Vibrational Modes of Graphitic Fragments and the Nucleation of Carbon Nanotubes

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OUTLINE

(1) Carbon nanotubes: synthesis methods and the problem of nucleation

(2) The Tight Binding Molecular-Dynamics method

(3) A mechanism for the nucleation of carbon nanotubes: spontaneous curvature induced by thermal fluctuations

(M. Volpe and F. Cleri, J. Chem. Phys. **115,** 3308 (2001))

SYNTHESIS OF CARBON NANOTUBES (CNTs)

Methods based on directed, high-energy processing - instantaneous nucleation ?
- laser evaporation of graphite targets
- arc-discharge between graphite electrodes

NON-EQUILIBRIUM

The inner reaction zone is under high temperature, surrounded by huge thermal and chemical gradients (not in equilibrium). It is unclear whether CNTs may nucleate during the high-T discharge, or in the thermalization step.

Methods based on 'chemical atmosphere' - constant-rate nucleation ?
- chemical vapor deposition (CVD)
- decomposition/pyrolisis of precursors on a heated substrate
- ...

EQUILIBRIUM

The reaction zone is at constant μ(,P,T), with μ the combined chemical potential of a complex chemical bath. CNT nucleation is a continuous, rate-dependent process.

ARC-DISCHARGE IN LIQUID NITROGEN

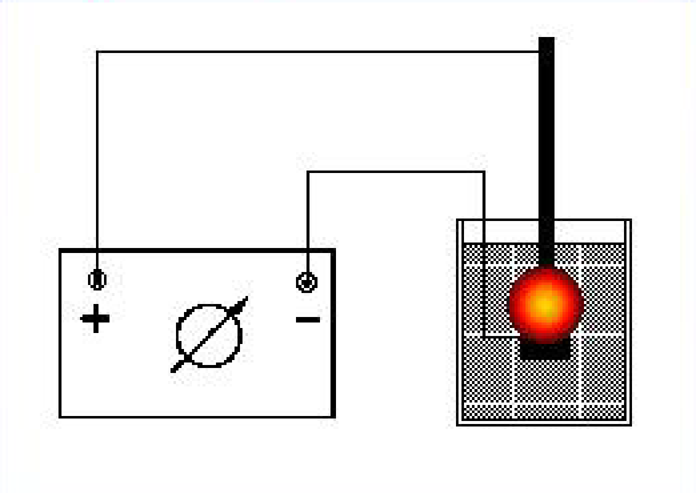
(ENEA Casaccia, M. Vittori-Antisari et al.)

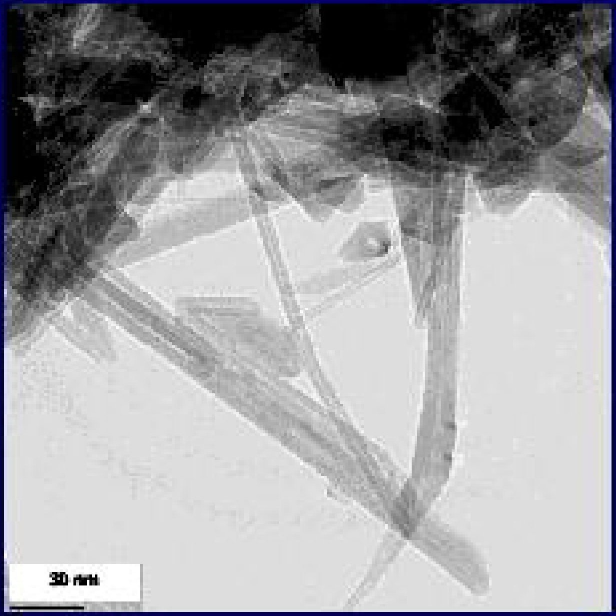
A simple and effective method to produce bulk quantities of carbon nanotubes.

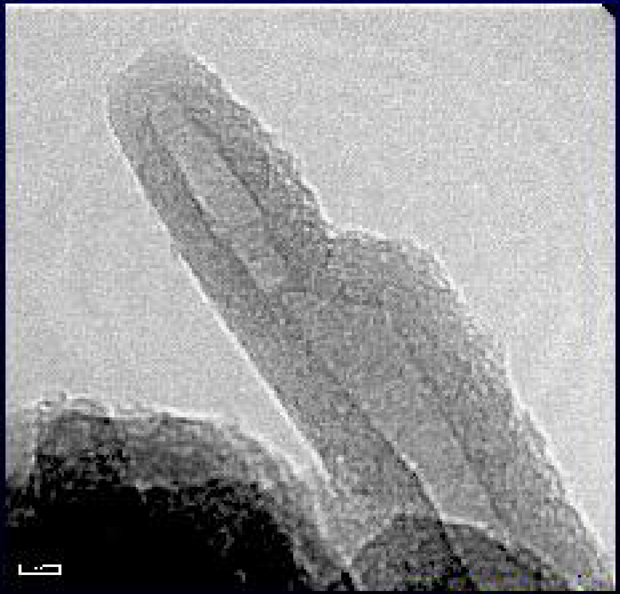
The reaction zoneis a bubble of N gas surrounded by cold liquid N, with a high gradient (~1000 K/cm).

