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nanomanufacturing – structures

① surface dominates at the nanoscale [Roduner]

e.g. a sphere, $\frac{SA}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} = \frac{6}{d}$

properties change/oscillate at/near a surface

these depend on the material, structure, strength of specific interactions (e.g. +/-)

⇒ e.g., melting point, electronic/optical properties

ballistic, s/c vs metal

plasmon resonances

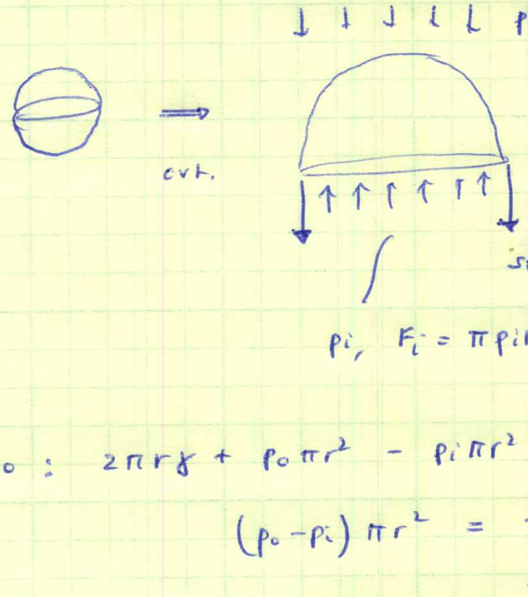
surface atoms are <u>less stable</u> than bulk atoms.

e.g., surface reconstruction of Si, Si is diamond cubic in bulk.

② surface gives a nanoparticle an internal pressure, like a droplet.

[Roduner]

p_o, $F_o = p_o \pi r^2$



surface tension γ [F/L], $F_\gamma = 2\pi\gamma r$

p_i, $F_i = \pi p_i r^2$

$$\Sigma F = 0 : \quad 2\pi r\gamma + p_o \pi r^2 - p_i \pi r^2 = 0$$

$$(p_o - p_i)\pi r^2 = -2\pi r\gamma$$

$$\therefore \quad p_o - p_i = \frac{-2\gamma}{r}$$

} — r ↓ ⇒ Δp ↑

smaller particles = higher internal pressure.

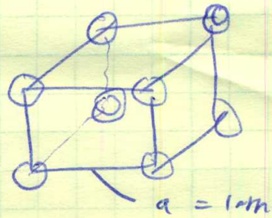
now lets see how this pressure really compresses a nanoparticle.

from solid Mechanics, bulk compressibility (κ)

(reciprocal of bulk modulus)

$$\kappa = \frac{\Delta V}{V\Delta p}$$

change in pressure



we can relate this to a change in lattice spacing, a

$$\underline{\underline{\frac{\Delta a}{a}}} = \frac{\Delta r}{r} = \frac{\Delta V}{3V} = \frac{\kappa\Delta p}{3} = \underline{\underline{\frac{-2\kappa\gamma}{3r}}}$$

$\gamma \approx g$

from $\frac{\Delta r}{r} = \frac{dV}{dr}\cdot\frac{dr}{3V} = \frac{\frac{4}{3}\cdot 3\pi r^2 dr}{3\cdot\frac{4}{3}\pi r^3} = \frac{dr}{r}$

chain rule.

More formally, $\gamma \cong g$ where noted above

g = surface stress $\approx \gamma + A\frac{d\gamma}{dA}$

$d\gamma/dA \approx 0$ because surface energy does not change with particle surface area.

the relationship $\frac{\Delta a}{a} = \frac{-2\kappa\gamma}{3r}$ is linear on a log scale

e.g. Roduner fig 2.8 for Au-NPs

typically in a NP, a decreases with particle size (radius), and also decreases with increasing ~~depth~~ distance from the particle ~~surface~~ center

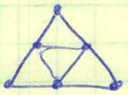
(hence pressure is ~~highest~~ lowest @ NP center)

③ "Magic" numbers [Teo and Sloane]

sizes of clusters are more frequently observed at discrete #'s of atoms which present geometrically closed shells.

this is simply atom counting; it has long been observed that some cluster sizes are preferential in abundance; these are more compact and symmetrical than other sizes.

let's start building triangles in 2D.



\# atoms = 1 3 6

n = 0 1 2 "frequency" n, (a ν_n triangle)

t_n = total # of atoms = $1 + 2 + 3 + \dots (n+1)$

$= \frac{1}{2}(n+1)(n+2)$ definition of series sum

t_n = "triangular numbers"

now generalize for 2D shapes. (polygons)

a polygon is a union of triangles

total atoms = $G_n = \frac{1}{2}Fn^2 + \frac{1}{2}pn + 1$

surface (edge) atoms = $s_n = pn$

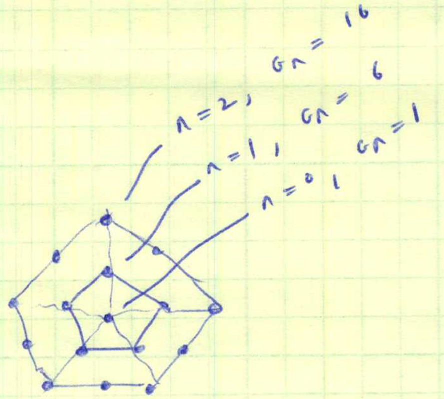
interior atoms, $G_n - s_n = I_n = \frac{1}{2}Fn^2 - \frac{1}{2}pn + 1$

where F = # of triangles

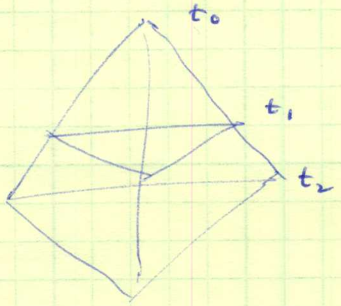
P = # of sides

n = frequency

e.g. a pentagon.



