$(C_{60})_N$@SWCNT

«peapods»

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Carbon: diamond, graphite, …

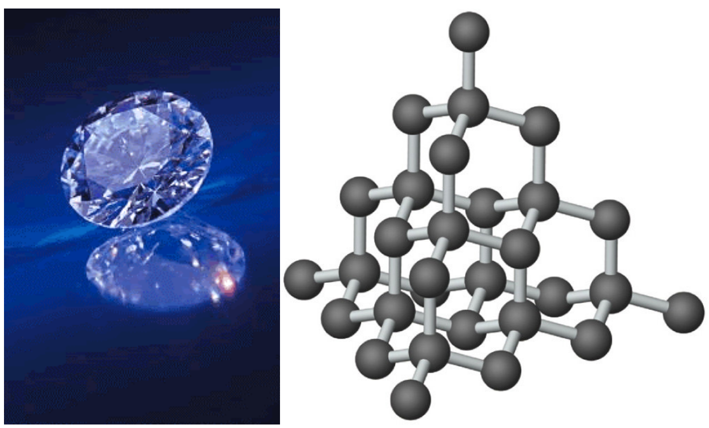
5	6	7
B	C	N
boron	carbon	nitrogen
10.811(7)	12.0107(8)	14.0067(2)
13	14	15

element nr. 6
<u>4 valence electrons</u>

1) organic compounds

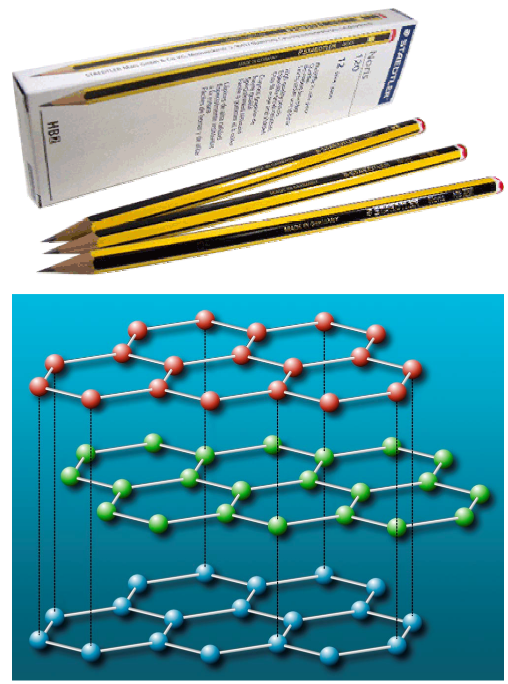
DNA, fuel, plastics, etc.

2) carbon-only compounds



diamond

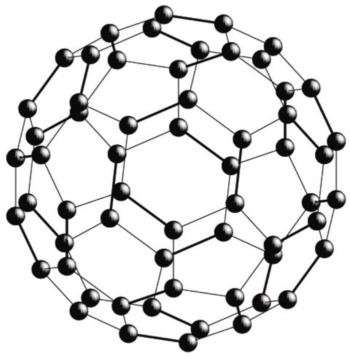
graphite



C_{60}

*H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, Nature **318**, 162 (1985)*

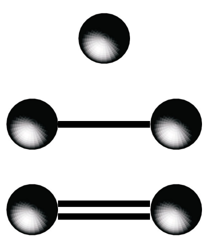
cage-like carbon clusters: **fullerenes**

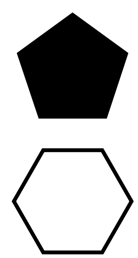


C_{60}:
buckminsterfullerene
a.k.a.
"buckyball"

truncated
icosahedron
a.k.a.
football

Richard
"Bucky"
Buckminster Fuller
(1895-1983)





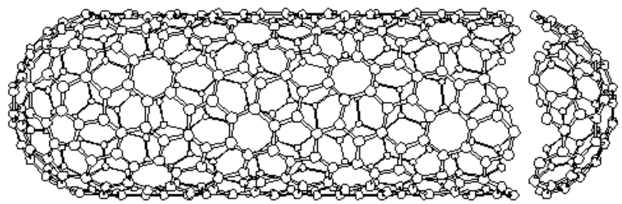
Solid C_{60}: Krätschmer, Huffman ... (1990)

