Simulations of Carbon Chain Growth and Evolution with Varying Temperature

PRINCETON PLASMA PHYSICS LABORATORY

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Computer simulations were used to study the growth of carbon nanotubes created by a plasma arc discharge. Density Functional Theory Tight-Binding (DFTB+) and Thermodynamics codes were used for the calculations, and the results of each code were compared. Quantum-classical molecular dynamics was carried out using the DFTB method and a Nose-Hoover thermostat. The thermal dynamics code uses the Gibbs ensemble to find the most probable states of the system. Evolution of the carbon chain length as a function of temperature was studied.

Background: Carbon chains and Nanotubes

- Carbon chains: the precursor to Carbon Nano-Tubes (CNTs)
- CNTs: Cylindrical Carbon allotrope with useful mechanical, electronic, optical properties
- One method of formation: Plasma arc discharge

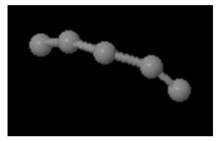


Fig 1. Visualization of a carbon chain of length 5 (C5 chain)[1]

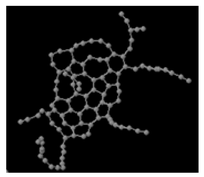


Fig 2. Partially formed Graphene flake, an intermediate between carbon chains and nanotubes

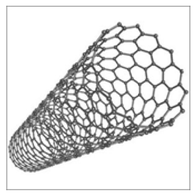
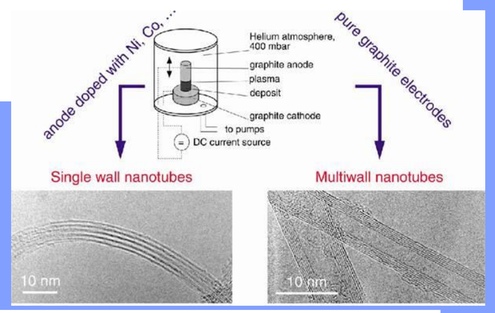


Fig 3. Molecular structure of a carbon nanotube[2]. (All atoms are carbon)



Background: Plasma arc discharge

- Involves two graphite electrodes immersed in a noble gas chamber.
- Current applied between electrodes, ionizing gas between them (creating a plasma).
- Can result in deposition of carbon nanotubes on the cathode.
- Amount and quality of nanotubes dependent on many parameters; we focused mainly on the temperature dependence.

Methods

- DFTB: Approximation to density functional theory (a quantum mechanical computational method).
- Used DFTB+ (one implementation of DFTB) to simulate plasma arc discharge formation of carbon chains:
  - Start with carbon lattice, heat to 6000 K
  - Put system under Nose-Hoover thermostat (constant temperature decrease down to 1000 K) (500 ps)
  - Keep system at 1000 K for a while to see how it evolves
- Used thermodynamic codes to predict the final composition of the system (what lengths of carbon chains there would be):
  - If system is kept under constant pressure and temperature, then minimizing Gibbs free energy (thermodynamic potential that is minimized in chemical equilibrium) should give the final composition
  - Gibbs free energies of formation for chains length 1-5 known[4], but need to estimate for longer chains

Gibbs Free Energy

- Gibbs Free Energy of an arbitrary system of N particles[5]:

$$G = -NkT\left(\ln Z - \ln N\right)$$

(k: Boltzmann's constant, T: temperature, Z: partition function (specific to a particular molecule))

- $\ln Z$ for a molecule of N atoms[6] ($N > 2$):

$$\ln Z = N \ln\left[\left(\frac{2\pi(\sum_i m_i)kT}{h^2}\right)^{3/2}\frac{Ve}{N}\right] + N\ln\left[\frac{\sqrt{\pi}}{\sigma}\cdot\left(\frac{T^3}{\theta_{rx}\theta_{ry}\theta_{rz}}\right)^{1/2}\right] - N\left[\sum\left[\frac{h\nu_i}{2kT} + \ln\left(1-\exp\left(-\frac{h\nu_i}{kT}\right)\right)\right]\right] + \frac{ND_e}{kT} + N\ln g_e$$

where m_i are the atomic masses, h is Planck's constant, V_e is electronic volume, σ is symmetry number, $\theta_{rx,y,z}$ are proportional to inverse moment of inertia, ν_i are vibrational frequencies, D_e is depth of the vibrational potential energy well, and g_e is the statistical weight of the electronic ground state.

- Unknown vibrational frequencies ν_i and well depth D_e, so approximation is needed

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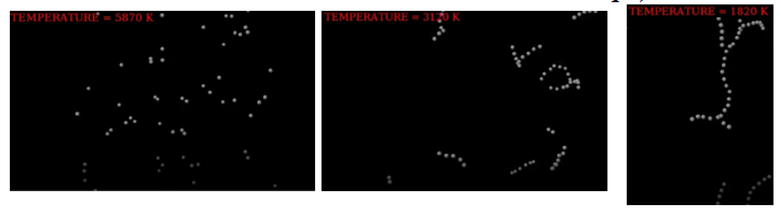
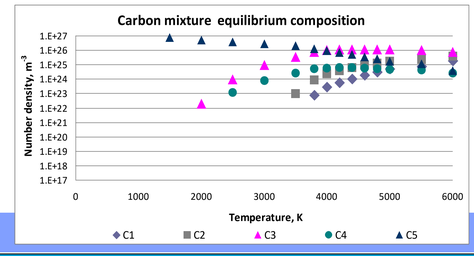
Results

•Chain evolution as function of temperature (system cooled from 6000 K down to 1000 K in 500 ps):



- Predicted final composition at 100 atm pressure (from thermodynamic code)—before condensation starts



Conclusions / Future Work

- Carbon chains grow longer as temperature decreases
- The predictions of final composition made with the thermodynamic code seem to agree with the DFTB+ simulations
- Moving to a semi-classical (molecular dynamics code) instead of a quantum mechanical one (like DFTB+) could immensely speed up computations (provided the correct potential function is used that accounts for quantum mechanical behavior).

References

1. Visualization courtesy of Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/
2. Image from http://www.cet-science.com
3. https://sites.google.com/site/nanomodern/Home/CNT/syncnt/arc-discharge
4. Gibbs free energies for chains length 1-5 were taken from *Malcolm W. Chase, Jr. NIST-JANAF Thermochemical Tables.* American Chemical Society ; American Institute of Physics for the National Institute of Standards and Technology, 1998.
5. Maecker, Heinz. *The Electric Arc.* 2009.
6. Gupta, M.C. *Statistical Thermodynamics.* 1990.