finally, in 3D we have expanding <u>tetrahedra</u> instead of triangles.



each tetrahedron is a series of triangles

$\underline{\underline{\sigma_n}}$ = total # of dots in the tetrahedron

$$= t_0 + t_1 + t_2 + t_3 + \ldots$$

$$= \underline{\underline{\frac{1}{6}(n+1)(n+2)(n+3)}}$$

$$\left(= \sum_{i=0}^{n} \frac{1}{2}(i+1)(i+2) \right)$$

it can be shown that for a general 3D shape made of tetrahedra

where c = # of tetrahedral cells

F_s = # of external triangular faces

V_i = # of interior vertices

$$G_n = \alpha n^3 + \frac{1}{2}\beta n + 1$$

$$\alpha = \frac{c}{6}$$

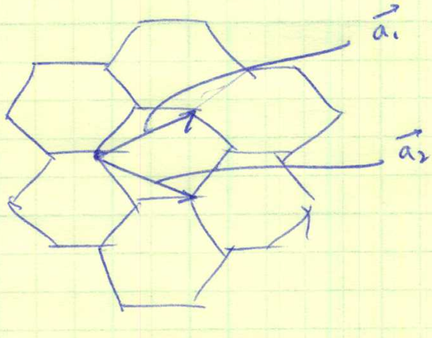
$$\beta = \frac{1}{2} F_s$$

example, cuboctahedron as FCC nanoparticle : observed in Au.

④ carbon nanotubes (CNTs) [Charlier, others]

chirality is denoted by the (n, m) indices ⇒ these completely define the structure

take a hexagonal lattice and place the unit vectors



$|\vec{a}_1| = \sqrt{3}\, a_{cc} = 2.46$ Å

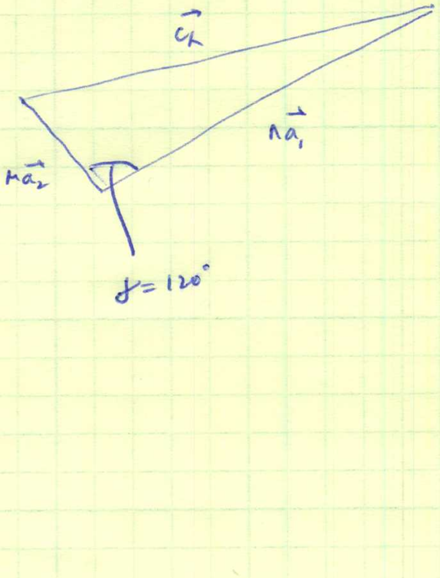
$a_{cc} = 1.44$ Å (1.42 Å in graphite)

define circumferential vector $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$

"wristband" for the CNT

diameter $d = \dfrac{|\vec{C}_h|}{\pi}$

now let's calculate d in terms of n, m



law of cosines

$$|\vec{C}_h|^2 = |n\vec{a}_1|^2 + |m\vec{a}_2|^2 - 2|n\vec{a}_1||m\vec{a}_2|\cos\gamma$$

$$\cos\gamma = -1/2$$

$$|\vec{a}_1| = |\vec{a}_2| = a = 2.46 \text{ Å}$$

$$|C_h|^2 = n^2a^2 + m^2a^2 + 2nma^2(1/2)$$

$\Longrightarrow$

$$|c_h| = a\sqrt{n^2+m^2+nm}$$

$$\Rightarrow \quad d = \frac{|c_h|}{\pi} = \frac{a}{\pi}\sqrt{n^2+m^2+nm}$$

define chiral angle, $\theta = [0,30]$ as θ between $\vec{c_h}$ and a_1

where $$\cos\theta = \frac{\vec{c_h}\cdot\vec{a_1}}{|\vec{c_h}||\vec{a_1}|} = \frac{\sqrt{3}\,m}{2\sqrt{n^2+m^2+nm}}$$

also define translation vector $\vec{T}$, $\vec{T}$ is ⊥ to c_h and ends at the next lattice point.

$\vec{c_h}$ and $\vec{T}$ bound the CNT unit cell ~ minimum axial repeating unit

therefore $\vec{c_h}\cdot\vec{T} = 0$, $\vec{a_1}\cdot\vec{a_1} = a^2$, $\vec{a_1}\cdot\vec{a_2} = a^2/2$

recall $\vec{c_h} = m\vec{a_1} + n\vec{a_2}$

define $\vec{T} = c\vec{a_1} + d\vec{a_2}$

then $$\vec{c_h}\cdot\vec{T} = mc\cancel{a^2} + md\frac{\cancel{a^2}}{2} + nc\frac{\cancel{a^2}}{2} + nd\cancel{a^2}$$

$$\therefore \quad mc + \frac{md}{2} + \frac{nc}{2} + nd = 0$$

$$c\left(m + \frac{n}{2}\right) + d\left(n + \frac{m}{2}\right) = 0$$

general relationship between c, d, m, and n

Therefore $$\vec{T} = \left(\frac{2m+n}{N_R}\right)\vec{a}_1 + \left(-\frac{2n+m}{N_R}\right)\vec{a}_2$$

$$N_R = \text{greatest common divisor of } \left\{(2m+n),\ (2n+m)\right\}$$

We can calculate the area of the unit cell and the # of atoms per unit cell based on definitions of $\vec{C}_h$ and $\vec{T}$

These are left as exercises for you.