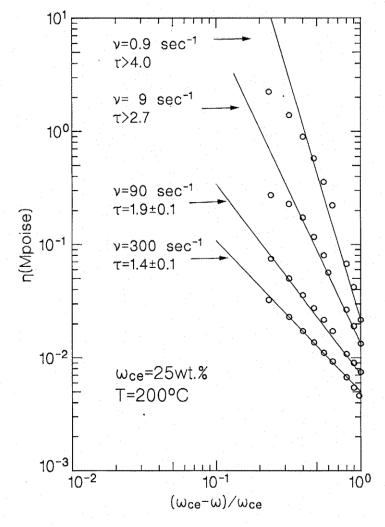
Figure 7. The main features of the RDF of non-interacting hard spheres (see figure 6) for a typical critical density of x = 0.4 (see [59, 60]). The solid curve represents the envelope of the contribution of the various nearest neighbours. In particular note that the integrated area between 1 and 1.05 sphere diameters (that has contributions up to the third nearest neighbours) provides, on the average, the critical two 'needed' near neighbours for a given particle. Also illustrated (by the dashed curve) is the parabolic RDF for the uniform concentration distribution (see figure 3) that is applicable to spheres with a diameter 2b that is negligible in comparison with the average nearest neighbours distance 2a.

The End



VISCOSITY vs. CONDUCTIVITY





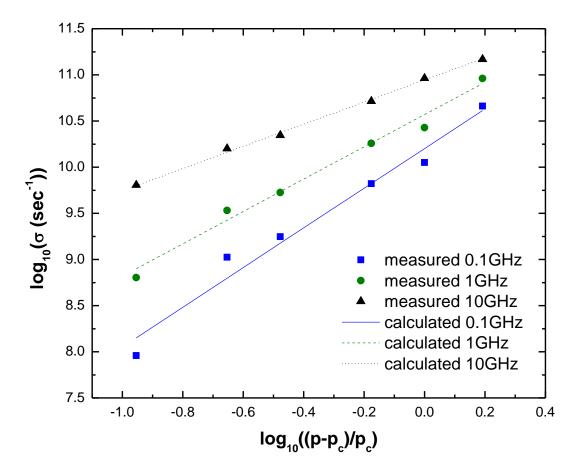
The differences between the different types of elongated Carbon particles

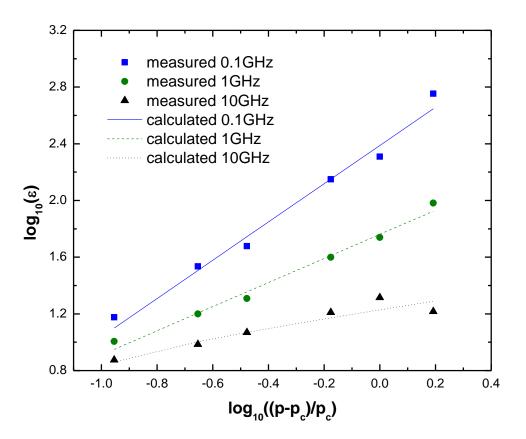
Property	VGCNF ^a	SWNT ^b	MWNT ^b	CF ^c
Diameter (nm)	50-200	0.6-1.8	5–50	7300
Length (µm)	50-100			3200
Aspect ratio	250-2000	100-10,000	100-10000	440
Density (g/cm³)	2	~1.3ª	∼1.75 ^e	1.74
Thermal conductivity (W/m K)	1950	3000-6000 ^f	3000-6000 ^f	20
Electrical resistivity (Ω cm)	1×10 ⁻⁴	$1 \times 10^{-3} - 1 \times 10^{-4}$	$2 \times 10^{-3} - 1 \times 10^{-4}$	1.7 × 10
Tensile strength (GPa)	2.92	50-500 ^g	10-60 ^g	3.8
Tensile modulus (GPa)	240	1500	1000	227
a From Refs. [1,20,62,66]. b From Ref. [2]. c Properties of Akzo Nobel Fortafil 243 PAN-based fibers [67].			For high structure carbon black the	
d From Ref. [33].			car bon black the	
From Ref. [68].			aspect ratio	is of the
From Ref. [69].			•	
g From Ref. [35].			order of 10	

The End

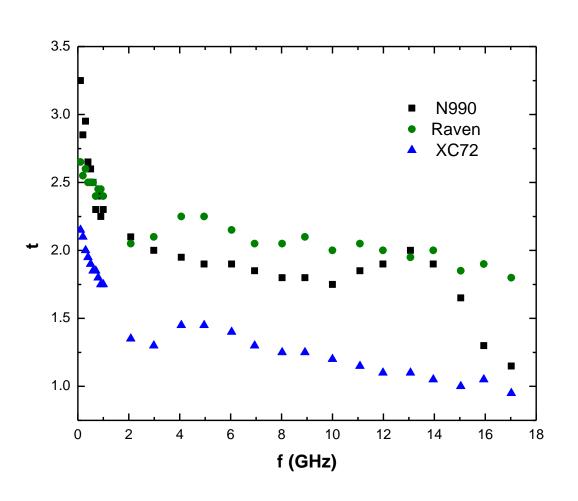


Recent results of the RF conductivity and permitivity of Carbon Black composites

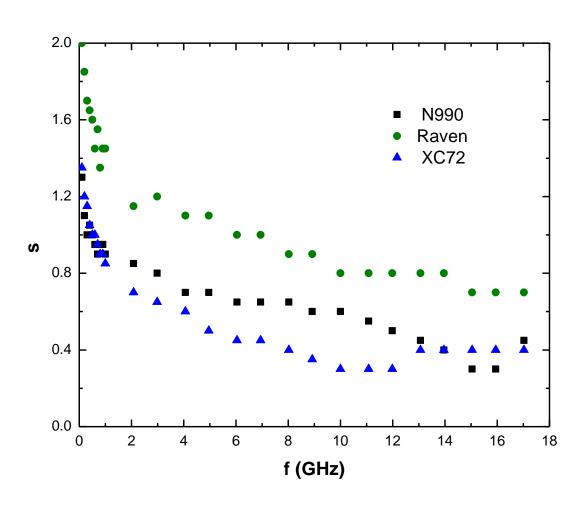




Conductivity exponent



Permitivity exponent





One – Day IVS Symposium & Folman Lecture Carbon Nanostructures –

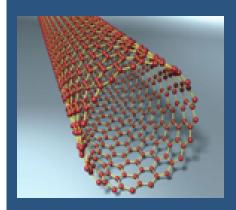
from fundamentals to applications

Thursday Jan. 13 2011, 8:45 - 17:30 Coler California Visitors Center, Technion, Haifa Speakers:

Ernesto Joselevich, Weizmann Institute
Yachin Cohen, Technion
Daniel Wagner, Weizmann Institute
Andrey Kaplan, University of Birmingham, UK
Rafi Kalish, Technion
Isaac Balberg, The Hebrew University of Jerusalem
Yeshayahu Lifshitz, Technion
Oded Hod, Tel Aviv University
Oren Regev, Ben Gurion University of the Negev
Daniel Nessim. Bar Ilan University

14:00-15:00 Folman Lecture: Prof. Reshef Tenne, Weizmann Institute 15:00-15:30 Get together

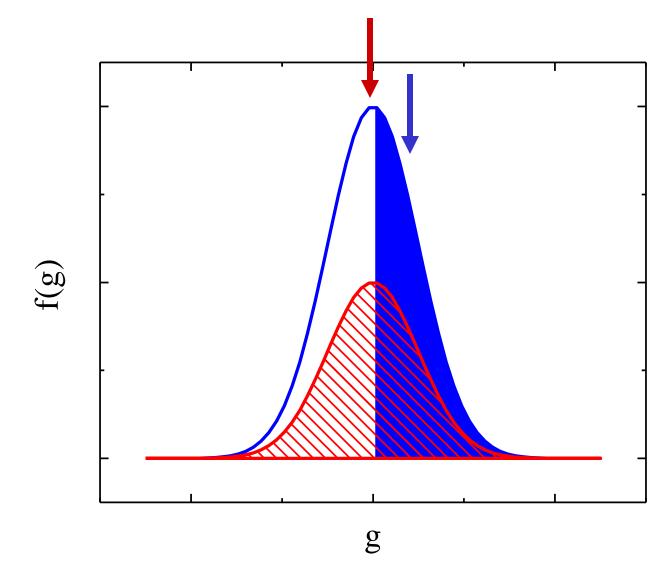
> Registration and Information: www.science.co.il/ivs/conferences/



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PROGRAM COMMITTEE
Eli Kolodney, Technion
Alon Hoffman, Technion

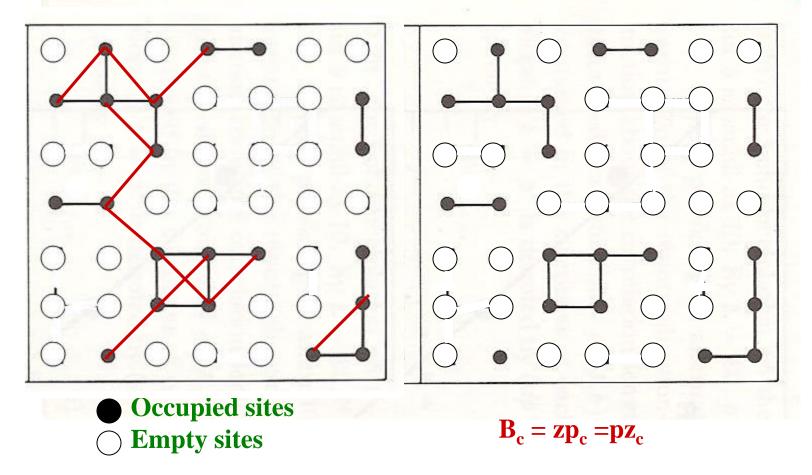
IVS - CONFERENCE SECRETARIAT

Galit Weizman: ivscon09@bs.technion.ac.il Phone: + 972- 54- 5580727



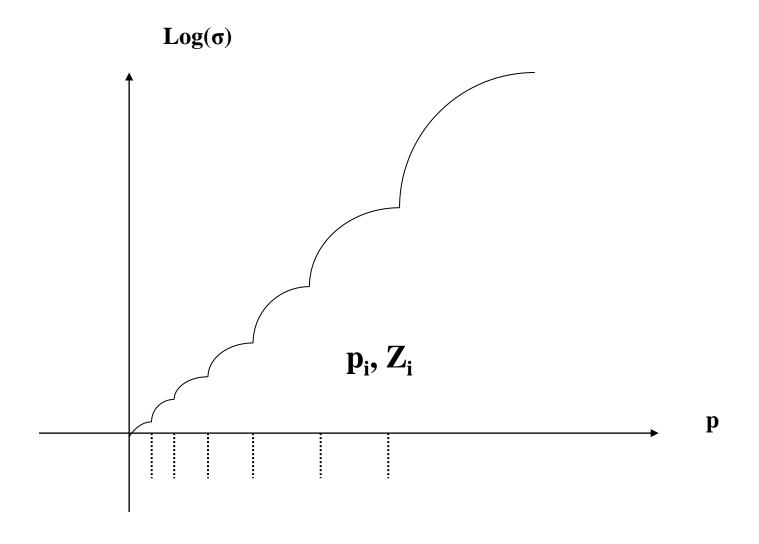
An illustration of the basic answer

Approach: Keeping p and going from \mathbb{Z}_1 to \mathbb{Z}_2 in the square lattice



If resistors $R_3 >> R_2 >> R_1$ are attached, the resultant resistance of the system will be dominated by R_2 , i.e., for a given p, an R_2 resistor will yield a threshold resistance of the system $(R_1 \rightarrow 0 \text{ and } R_3 \rightarrow \infty)$.