- No need to work with high vacuum condition => the techique is low-cost and easily scalable.

- Drawback: poor control on the quality of the resulting CNT material... Typically, a matrix containing 20-30% of CNTs with spherical particles and amorphous carbon.



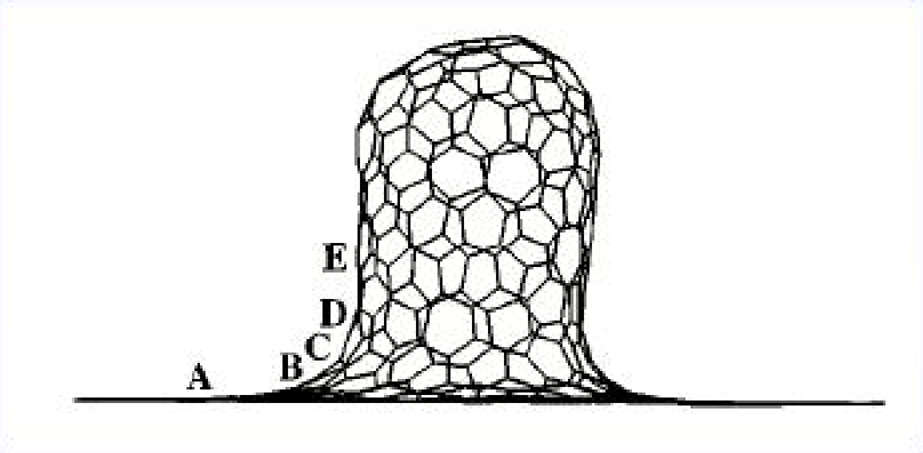




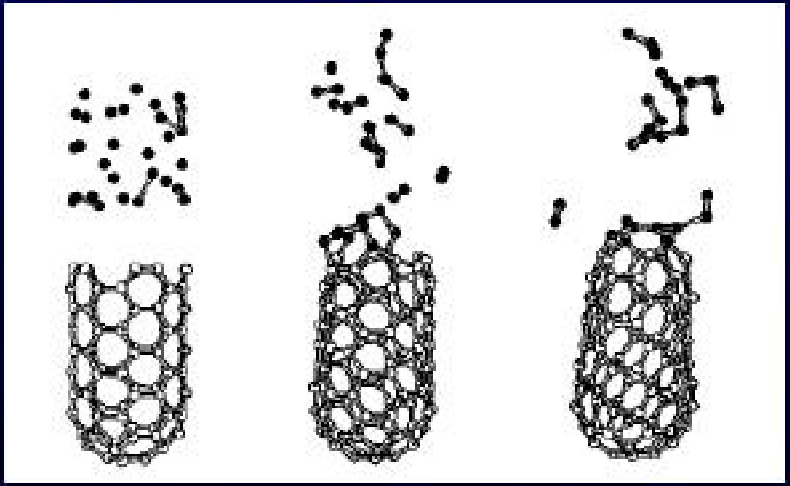
THE PROBLEM OF NUCLEATION AND GROWTH

Several models have been put forward to explain the microscopic mechanisms of CNT **growth** Compared to growth, however, the process of **nucleation** of CNTs has received much less attention.

Most growth models assume a pre-existing hemispherical cap, or a cylindrical seed, attached to a substrate or to a catalytizer particle,e.g. the 'root-growth' model ...