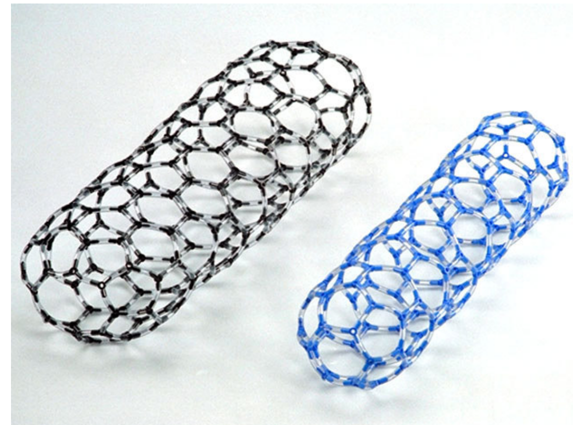
Carbon nanotubes

*S. Iijima, Nature **354**, 56 (1991)*

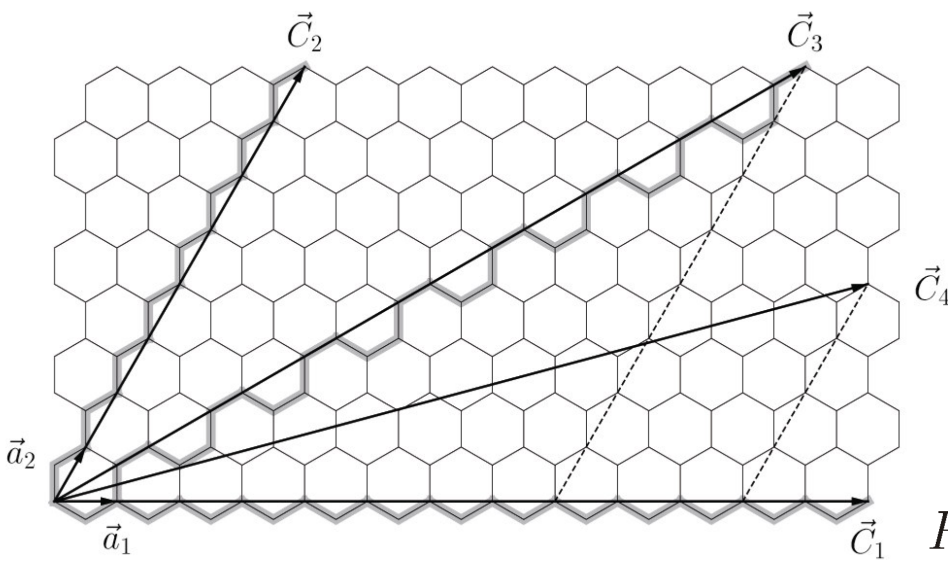
tube-like carbon clusters: **carbon nanotubes**

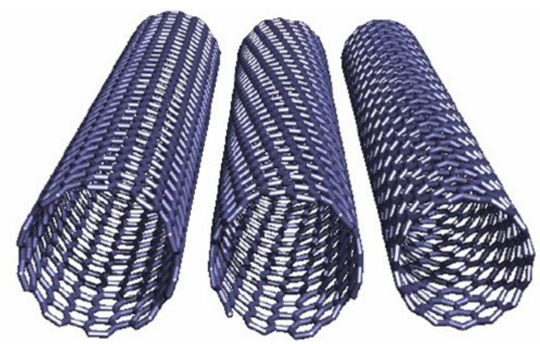
nanotube = long fullerene





nanotube = rolled-up graphene sheet





$$\vec{C}(n,m) = n\vec{a}_1 + m\vec{a}_2$$

$$R_T(n,m) \propto \sqrt{n^2 + nm + m^2}$$

$(C_{60})_n$@SWCNT = **peapod**

B.W. Smith, M. Monthioux, and D.E. Luzzi, Nature ***396****, 323 (1998)*

C_{60}@SWCNT: “crystal field”

potential energy of a C_{60} molecule inside a SWCNT:
“crystal field”

$$V_{\mathsf{CF}}(\alpha, \beta, \gamma; n, m)$$

molecular orientation: **Euler angles** (α, β, γ)

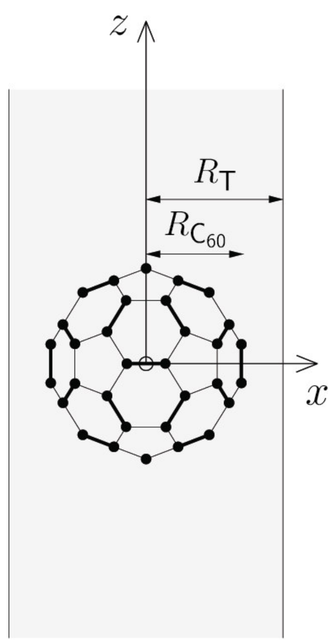
SWCNT structure: **indices** (n, m)

SWCNT:
uniform “carbonic” cylinder

$$V_{\mathsf{CF}}(\alpha, \beta, \gamma; R_{\mathsf{T}})$$

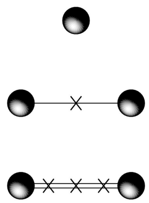
theoretical reason: **cylindrical symmetry** $(D_{\infty h})$

experimental justification: **SWCNT mixture** $(\{(n, m)\})$



C_{60} molecule:
icosahedral cluster of
atoms, double bonds and single bonds

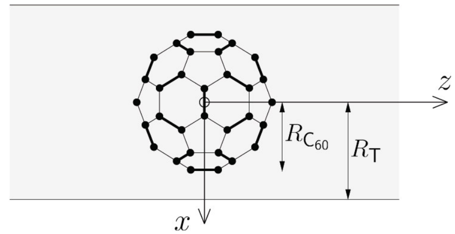
C_{60}@SWCNT: standard orientation



t = ‘a’

t = ‘sb’

t = ‘db’



$$\vec{\rho} = (\rho, \Phi, Z)$$
$$\vec{r}_{\Lambda_t} = (r_{\Lambda_t}, \theta_{\Lambda_t}, \phi_{\Lambda_t})$$

We consider **atom – wall** interactions ... v.d. Waals

$$V_{\mathsf{CF}}^{\mathsf{a}}(R_{\mathsf{T}}) = \sum_{\Lambda_a=1}^{60} \int_0^{\infty} \rho d\rho \int_0^{2\pi} d\Phi \int_{-\infty}^{+\infty} dZ u^{\mathsf{a}}\left(|\vec{\rho} - \vec{r}_{\Lambda_a}|\right) \sigma \delta(\rho - R_T)$$

$$u^{\mathsf{a}}(r) = C_1^{\mathsf{a}} e^{-C_2^{\mathsf{a}} r} - \frac{B^{\mathsf{a}}}{r^6}$$

$\sigma = 0.38$ Å^{-2} (graphite)

... as well as **double - and single bond – wall interactions**.