The staircase in a lattice

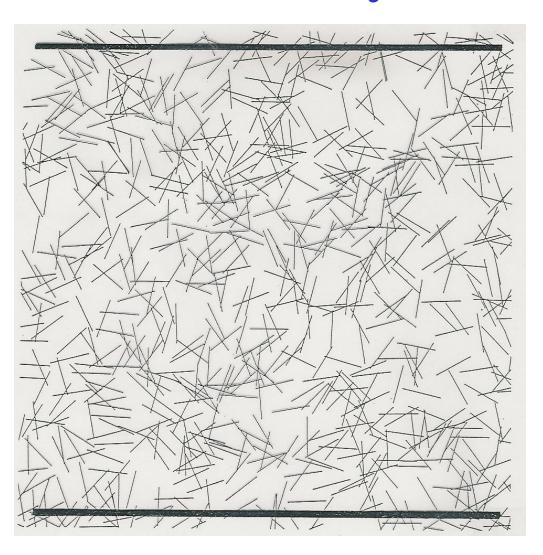


The change of the average local resistance upon threshold approach (the bypassing network)

- 1) Start from $p > p_c$
- 2) Consider the g's in descending order
- 3) The largest p_c of them yield percolation
- 4) The smallest g in this subset is g_c .
- 5) If there is a distribution, g_c decreases as $p \rightarrow p_c$.
- 6) At $p = p_c$ the resistor of smallest g must be included
- 7) If it is $g \to 0$ it may result that $\langle \mathbf{r} \rangle \to \infty$

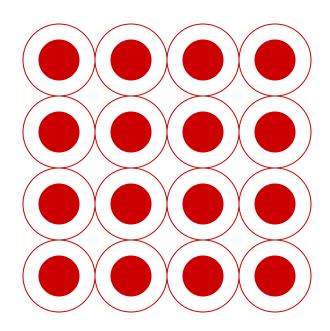
UPON $p \rightarrow p_c$ NOT ONLY THE NETWORK SHRINKS BUT THE AVERAGE RESISTANCE INCREASES AND MAY DIVERGE

A typical (pencil generated) continuum system

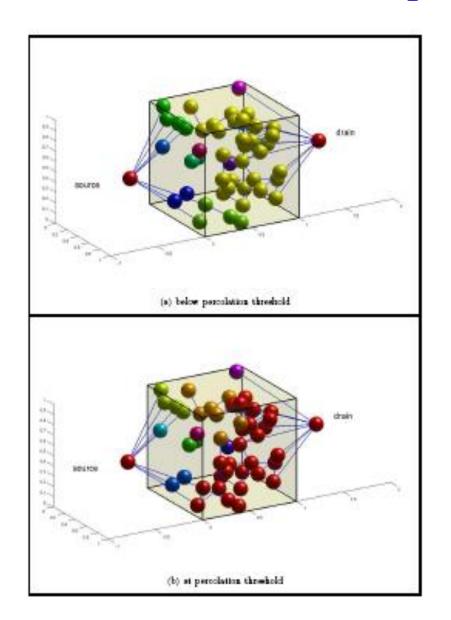


No p
no φ.
and N is not
informative

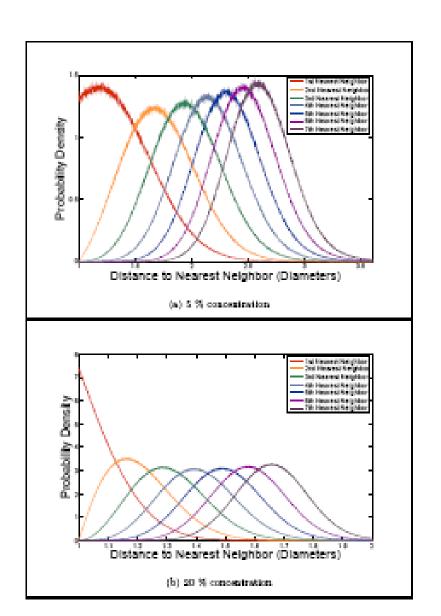
The lattice composite model



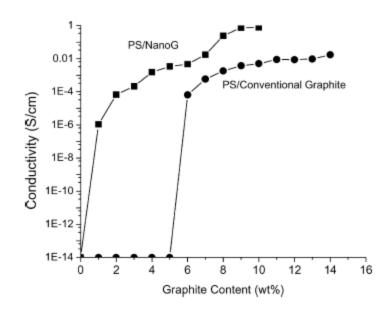
Statistics and conductance of a composite system



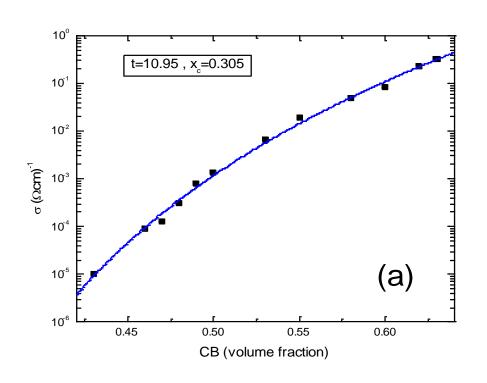
RDF of spherical particles

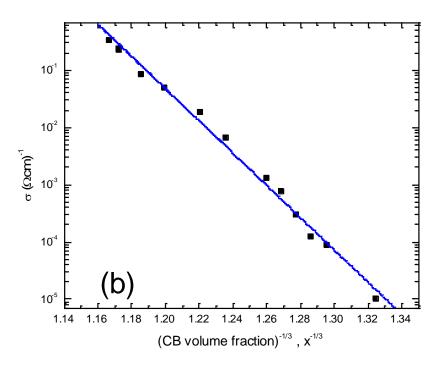


Staircase structure in nano Graphite composites

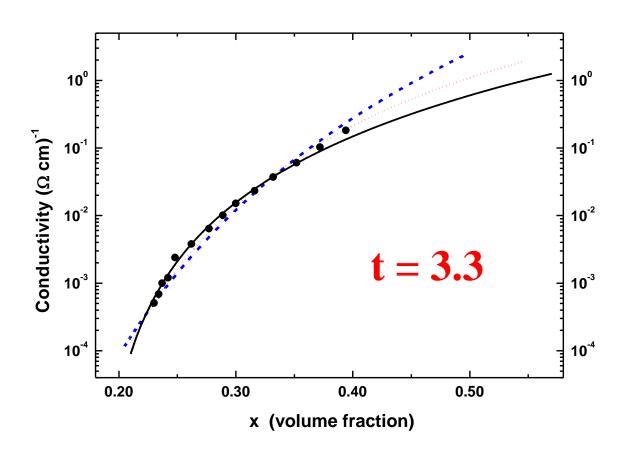


Non Universal and Hopping Interpretations





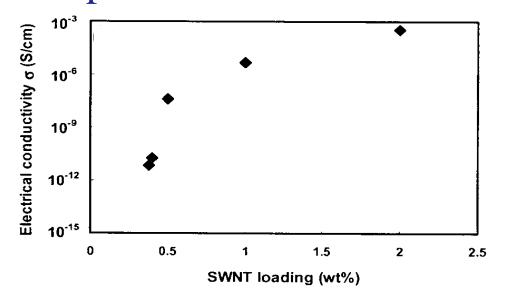
Ni-SiO₂



Two fundamental questions

1) What determines the percolation threshold?