Maiti, Brabec and Bernholc, PRB 55, R6097 (1997)

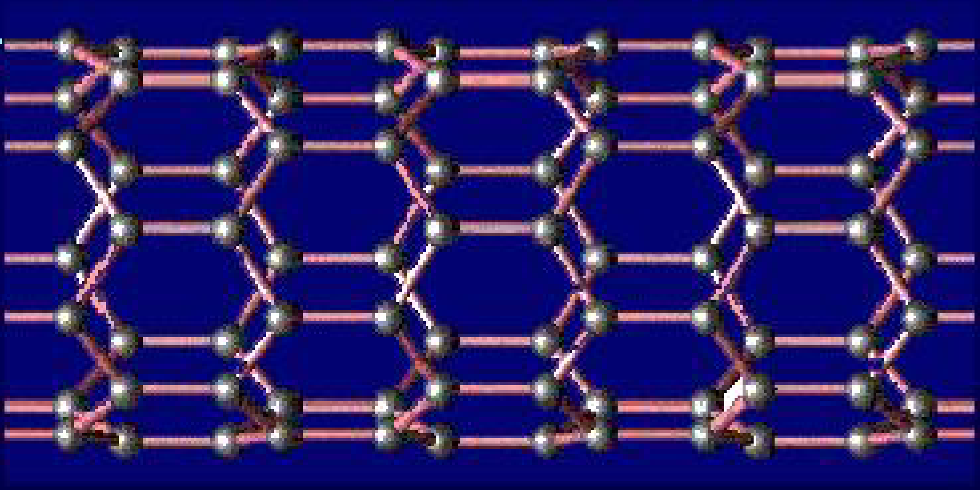


Oh and Lee, PRB 58, 7407 (1998)

BUT ... where does such a cap or cylinder comes from, in the first place ???

ATOMISTIC MODEL OF CARBON NANOTUBES

A CNT is represented by a closed cylinder formed by wrapping one graphite sheet around a given axis, defined by the so-called ‘**chiral vector**’

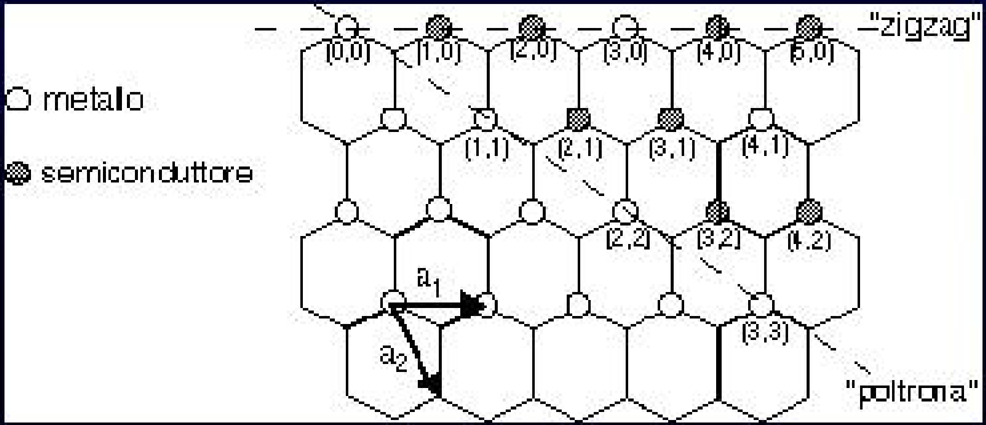


The system is fully closed in the two perpendicular dimensions (no dangling bonds) and infinite (by means of periodic border conditions) along the wrap axis.

Definition of the **chiral vector**

$$C_h = na_1 + ma_2$$

(n,m) **chiral index**



THE TIGHT-BINDING METHOD FOR TOTAL ENERGY AND MOLECULAR DYNAMICS CALCULATIONS

TIGHT-BINDING MODEL OF C-C INTERACTIONS

- The tight binding formulation reduces the Hamiltonian of the system to a sum of one-electron Hamiltonians:

$$H = \Sigma_i H_i$$

- The one-electron wavefunctions $|\psi_i>$ are written as a linear combination of atomic orbitals on the restricted basis of the valence orbitals $\{s, p_x, p_y, p_z\}$.
- The Schroedinger equation is turned into a saecular problem to be diagonalized:

$$<\psi_i|\, H_i \,|\psi_j> - \varepsilon <\psi_i|\psi_j> = 0$$

- Once the eigenvalues ε_i are obtained, the band-structure energy is:

$$E_{BS} = 2\ \Sigma_i^{(occ)}\ \varepsilon_i$$

Approximations

- a cut-off radius is assumed for the radial dependence of $<\psi_i|\, H \,|\psi_j>$
- the basis of atomic orbitals is restricted to the valence orbitals
- the matrix elements $<\psi_i|\, H \,|\psi_j>$ are fitted numerical constants
- three-center integrals are neglected

A TIGHT-BINDING MODEL FOR CARBON

(C.H. Xu, C.Z. Wang, C.T. Chan and K.M. Ho, J. Phys. Cond. Matt. **4**, 6047 (1992))