$$V_{\mathsf{CF}}(R_{\mathsf{T}}) = \sum_{\mathsf{t=a,db,sb}} \sum_{\Lambda_t=1}^{N_t} \boxed{\sigma R_{\mathsf{T}} \int_0^{2\pi} d\Phi \int_{-\infty}^{+\infty} dZ \, u^{\mathsf{t}}\left(|\vec{\rho} - \vec{r}_{\Lambda_t}|\right)\Big|_{\rho=R_{\mathsf{T}}}}$$

$$\equiv U^{\mathsf{t}}(\theta_{\Lambda_t}) = \sum_{\substack{l=0 \\ l \text{ even}}}^{\infty} v_l^{\mathsf{t}}(R_{\mathsf{T}}) Y_l^{m=0}(\theta_{\Lambda_t})$$

spherical harmonics $Y_l^m(\theta, \phi)$

C_{60}@SWCNT: arbitrary orientation

$$V_{\mathsf{CF}}(\alpha,\beta,\gamma;R_{\mathsf{T}}) = \mathcal{R}(\alpha,\beta,\gamma)V_{\mathsf{CF}}(R_{\mathsf{T}})$$

$$= \sum_{\mathsf{t=a,db,sb}} \sum_{\Lambda_{\mathsf{t}}=1}^{N_{\mathsf{t}}} \sum_{\substack{l=0 \\ l\ \mathsf{even}}}^{\infty} v_l^{\mathsf{t}}(R_{\mathsf{T}}) \boxed{\mathcal{R}(\alpha,\beta,\gamma)Y_l^{m=0}(\theta_{\Lambda_{\mathsf{t}}})}$$

$$\|$$

$$\sum_{n=-l}^{l} \boxed{\mathcal{D}_{n,m=0}^{l}(\alpha,\beta,\gamma)} Y_l^n(\theta_{\Lambda_{\mathsf{t}}},\phi_{\Lambda_{\mathsf{t}}})$$

$$\|$$

$$\sqrt{\frac{4\pi}{2l+1}}\left[Y_l^n(\beta,\gamma)\right]^*$$

Wigner D-functions $\mathcal{D}_{n,m}^{l}(\alpha,\beta,\gamma)$

α, β, γ: Euler angles

$$V_{\mathsf{CF}}(\beta,\gamma;R_{\mathsf{T}}) = \sum_{l=0,6,10,\ldots} w_l(R_{\mathsf{T}})\mathcal{U}_l(\beta,\gamma)$$

$$\approx w_0(R_{\mathsf{T}})\mathcal{U}_0(\beta,\gamma) + w_6(R_{\mathsf{T}})\mathcal{U}_6(\beta,\gamma) + w_{10}(R_{\mathsf{T}})\mathcal{U}_{10}(\beta,\gamma) + w_{12}(R_{\mathsf{T}})\mathcal{U}_{12}(\beta,\gamma)$$

symmetry-adapted rotator functions (SARFs) $\mathcal{U}_l(\beta,\gamma)$

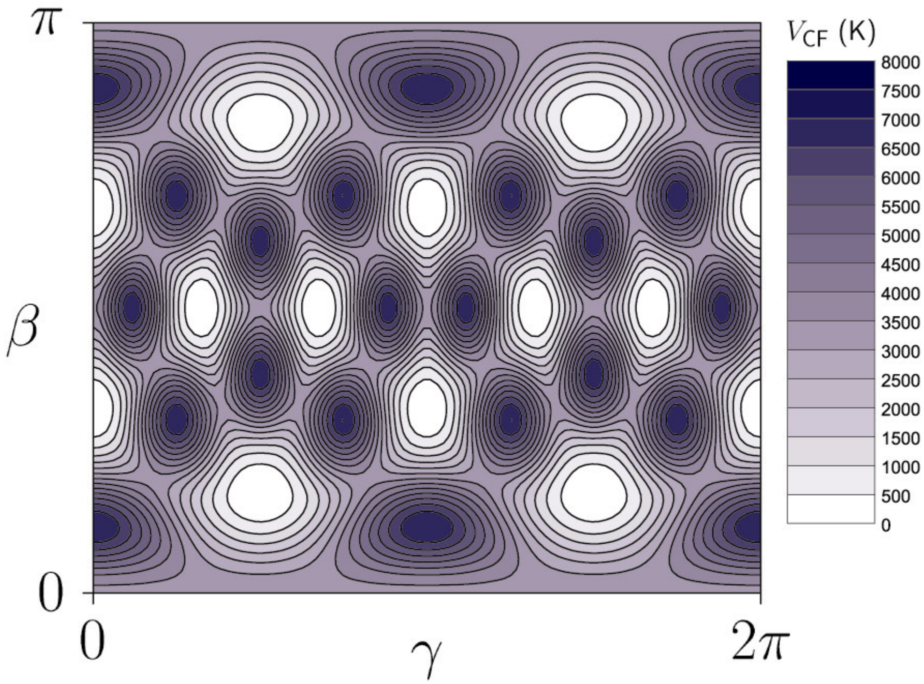
icosahedral C_{60} symmetry: $l = 0, 6, 10, \ldots$

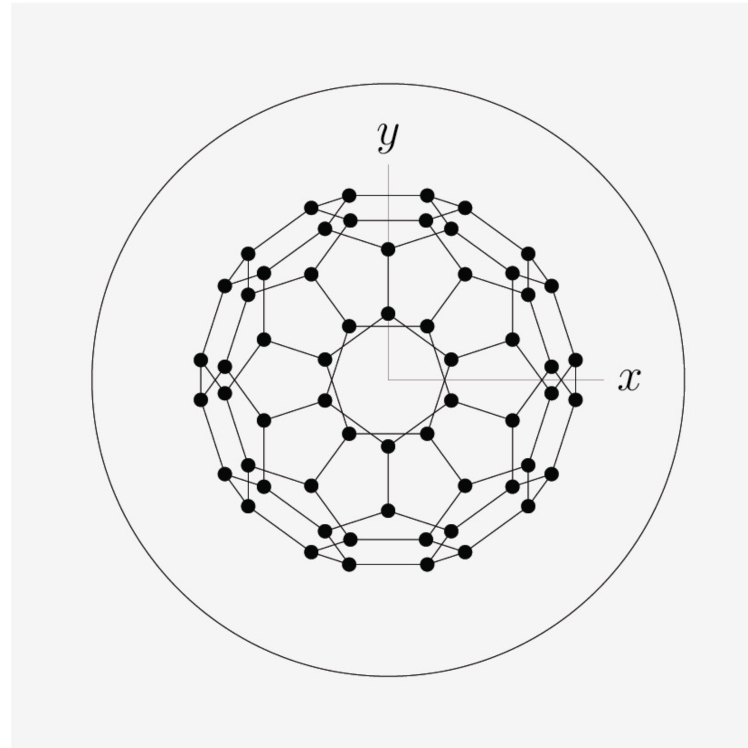
cylindrical tube symmetry: no α dependence