2) What determines the shape of the $\sigma(x)$ dependence?



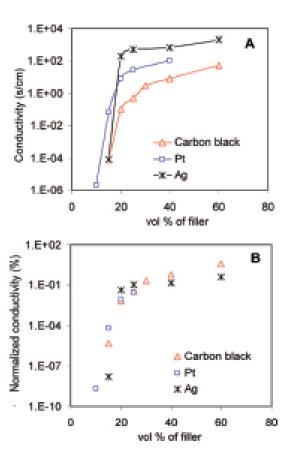
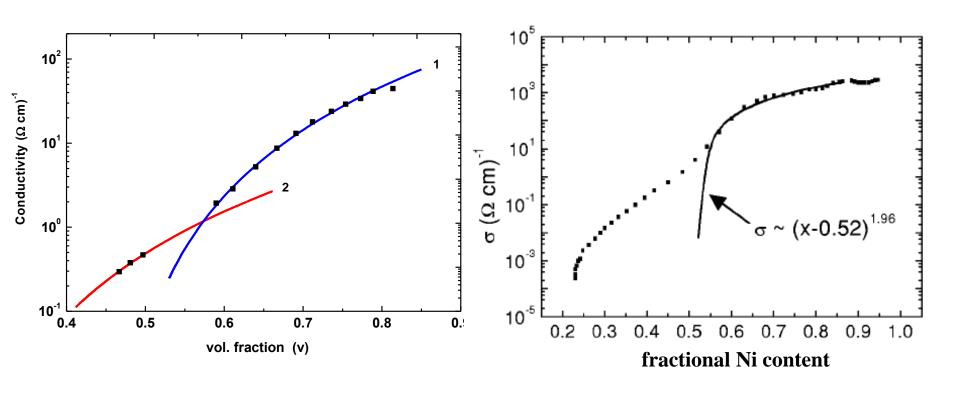


FIGURE 2. (A) Conductivity of polymer/filler composites as functions of volume fraction of fillers. (B) Composite conductivity normalized to that of the bulk fillers as functions of volume fraction of fillers.

Another a priori unexpected behaviors



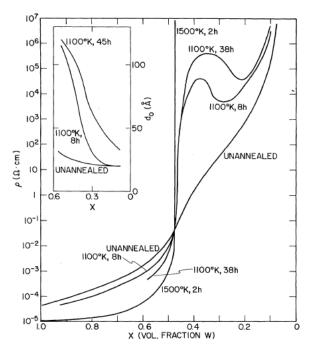


FIG. 2. Resistivity, ρ , of granular W-Al₂O₃ films as a function of volume fraction, x, of W. For the sake of clarity data points are left out and only smoothed curves are shown. The annealing time and temperature are indicated. The inset shows the average W grain size, determined by x-ray diffraction, as a function of x before and after annealing.

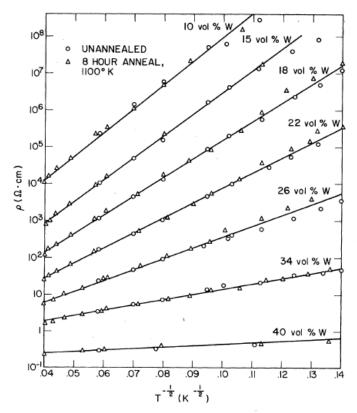


FIG. 4. $\ln \rho$ versus $1/\sqrt{T}$ for several compositions of W-Al₂O₃, before and after annealing for 8 h at 1100°K. The resistivities of the annealed samples are normalized at 300°K to the resistivity value determined on the same sample before annealing.

Percolation and tunneling -percolation

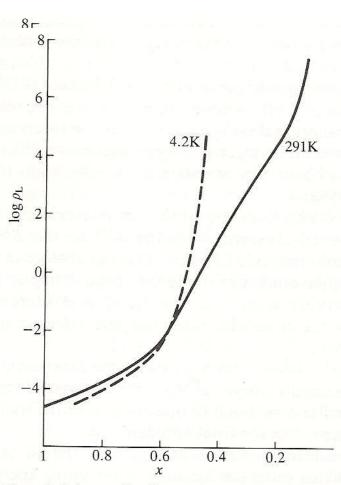
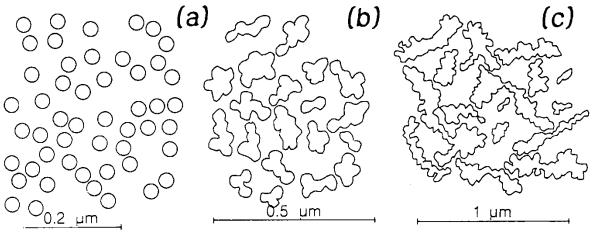


Fig. 3.7. Low-field resistivity ρ_L in Ω cm as a function of volume fraction x of Ni in Ni–SiO₂ sputtered films, at the temperatures shown (Abeles and Ping Shen 1974).