- Set of six semi-empirical parameters fitted on accurate *ab-initio* results for C band structure: E_s , E_p *(self-energies)* + $V_{ss\sigma}, V_{sp\sigma}, V_{pp\sigma}, V_{pp\pi}$ *(hopping integrals)*

- $$s(r) = \left(\frac{r_0}{r}\right)^n \exp\left\{n\left[-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right]\right\}$$

  Radial scaling law for the hopping integrals

- $$U_{rep} = \sum_i f\left[\sum_j \phi(r_{ij})\right]$$

  Many-body repulsive potential

  $$\phi(r) = \phi_0\left(\frac{d_0}{r}\right)^m \exp\left\{m\left[-\left(\frac{r}{d_c}\right)^{m_c} + \left(\frac{d_0}{d_c}\right)^{m_c}\right]\right\}$$

CLASSICAL MOLECULAR DYNAMICS WITH QUANTUM MECHANICAL FORCES

$$m\ddot{r}_i(t) = -\frac{\partial U\left(\left\{r_k(t)\right\}_{k=1..N}\right)}{\partial r_i(t)} = F_i\left(\left\{r_k(t)\right\}_{k=1..N}\right)$$

Ion-ion forces derived from the fully quantum-mechanical electronic states

$$\boxed{U_{TOT} = E_{BS} + U_{rep}}$$

Band-structure energy

(Short-range) repulsive energy

Quantum mechanical forces are derived from the Hellmann-Feynman theorem for the band-structure term.

LINEARLY-SCALING FERMI PROJECTOR METHOD

The diagonalization of the full hamiltonian is impractical for large number of atoms (N>2–300) since the computational load scales as N^3.

For the MD study of large systems we adopt a linearly-scaling formulation of the total energy based on the Fermi projection-operator method:

$$E_{BS} = 2\ \Sigma_i\ \varepsilon_i\ F_\beta(\varepsilon_i) = Tr\ [\ F \times H\ ]$$

with the Fermi operator given by:

$$F_\beta(\varepsilon_i) = [\exp\ \beta(\varepsilon_i - \mu)]^{-1}$$

The Fermi operator can be approximated by an orthogonal expansion:

$$F\,|\psi_j> \sim \Sigma_k\ c_k\ T_k\ (H)\,|\psi_j> = \Sigma_k\ c_k\,|\phi_k>$$

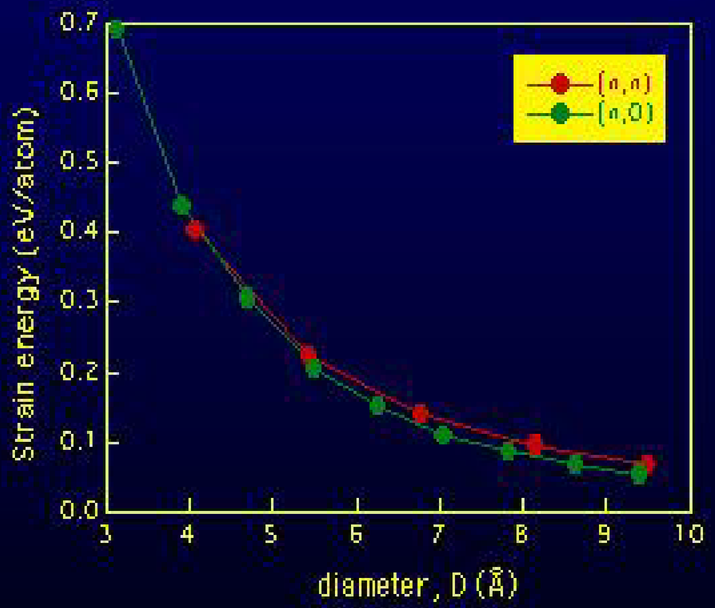
… the great news is that the 'effective orbitals' $|\phi_k>$ (indeed, the columns of the Fermi operator in matrix representation) are **well localized** below a cutoff radius with exponential decay (in insulators).