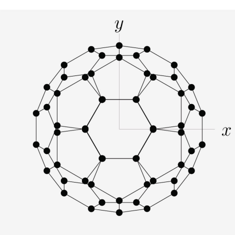
C_{60}@SWCNT: Mercator* map #1

$$V_{\mathrm{CF}}(\beta, \gamma; R_{\mathrm{T}})$$

$R_{\mathrm{T}} = 6.0$ Å







20 energy maxima

hexagons ⊥ tube axis

12 energy minima

pentagons ⊥ tube axis

C_5 // tube axis

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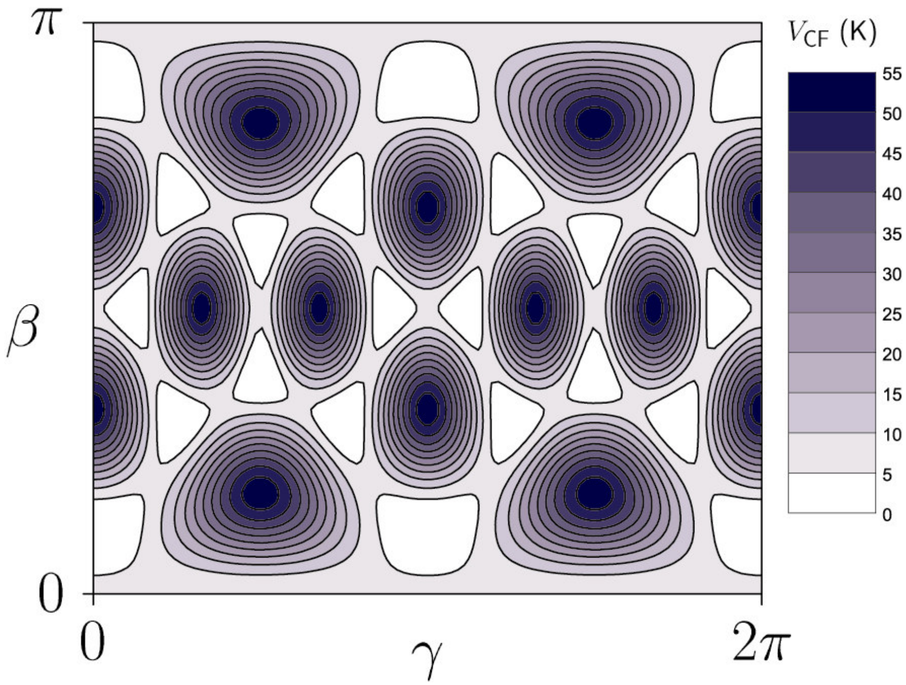
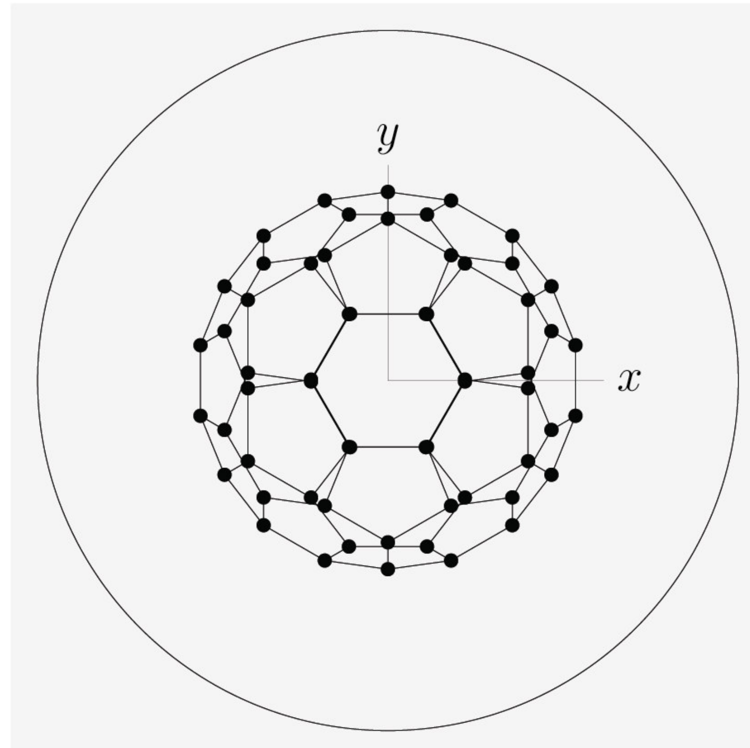
* Gerardus Mercator (1512-1594): Flemish cartographer, inventor of the cylindrical projection.