Various carbon blacks



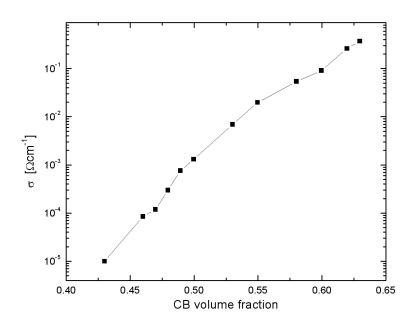


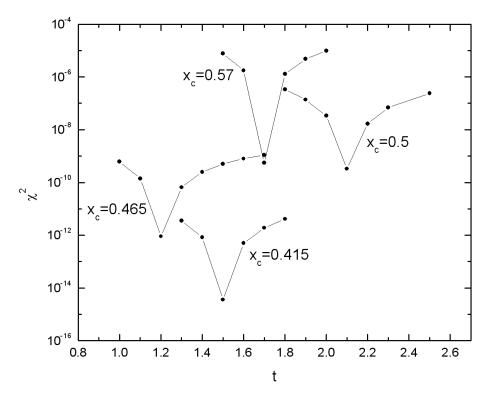
Two Conclusions

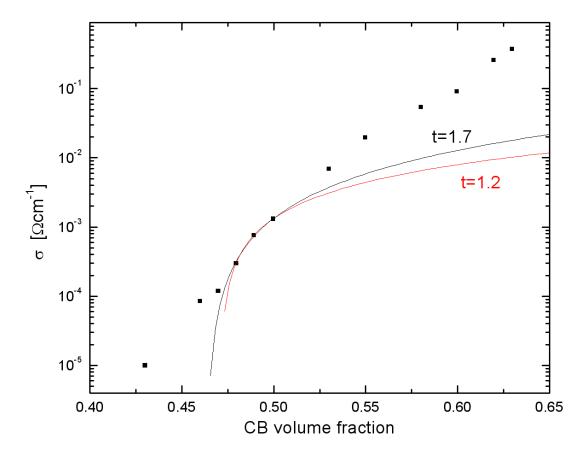
The understanding of the conductivity dependence on the content of the carbon filler in terms of percolation theory is based on:

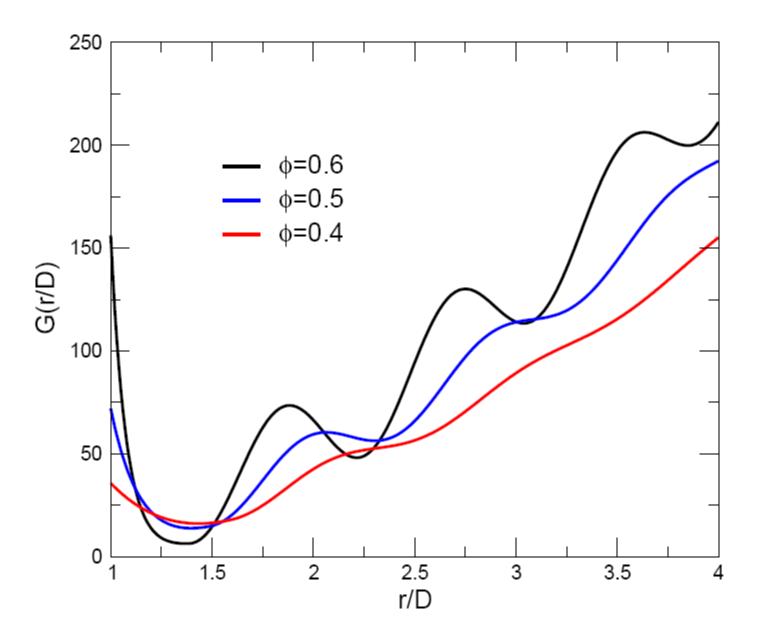
$$\sigma \propto (\Phi - \Phi_c)^t$$

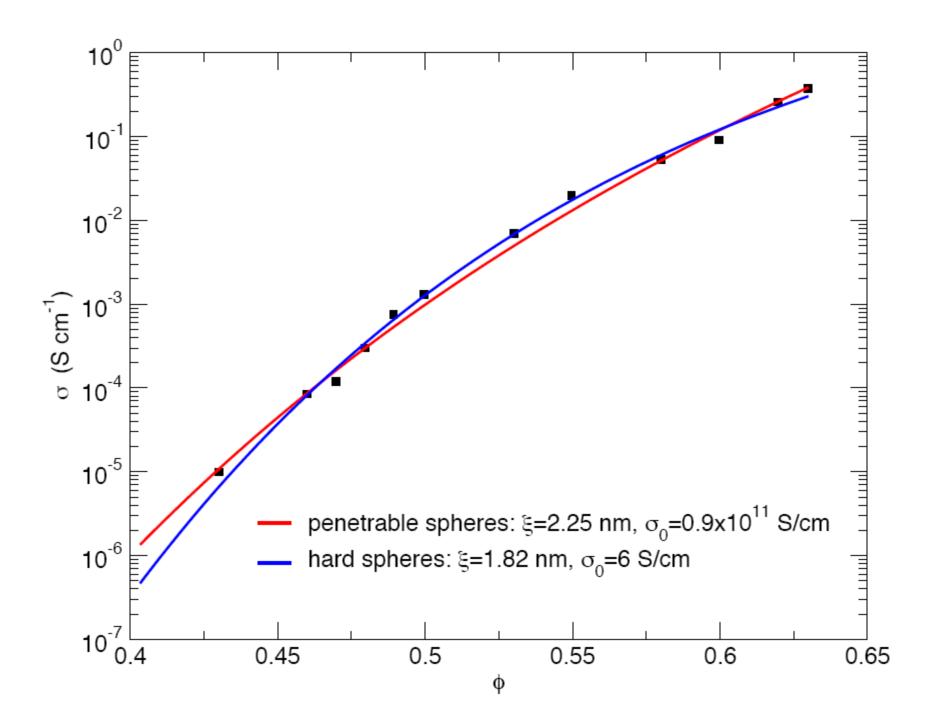
- 1) The larger the aspect ratio and the isotropy the smaller the percolation threshold (the smaller the content of carbon particles needed for the onset of large conductivity), the "excluded volume" argument.
- 2) The Behavior of the conductivity is determined by the distribution of the tunneling conductances (or interparticle distances) which is manifested by the deviation of the critical exponent t from its universal value.