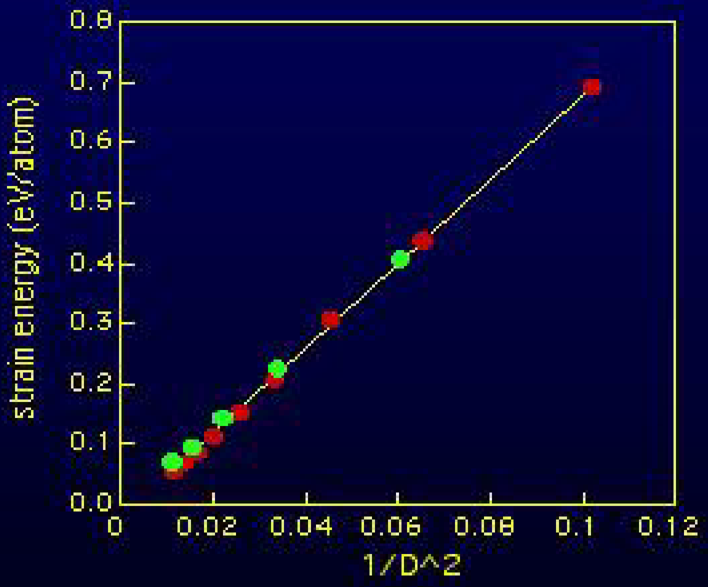
THE STRAIN ENERGY, or ENERGY OF CURVATURE

We calculated the “strain energy”, i.e. the difference in energy/atom between CNTs of different chirality and a flat (infinite) graphite plane.

The tube diameter for each chirality is given by:

$$D=(\sqrt{3}\, a_0/\pi)\ (n^2+nm+m^2)^{1/2}$$





The energy barriers against curvature are of the order of 0.3 eV/atom or less for any experimentally realized nanotube size.

Such barriers could be overcome by thermal fluctuations....

TIGHT-BINDING CALCULATION OF THE VIBRATIONAL SPECTRA OF GRAPHENE

ATOMISTIC CALCULATION OF VIBRATIONAL SPECTRA

(1) Diagonalization of the force-constant matrix, $[F] = \left\| \frac{\partial^2 U_{TOT}}{\partial x_\alpha \partial x_\beta} \right\|$ and integration over many k-points.

Extremely expensive, requires analytic knowledge of second derivatives….

(2) Calculation of the velocity auto-correlation function (VAF) from a MD trajectory:

First, the atom velocities $v_i(t)$ are recorded at time-slices $\tau = 0.03$ fs during a MD simulation at temperature T ; then the VAF is obtained as:

$$C(t,T) = \sum_{\tau} \left\langle \vec{v}_i(\tau) \cdot \vec{v}_i(\tau + t) \right\rangle_T$$

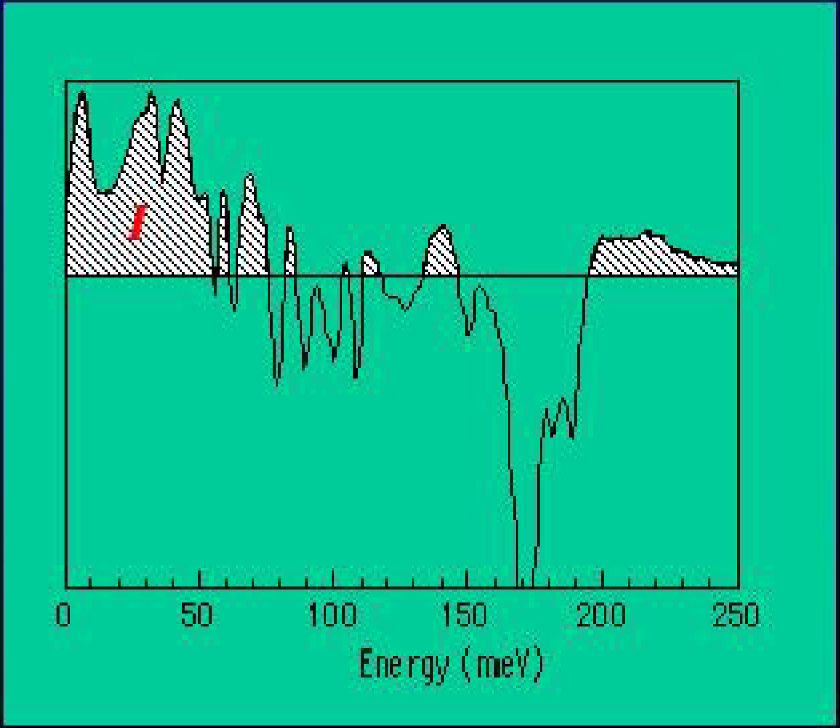
from which the vibrational spectrum can be obtained via Fourier transform:

$$g(\omega,T) = \frac{2}{\pi} \int_0^{t_0} C(t,T) \cos \omega t \, dt$$

VIBRATIONAL SPECTRA OF GRAPHITE vs. ‘GRAPHENE’

... infinite vs. finite size

We compared thevibrational spectra of finite-sizegraphene with an infinite graphite sheet at T=4000 K.



