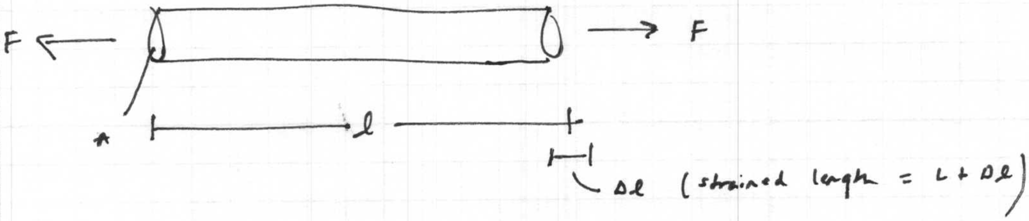
NM 05 – mechanical properties

in a macroscopic solid, we have simple linear – elastic behavior

e.g. a bar in uniaxial tension



young's modulus [N/m²]

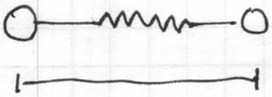
$$\sigma = \frac{F}{A} = E\varepsilon$$

$$\varepsilon = \frac{\Delta l}{l}$$

$$\frac{F}{A} = E\frac{\Delta l}{l} \Rightarrow \underline{\Delta l = \frac{FL}{AE}}$$ ~ we'll return here later.

at a far smaller scale, let's consider a material as a massive array of springs

→ each bond is like a spring



this is modeled by an interatomic potential,

e.g., the morse potential

$$U = D\left[\left(1 - e^{-\beta(r-r_0)}\right)^2 - 1\right]$$

well "depth"

β = well width.

$U(x)$ = energy [J]

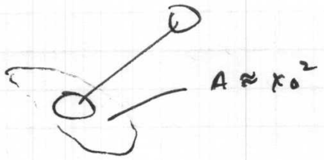
$\frac{dU}{dx}$ = force [N]

$\frac{d^2U}{dx^2}$ = stiffness [N/m]

thus, if our 'material' is a single bond spring

the restoring force $$F = \underset{\text{stiffness.}}{s}\,(x - \underset{\text{equilibrium length.}}{x_0})$$

define "area" = $\frac{1}{x_0^2}$



then stress = $$\frac{F}{A} = \frac{F}{x_0^2} = \frac{s(x - x_0)}{x_0^2} = \underbrace{\frac{s}{x_0}}_{\text{modulus } [N/m^2] = E}\overbrace{\left(\frac{x - x_0}{x_0}\right)}^{\text{strain} = \frac{\Delta l}{l} = \varepsilon}$$

let's approximate some real values.

based on interatomic potentials.

covalent bonds, $s = 20 - 200$ N/m

metal/ionic bonds, $s = 15 - 100$ N/m

polymers, $s = 0.5 - 1$ N/m } C-H bonds dominate springs in series

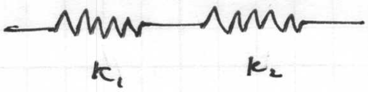
(C-H bonds are weak)

thus, if $E \approx \frac{s}{x_0}$

$x_0 = 0.2$ nm

$s \approx 200$ N/m.

$E \approx 1000$ GPa = graphite!



$$k_{eff} = \left(\frac{k_1 + k_2}{k_1 k_2}\right)^{-1}$$

if $k_1 \ll k_2 \Rightarrow k_{eff} = k_1$

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stiffness can typically be close to the theoretical limit

strength, no.. it is governed by defects, slip (e.g. grain boundaries) and can be as low as $10^{-4}E$; in nanoscopic materials, we can reach theoretical strength limits.

strength, lets say bonds break @ 10% elongation.

$$\sigma = \frac{S}{x_0}\underbrace{\left(\frac{x - x_0}{x_0}\right)}_{=0.1} \Rightarrow \sigma \approx 0.1\,E \rightarrow \text{see Ashby plot.}$$

in polymer fibers, chain alignment is very high ⇒ we approach theoretical stiffness, but are away from strength limit, which is probably governed by chain-chain gaps.

defects are stress concentrators.

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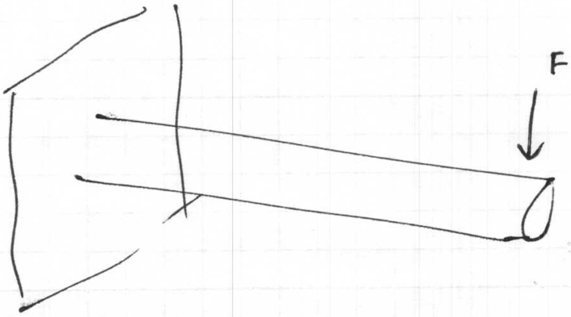
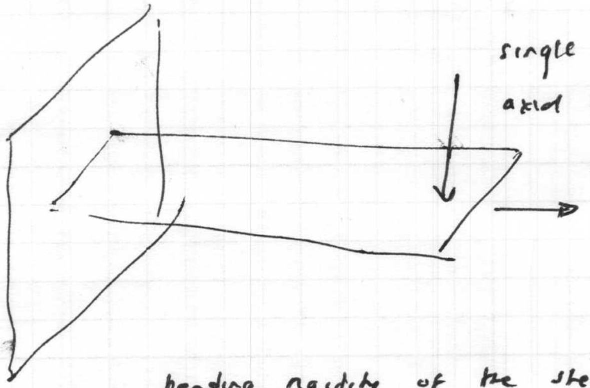
case study: consider CNTs as beams? w/ "continuum properties"?

assume yes - CNT is a continuous isotropic hollow cylinder.



$$\delta = FL^3/3EI$$

this is true if we choose E and t correctly



single graphene sheet ⇒ will have different axial (in-plane) and bending rigidities.