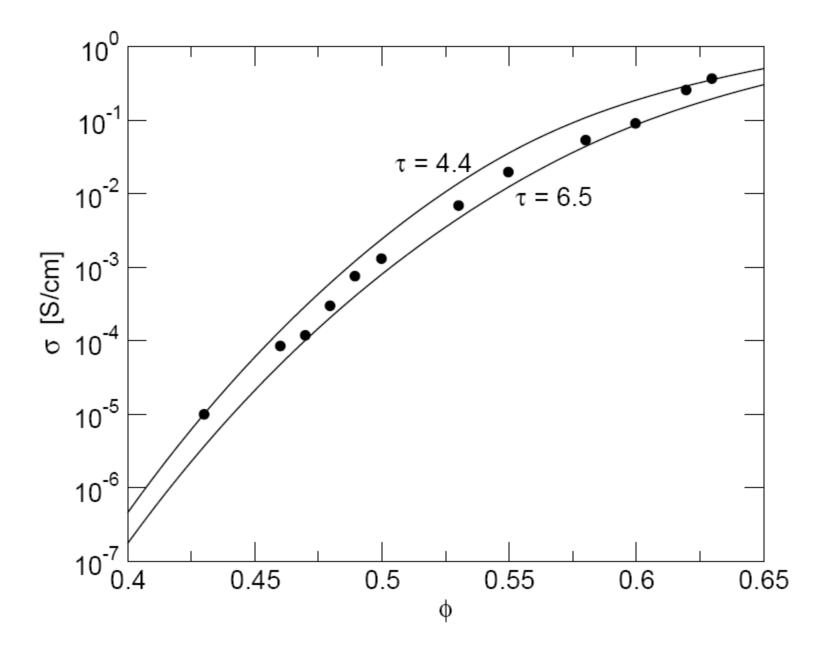


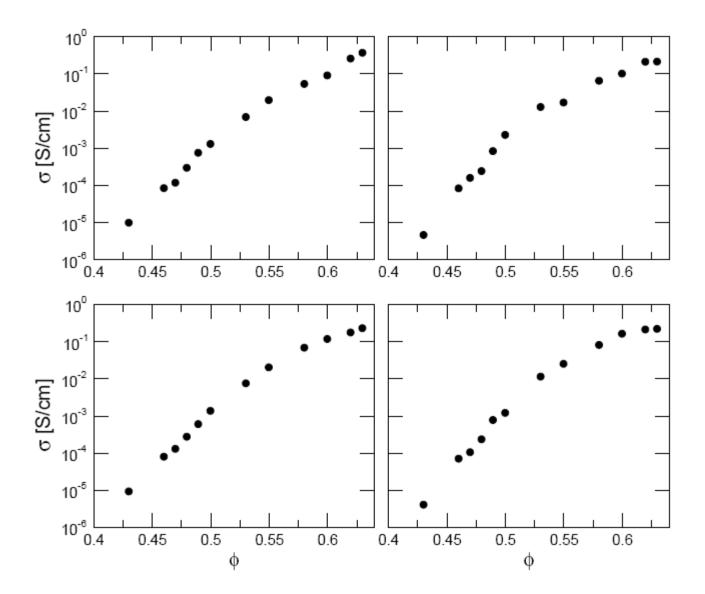












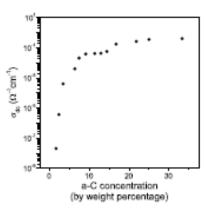


Fig. 8. The d.c. conductivity vs. concentration of a-C.

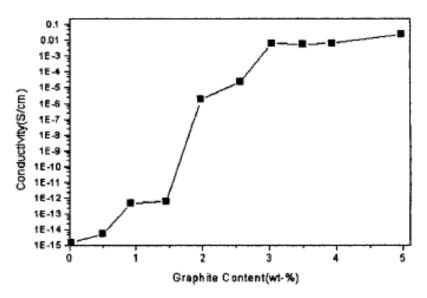


Figure 7. Electrical conductivity of PS-expanded graphite as a function of graphite content.

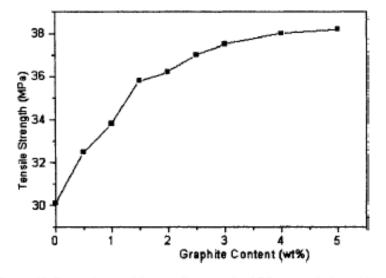


Figure 13. Dependence of the tensile strength of PS-expanded graphite nanocomposite on the graphite content.

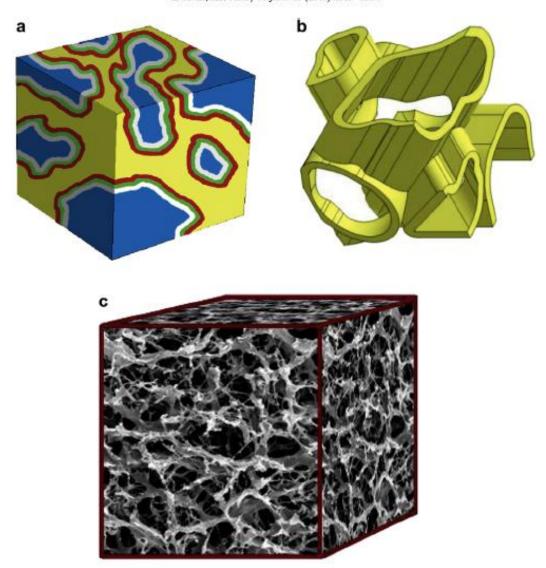


Fig. 12. a) Schematic representation of quinary multi-percolated morphology, the yellow phase is PANI, the blue phase is HDPE, and all other phases are located between them, b) schematic of a PANI network obtained after removal of all phases except PANI, and c) a 3D image constructed from 2D SEM images of the interconnected PANI network in the quinary 15/20/15/25/25 PS/PS-co-PMMA/PMMA/PVDF/PANI blend after extraction of all other phases.

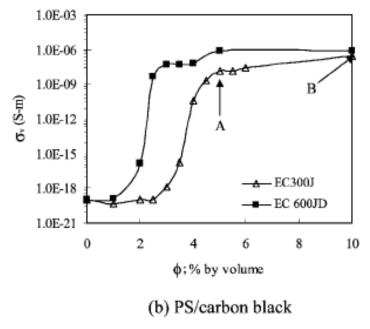


Fig. 5. Volume conductivity of (a) PP and (b) PS/carbon black conductive compounds. Sample specimens were prepared by compression molding.