The difference-spectrum shows that the vibrational spectra of finite-size fragments have a large content of low-energy modes

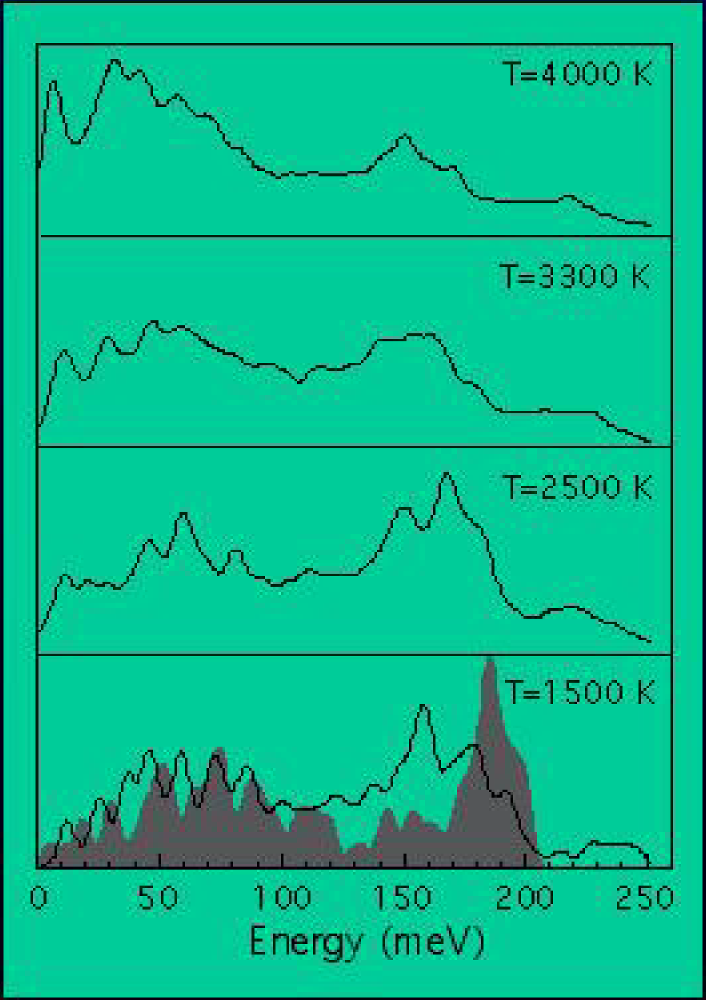
The excess of high-frequency modes originates from the dangling bonds in the free fragment.

I is defined as the integral of thevibrational spectrum in the range 0-50meV.

VIBRATIONAL SPECTRA OF GRAPHENE: ROLE OF TEMPERATURE

The vibrational spectrum of graphene (here the case of a 96 atoms fragment) as a function of temperature.

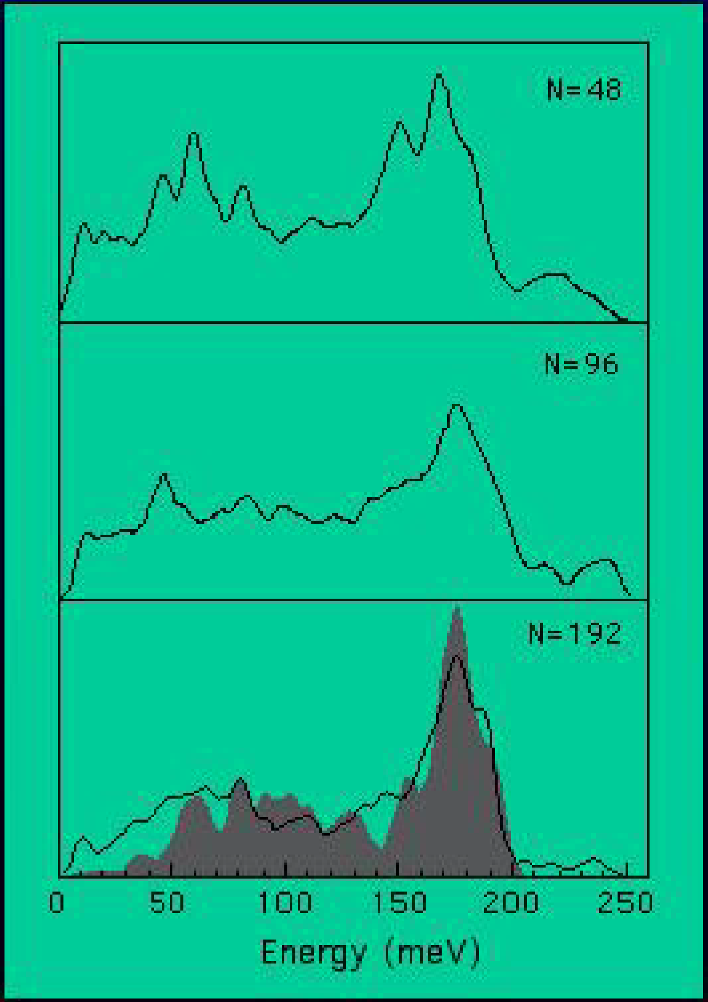
The spectral density is red-shifted and the low-frequency band grows as $I - T$.