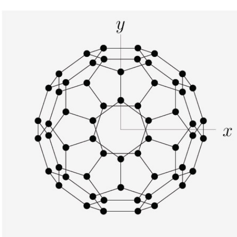
C_{60}@SWCNT: Mercator map #2

$$V_{\mathrm{CF}}(\beta, \gamma; R_{\mathrm{T}})$$

$R_{\mathrm{T}} = 8.0$ Å







12 energy maxima

pentagons ⊥ tube axis

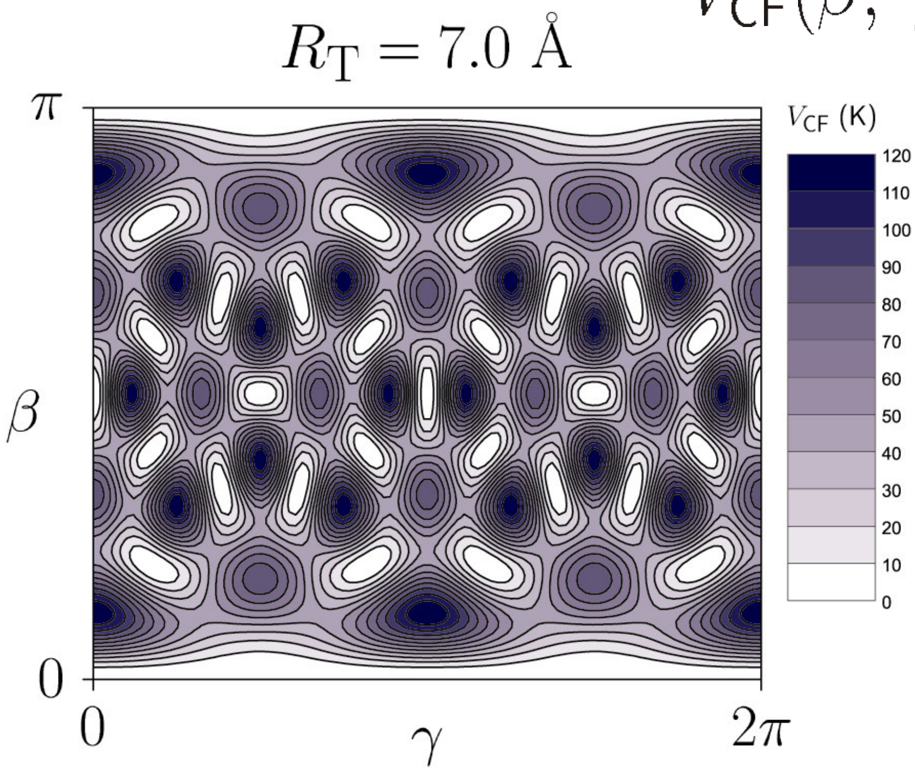
20 energy minima

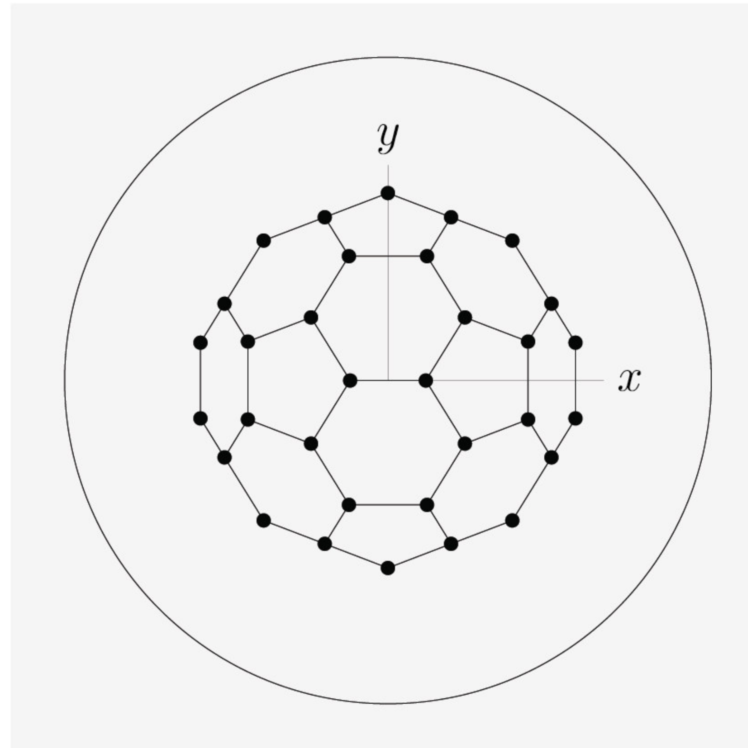
hexagons ⊥ tube axis

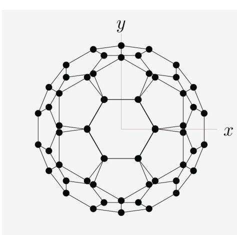
C_3 // tube axis

C_{60}@SWCNT: Mercator map #3

$$V_{\mathrm{CF}}(\beta, \gamma; R_{\mathrm{T}})$$







20 energy maxima

hexagons ⊥ tube axis

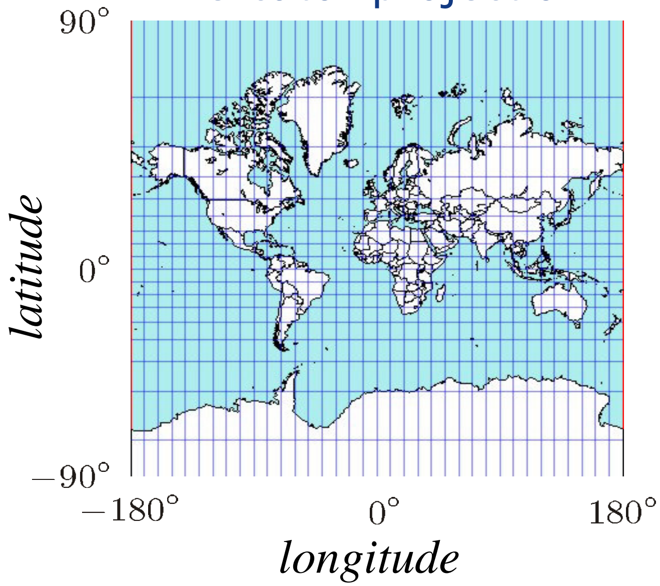