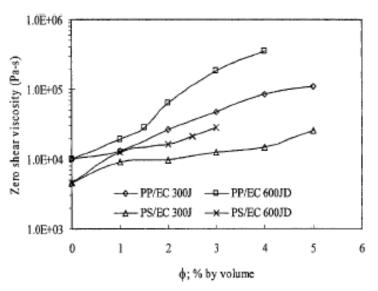
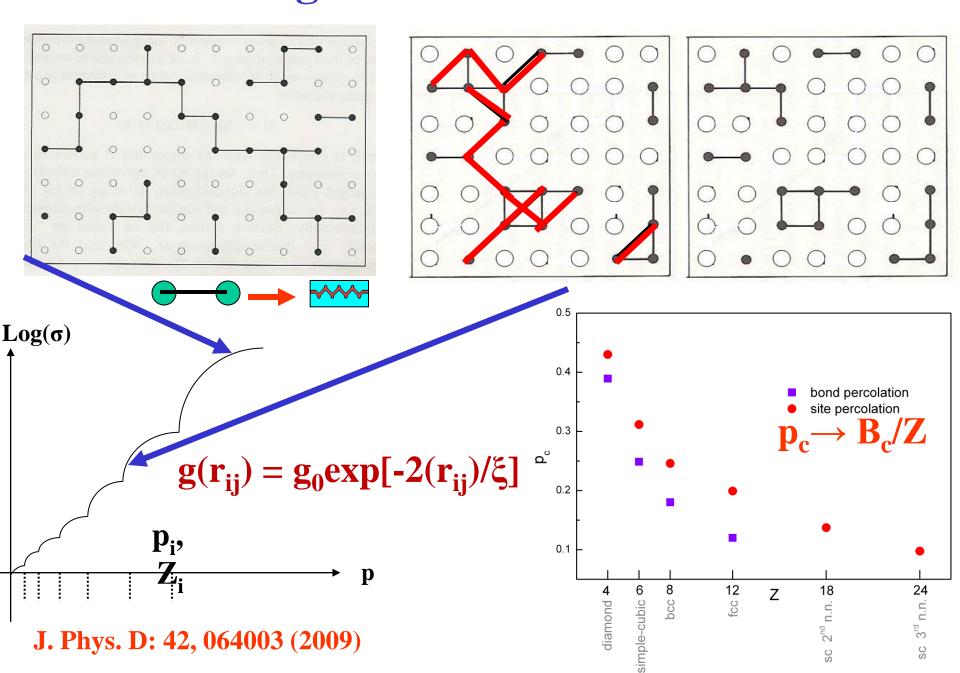
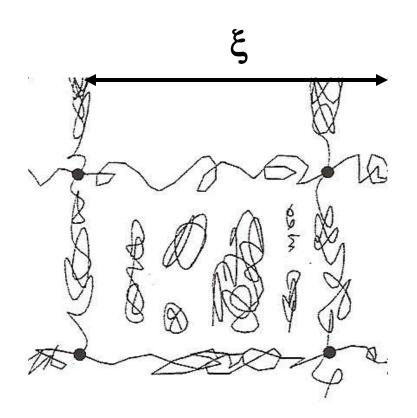


Fig. 6. Zero shear viscosity of PP and PS compounds with EC 300J and 600JD carbon black particles measured at 200°C using ARES Rheometrics cone and plate rheometer.

The origin of the staircase model



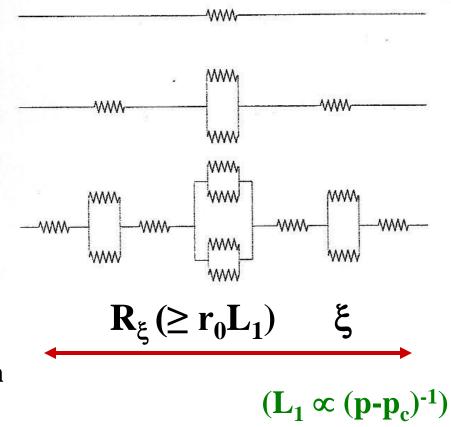
The NLB Model



$$R_{L} = R_{\xi}(L/\xi)/(L/\xi)^{D-1}$$

$$\propto (p-p_{c})^{-[\zeta + (D-2)\nu)]} \propto (p-p_{c})^{-tun}$$

A model for the links



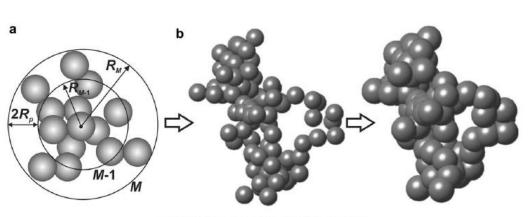


Fig. 1. Algorithm for simulation of aggregate arrangement.

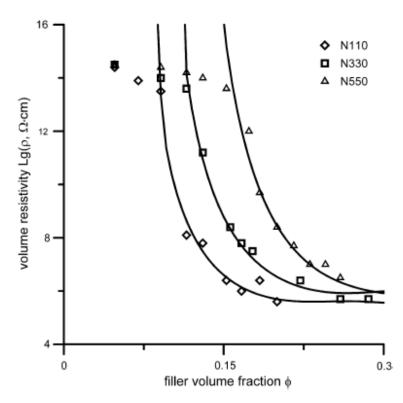


Fig. 8. Experimental relationships of Ref. [17] (single markers) and approximations (solid lines), Eq. (5) of volume resistivity versus filler volume fraction.

TABLE 2. Scaling parameters calculated for Cu-PMMA composites containing different particle size.

Composite	$f_{\mathbf{C}}$	t	R (correlation coefficient)
Cu-PMMA (78 nm)	13.95	2.0 ± 0.097	0.997
Cu-PMMA (0.2-0.3 µm)	11.00	2.0 ± 0.100	0.996
Cu-PMMA (3.25-4.75 µm)	9.28	2.0 ± 0.100	0.997

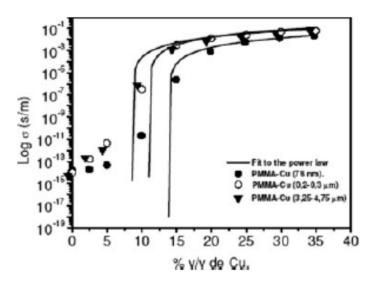


FIG. 7. Fit of electrical conductivity data to the power law. Cu-PMMA (78 nm), Cu-PMMA (0.2–0.3 μ m), Cu-PMMA (3.25–4.75 μ m).

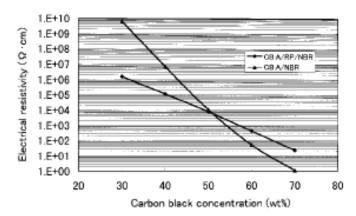


Fig. 2. Electrical resistivity of the thin NBR layers which contain carbon black A with and without polymer grafting as a function of carbon black concentration. CB, carbon black; RP, reactive polymer; NBR, acrylonitrile-butadiene rubber.