VIBRATIONAL SPECTRA OF GRAPHENE: ROLE OF SIZE

The vibrational spectrum of graphene at 2500 K as a function of the fragment size.

The spectral density is blue-shifted and the low-frequency band decreases as $I \sim N^{-0.4}$.



The analysis of the vibrational spectra of finite-size graphene fragments shows that:

- finite-size fragments have a characteristic low-frequency band which is absent in infinite graphite sheets
- the integral I of such low-ω band grows linearly with temperature
- the integral I also decreases with fragment size as $N^{-0.4}$

If such low-frequency modes can be held responsible of the bending effect leading to closed-shape carbon fragments (i.e. nanotube precursors), the above findings imply the existence of a

preferential fragment size (=>nanotube diameter) for each temperature.

From simple considerations, one can deduce that

low-frequency modes should correspond to large-amplitude vibrations.

Consider an ideal system with only one low-frequency phonon (L) which is excited at high temperature, and one high-frequency (H) phonon excited at low temperature; assume that by raising the temperature all the vibrational energy $E=N\hbar\omega$ goes from the H-mode to the L-mode.

Then, the ratio of the phonon number densities is inversely proportional to the ratio of the frequencies,

$$N_L/N_H = \omega_H/\omega_L$$

In classical oscillator terms, $E=1/2\,k<x^2>$ with $k=m\omega^2$, the vibrational amplitudes are in the ratio

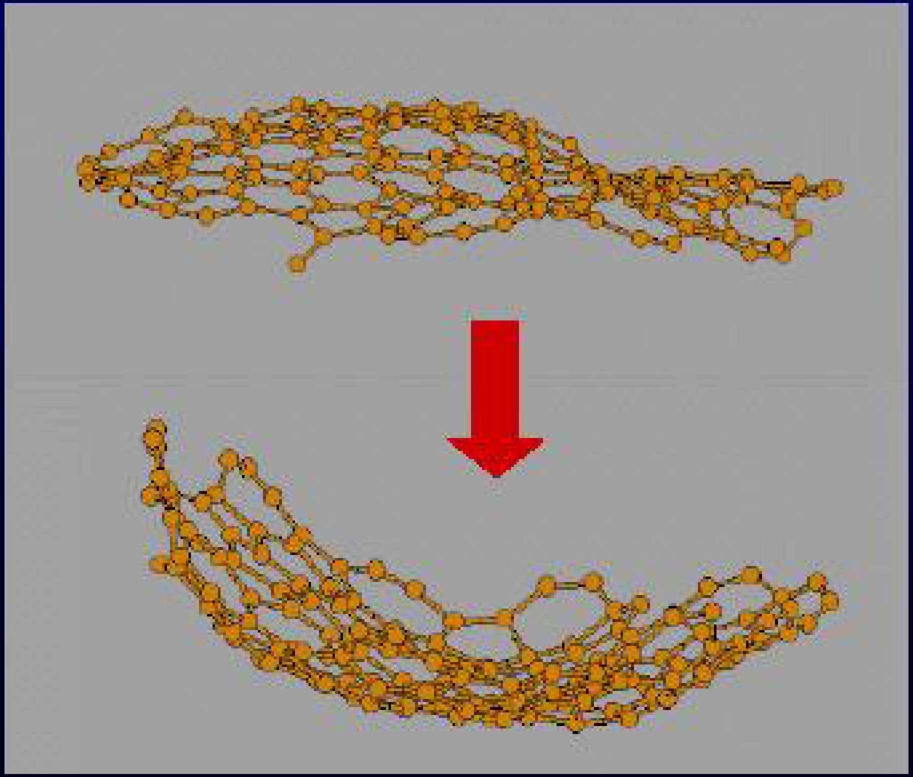
$$<x>_L\,/<x>_H = \omega_H/\omega_L$$

TIGHT-BINDING MOLECULAR DYNAMICS SIMULATIONS OF THE ABLATION OF GRAPHITE NANOFRAGMENTS

FREE OSCILLATION OF A GRAPHENE (FINITE-SIZE GRAPHITE)

As a direct confirmation of the deductions of the preceding study, we performed TB-MD simulations of the free oscillation of a graphene at high temperature (T~4000 K) and observed the existence of large-amplitude, low-frequency modes.