30 energy minima

double bonds ⊥ tube axis

C_2 // tube axis

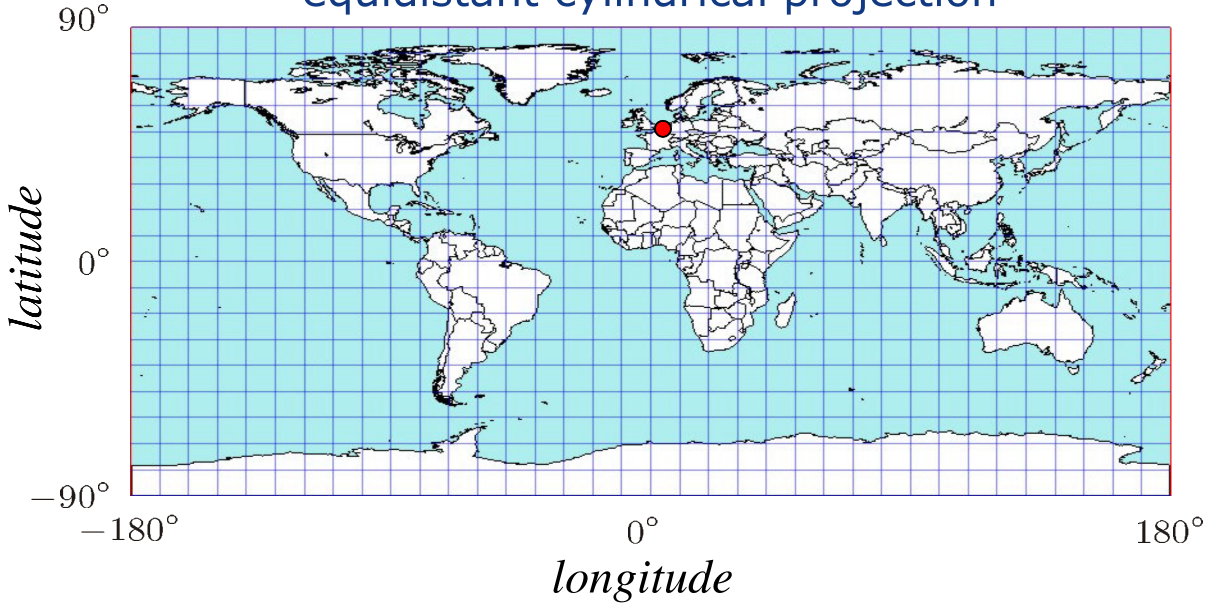
Mercator maps

Mercator projection



Gerardus Mercator
(1512-1594)

equidistant cylindrical projection



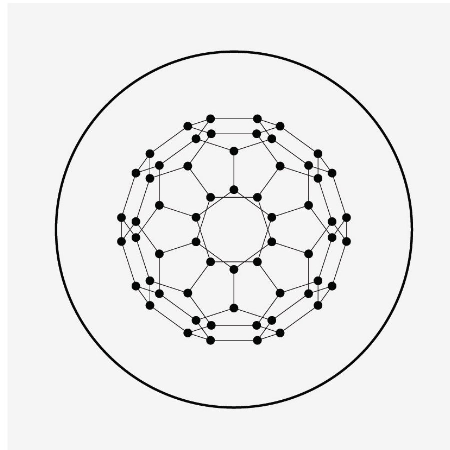
Antwerp

$\text{latitude} = 51.20^\circ$

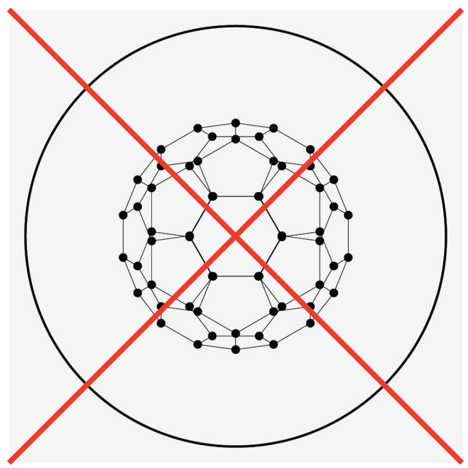
$\text{longitude} = 4.47^\circ$

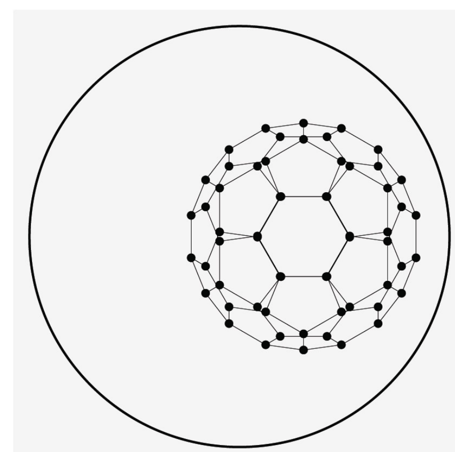
C_{60}@SWCNT: sticking

small tube radius

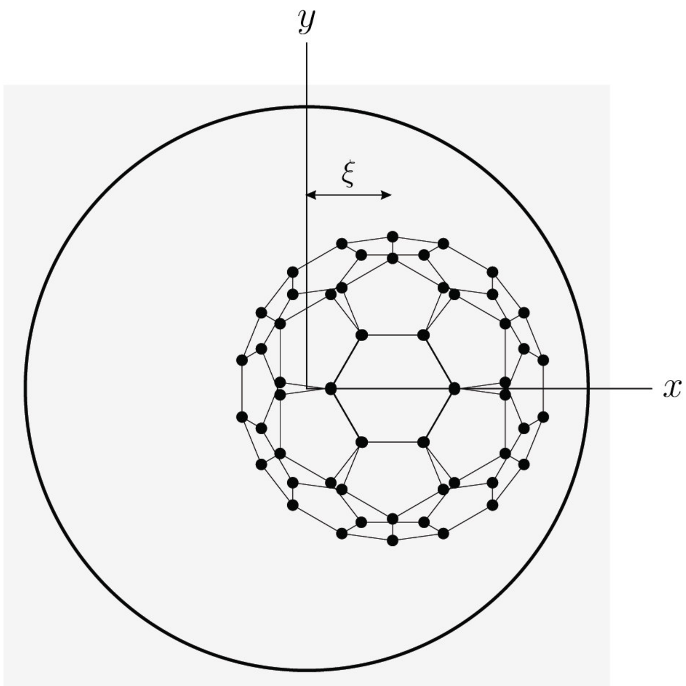


large tube radius





C_{60}@SWCNT: sticking



crystal field:

$$V_{\mathsf{CF}}(\alpha, \beta, \gamma; \xi; R_{\mathsf{T}})$$

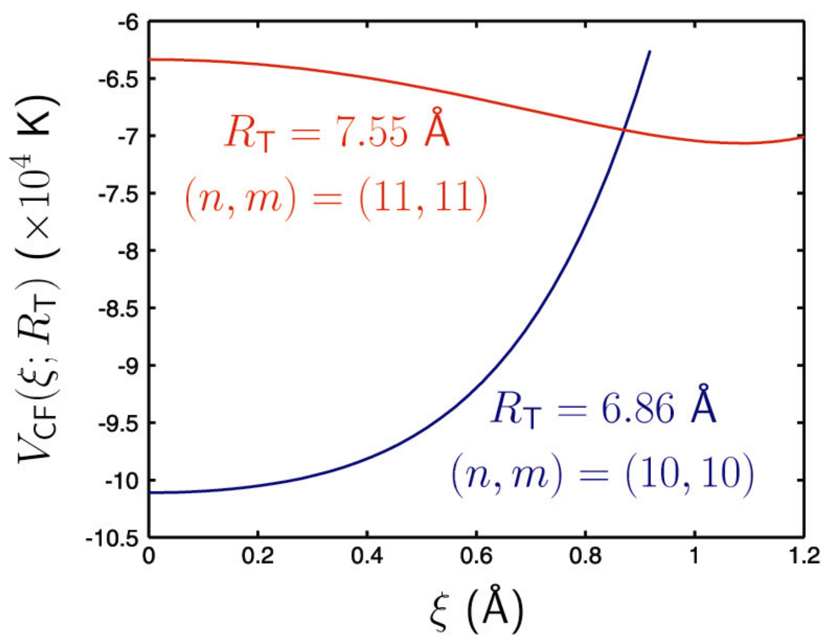
(α, β, γ) **dependence negligible:**

$$V_{\mathsf{CF}}(R_{\mathsf{T}}; \xi)$$

critical tube radius: $R_{\mathsf{T}} \approx 7$ Å

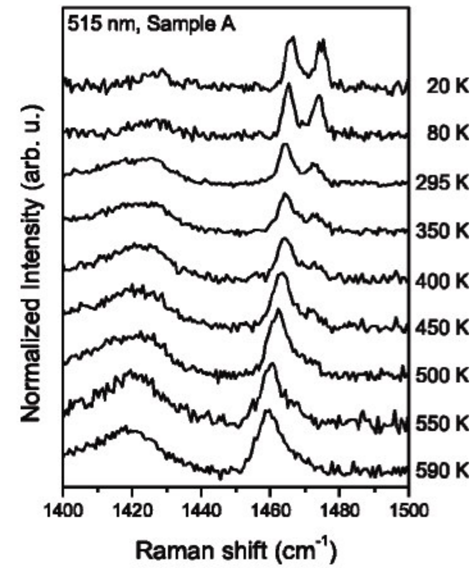
$R_{\mathsf{T}} > 7$ Å**: off-axis arrangement**

$R_{\mathsf{T}} < 7$ Å**: on-axis arrangement**



$(C_{60})_n$@SWCNT: resonant Raman scattering

*R. Pfeiffer et al., Phys. Rev. B **69**, 035404 (2004)*



"Splitting" of $A_g(2)$ Raman active mode ...

$$A_g(2) \rightarrow A_g(2)' + A_g(2)$$

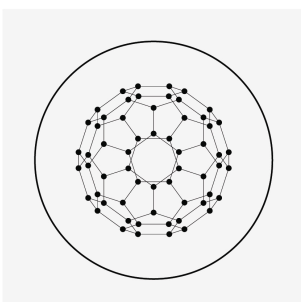
... but $A_g(2)$ mode non-degenerate!?

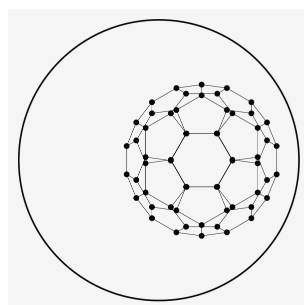
Different tube radii ...

$R_\mathrm{T} < 7$ Å $R_\mathrm{T} > 7$ Å

... result in different C_{60} arrangements ...

on-axis off-axis



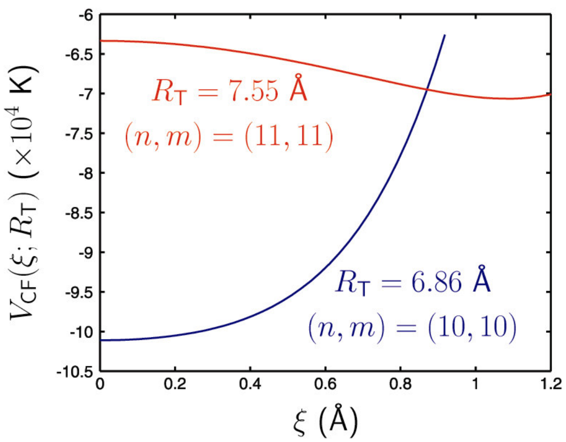


... and in **different vibrational frequencies** (at sufficiently low T).

$(C_{60})_n$@SWCNT: a 1D system

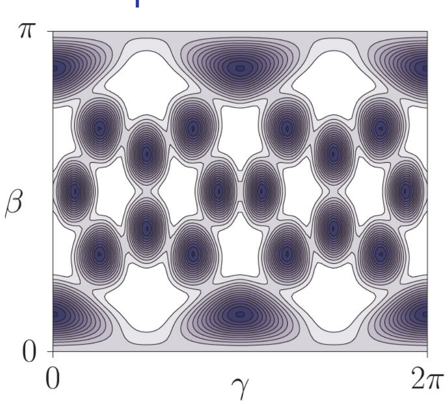
$R_\mathsf{T} < 7$ Å: crystal field $V_\mathsf{CF}(\beta, \gamma; R_\mathsf{T})$ = confinement potential