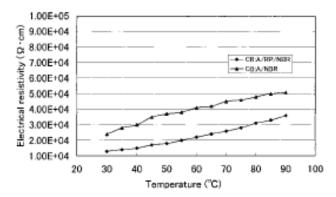


Fig. 5. Electrical resistivity of the thin NBR layers which contain carbon black A of 50 wt.% with and without polymer grafting as a function of temperature. CB, carbon black; RP, reactive polymer; NBR, acrylonitrile-butadiene rubber.

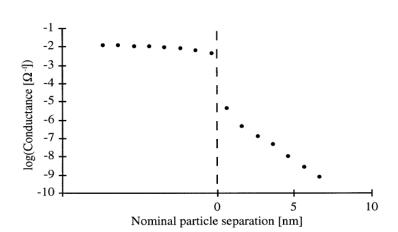


Figure 2. The conductance between two gold particles as a function of their nominal separation.

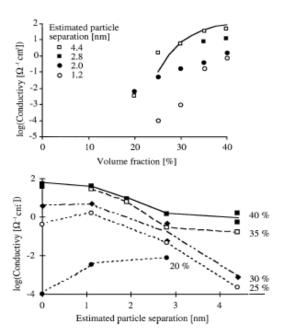
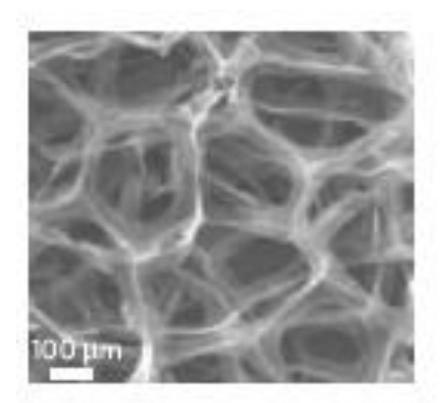
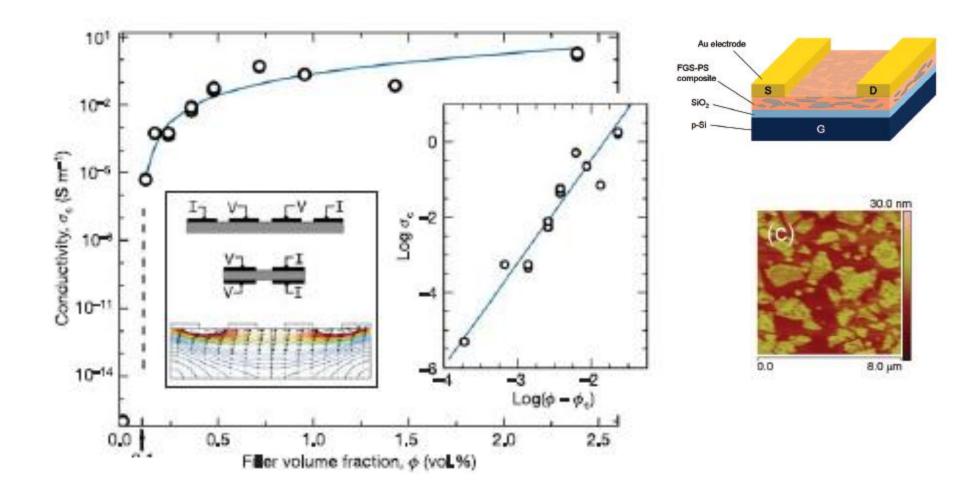


Figure 4. Effect of an alkanethiol monolayer coating the surface of particles on the mean conductivity of a polymer charged with the coated particles: (a) as a function of filler content for different layer estimated layer thicknesses, along with the model curve for uncoated particles; (b) as a function of layer thickness for the different filler volume fractions indicated.

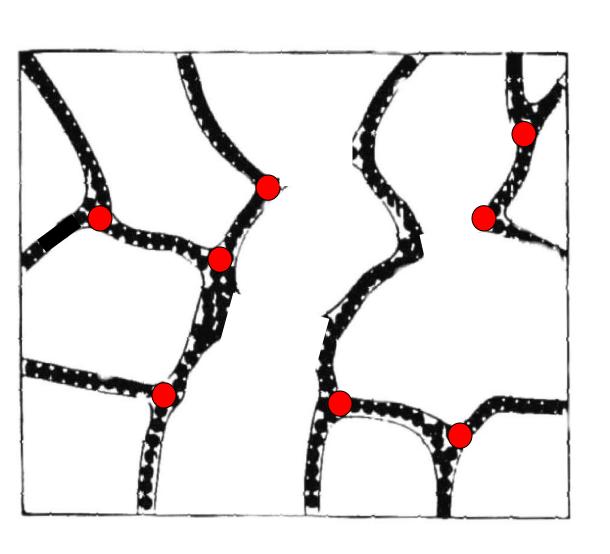


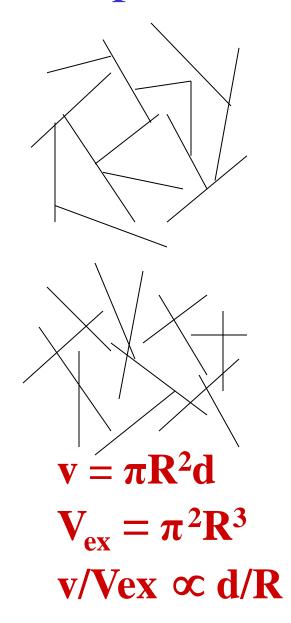
Graphene-based composite materials

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An illustration of a Graphene composite





The Graphene-composite problem

- For example, for high density spheres
- $\delta_c = B_c D/24$,
- for cylinders $\delta_c \approx B_c R[(R/L) < \sin \theta >] \Phi^{-1}$ and
- for discs Bc = $\pi^2(3b^2\delta+3b\delta^2+\delta^3)N$ so that
- $\delta/t \approx B_c/(3\pi\Phi)$, or $\approx \Phi \approx [t/5\delta)$], or $\delta \approx tB_c/(3\pi\Phi)$,