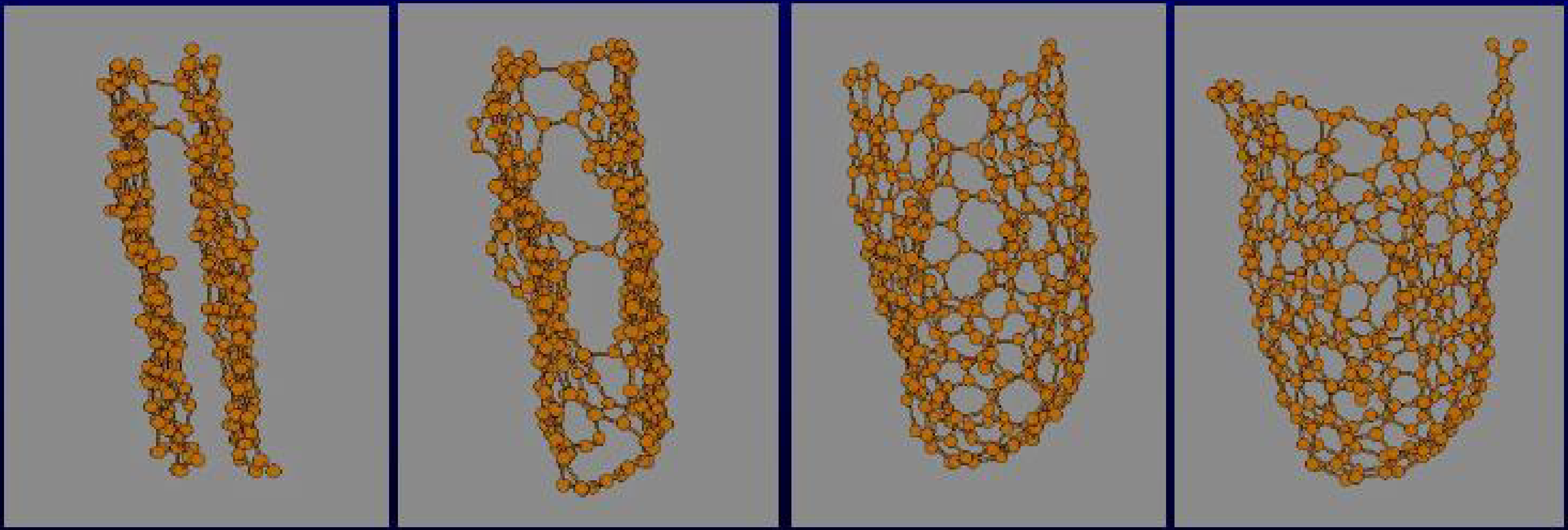
Such modes tend to invert the curvature of the fragment, thus suggesting the possibility that a fragment could get spontaneously rolled into a closed carbon nanostructure during thermal fluctuations.



Tight-binding MD simulation of the free vibration of a graphene (fragment of graphite) with 160 atoms.

N_{tot} = 160 atoms
Total time = 0.03 ns
$\Delta t = 10^{-15}$ sec/time step
{NVT} at T=4000 K

SPONTANEOUS CLOSURE OF A GRAPHITE FRAGMENT INTO A NANOCAP (the seed of a nanotube ...?)



t=2 ps t=5 ps t=10 ps t=50 ps

MD simulation of two parallel graphenes with 160 atoms each at T=4000 K

Tight-binding MD simulation of the nucleation of two parallel nanotubes from a fragment of graphite made of four parallel planes with 160 atoms each.

N_{tot} = 640 atoms
Total time = 0.1 ns
$\Delta t = 10^{-15}$ sec/time step
{NVT} at T=4000 K

CONCLUSIONS

- A possible mechanism for the spontaneous nucleation of carbon nanotubes from high-energy processing of graphite has been individuated: graphite nanofragments can generate nanotube precursors by means of low-frequency, large-amplitude oscillations, as confirmed by direct TBMD simulations.

- Finite-size fragments display a peculiar low-frequency vibrational band which is absent in the infinite graphite sheet. The importance of such vibrational band increases with temperature and decreases with fragment size, indicating a preferential nanotube size at each temperature.

- TBMD simulations of the high-temperature dynamics of several parallel graphenes also suggest a possible path to the formation of bundles of parallel single-wall nanotubes.