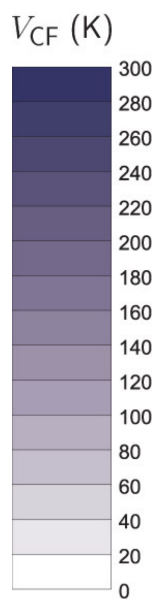
1) on-axis confinement

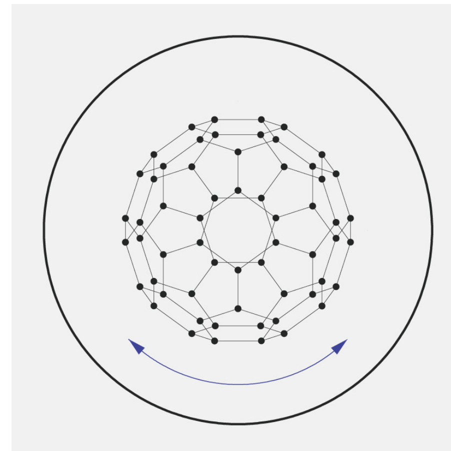


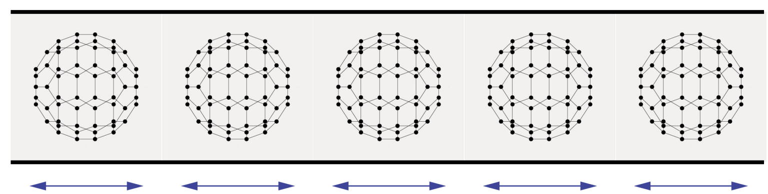
2) orientational confinement

$R_\mathsf{T} = 6.86$ Å









$(C_{60})_n$@SWCNT:
a physical realization of
a 1D system with
translational and orientational
degrees of freedom

$(C_{60})_n$@SWCNT: degrees of freedom

1) translational degrees of freedom (translations): Taylor series

$$V(n+1,n) = V + V'\big[u(n+1) - u(n)\big] + \frac{1}{2}V''\big[u(n+1) - u(n)\big]^2 + \ldots$$

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2) orientational degrees of freedom (rotations): Fourier series

$(s=5)$

$$V = V\big(\psi(n+1) - \psi(n)\big) = A_0 + A_5 \cos\Big(5\big[\psi(n+1) - \psi(n)\big]\Big) + \ldots$$

$$V' = V'\big(\psi(n+1) - \psi(n)\big) = A'_0 + A'_5 \cos\Big(5\big[\psi(n+1) - \psi(n)\big]\Big) + \ldots$$

$$V'' = V''\big(\psi(n+1) - \psi(n)\big) = A''_0 + \ldots$$

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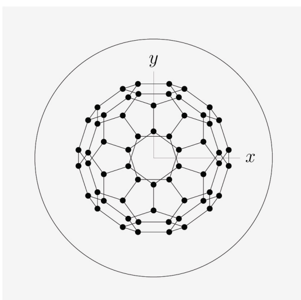
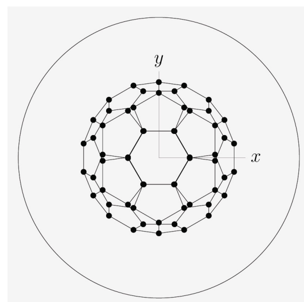
equilibrium lattice constant: $A'_0(a) = 0$



$s = 5$

$a = 10.033$ Å



$s = 3$

$a = 10.200$ Å

$(C_{60})_n$@SWCNT: 'torsio-thermo mechanics'

crystal sum: hamiltonian

$$\sum_{n=1}^{N-1} V(n+1,n) = (N-1)A_0 + V^{\mathrm{RR}} + V^{\mathrm{TT}} + V^{\mathrm{RRT}} + \dots$$

$(s=5)$

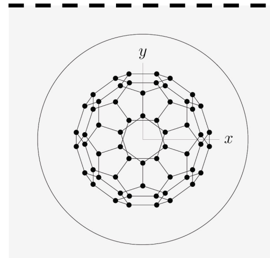
$$V^{\mathrm{TT}} = \frac{A_0''}{2}\sum_n \left[u(n+1) - u(n)\right]^2$$

V. Emery, J. Axe (1978)

$$V^{\mathrm{RRT}} = A_5' \sum_n \vec{S}(n+1)\cdot\vec{S}(n)\left[u(n+1)-u(n)\right] \approx A_5'\Gamma(1)\sum_n \left[u(n+1)-u(n)\right]$$

lattice contraction

$$\left\langle u(n+1) - u(n)\right\rangle = -\frac{A_5'\Gamma(1)}{A_0''}$$



$s = 5$

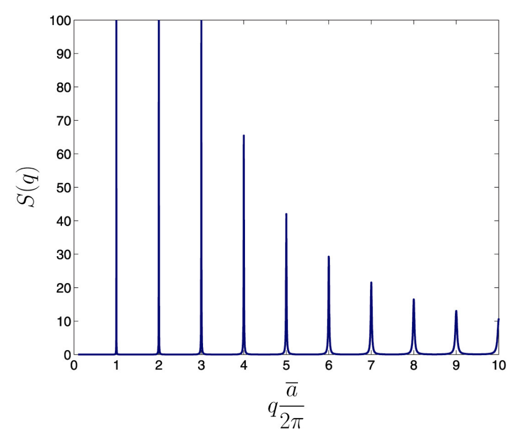
$T = 300$ K

$\left\langle u(n+1) - (n)\right\rangle = -0.0003$ Å

elastic scattering law

$$S(q) = \frac{1}{N}\sum_n\sum_{n'} e^{-iqa(n-n')}\left\langle e^{-iq[u(n)-u(n')]}\right\rangle$$

$$\bar{a} = a - \frac{A_5'\Gamma(1)}{A_0''}$$



Summary

C_{60}@SWCNT

- dependence of crystal field on tube radius
  distinct molecular orientations

- on-axis vs. off-axis C_{60} molecules depending on tube radius
  resonance Raman scattering measurements

- low tube radii
  $(C_{60})_n$@SWCNT 1D system