⇒ is this true for a SWNT too?

bending rigidity of the sheet = $D = \dfrac{Et^3}{12(1-\nu^2)}$ [N·m]

$\nu = 0.16 - 0.34$

in-plane rigidity $C = Et$

Both can be calculated based on bond rigidity (C–C hexagons) with no specification of t.

combining theory and experiment, for graphene we get

$E = 5$ TPa.

$t = 0.07$ nm

for a <u>single layer</u>

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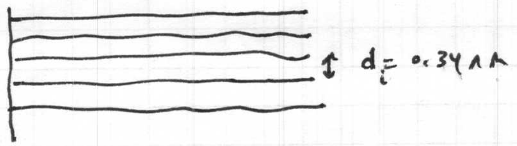
if we have multiple layers,



$\Longrightarrow E = 1$ TPa, $d = 0.34$ nm.

back to the CNT in bending,

the flexural rigidity $EI = \underbrace{E\pi \frac{D_o^4}{64}\left(1-\left(\frac{D_i}{D_o}\right)^4\right)}_{\text{from } E = \frac{\pi D_o^4}{64} - \frac{\pi D_i^4}{64}.} = E\pi \frac{D_o^4}{64}\left(1-\left(1-\left(\frac{2t}{D_o}\right)\right)^4\right)$

if $t \ll D_o$, $\left(1-\frac{2t}{D_o}\right)^4 \approx 1 - 4\left({}^{2t}/_{D_o}\right)$

$$\Longrightarrow EI = \frac{E\pi D_o^4}{64} \cdot {}^{8t}/_{D_o} = \frac{\pi}{8} D_o^3 \underbrace{Et}$$

Et = in-plane graphene stiffness × thickness.

so, we can use (1 TPa, 0.34 nm)

or (5 TPa, 0.07 nm)

$\Longrightarrow$ and for many-walled CNTs,

$$E_N = \frac{N}{N-1+\left({}^{t}/_{d_i}\right)} \cdot \frac{t}{d_i} E$$

$t = 0.07$ nm

5 TPa

d_i = interlayer spacing

as $N \rightarrow$ large,

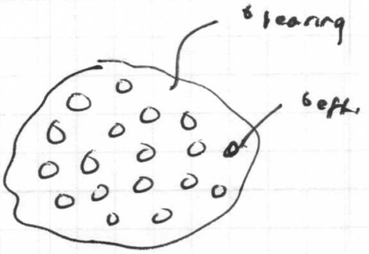
$$E_N \Longrightarrow \frac{t}{d_i} E \Longrightarrow E_N = 1 \text{ TPa}.$$

now, let's consider packing effects on effective stiffness and strength

For a SWNT, the true engineering area is d_o^2

so, $\sigma = F/A \leftarrow$ but this is the load-bearing area, $\pi(d_o^2 - d_i^2)$

so, $\sigma_{effective} = \sigma_{bearing}\left(\dfrac{\pi d_o^2}{\pi(d_o^2 - d_i^2)}\right)$



similarly, for $\Delta l = \dfrac{FL}{AE} \leftarrow E = E_{effective}$

e.g. for 1 nm dia SWNT, $E_{eff} = 0.5$ TPa

AND, we need to consider the <u>tightness of packing</u>

now, consider strength.

2 things : 1 - "top-down" grain size effects. ⇒ hall-petch.

2 - "bottom up" defect statistics in small volumes. ⇒ weibull.

1 - Hall-petch relation

strength of a bulk material increases as its grain size decreases . . . (to a point.)

"grain boundary strengthening"

- grain boundaries hinder dislocation motion
- different grains have different crystal orientations
- dislocations "pile up" at grain boundaries

Hall-petch relation

strengthening coefficient

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

grain size

material specific "starting stress"

heat treatment, quenching affect grain size

also can introduce particles or nucleants.

crystals have theoretically high strength, but defects weaken crystals ⇒ grain boundaries "stop" failure.

but as grain size decreases below 10 - 100 nm, Hall - Petch breaks down, ⇒ can have $k < 0$

- no consensus on mechanism
- grain boundary sliding
- diffusion (lots of surface atoms)

2 – statistics of failure

weibull statistics

probability of failure $F(\sigma_f) = 1 - \exp\left(-\left(\frac{\sigma_f}{\alpha}\right)^{\beta}\right)$ volume or surface flaws?

β = "shape" parameter (dimensionless)

α = scale parameter.

QFM model: $\sigma_f(n) = \sigma_c\left(1 + \rho/2a\right)^{1/2}(1+n)^{-1/2}$

ρ = "rupture radius"

a = lattice parameter

σ_c = perfect (defect-free) strength

n = # atoms

$\Longrightarrow$ see Asteri paper.

finally, how many defects are there.

activation energy $\Longrightarrow$ vacancy (just one type of defect – there are many)

c_v = equilibrium concentration = $\exp(-q/kT)$ vacancy formation energy

for a sphere, $N_{atoms} = n_v\left(\frac{4\pi}{3}\right)r^3$

if $c_v N_{atoms} < 1$, <u>no vacancies</u>

$$n_v \left(\frac{4}{3}\pi\right) r^3 \exp\left(-q/kT\right) < 1$$

$$r < \left\{\exp\left(q/kT\right)\left(\frac{3}{4\pi}\right)\right\}^{1/3}$$

$\Rightarrow$ for Al, $q = 0.66$ eV, 900 K $\Rightarrow$ $d = 6$ nm.

CNTs : 1 nm diameter, very long defect-free segment!

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