Cluster model expanded to C-nanostructures: Fullerenes, tubes, graphenes and their buds

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Abstract

The existence of nanographene (GR) and GR-fullerene bud (GR-BUD) in cluster form is discussed in organic solvents. Theories are developed based on columnlet, bundlet and droplet models describing size-distribution functions. The phenomena present a unified explanation in columnlet model, in which free energy of GR involved in cluster comes from its volume, proportional to number of molecules n in cluster. Columnlet model enables describing distribution function of GR stacks by size. From purely geometrical considerations, columnlet (GR/GR-BUD), bundlet [single-wall carbon nanotube (SWNT) (CNT) (NT) and NT-fullerene bud (NT-BUD)] and droplet (fullerene) models predict dissimilar behaviours. Interaction-energy parameters of GR/BUD are taken from C_{ngr}. An NT-BUD behaviour or further is expected. Solubility decays with temperature result smaller for GR/GR-BUD than SWNT/NT-BUD than C_{ngr} in agreement with lesser numbers of units in clusters. Discrepancy between experimental data of the heat of solution of fullerenes, CNT/NT-BUDs and GR/GR-BUDs is ascribed to sharp concentration dependence of the heat of solution. Diffusion coefficient drops with temperature result greater for GR/GR-BUD than SWNT/NT-BUD than C_{ngr} corresponding to lesser number of units in clusters. Aggregates (C_{ngr}), SWNT/NT-BUD, and GR/GR-BUD, are representative of droplet, bundlet and columnlet models.

Keywords: Solubility of graphene-fullerene bud; Columnlet cluster model; Bundlet cluster model; Droplet cluster model; Nanobud; Fullerene.

Introduction

Nanoparticles interest arose from shape-dependent physical properties of nanoscale materials [1,2]. Single-wall C-nanocones (SWNCs) (CNCs) allowed curved-structures nucleation/growth suggesting pentagon role that, introduced into nanographene (GR) via extraction of a 60º sector, forms a cone leaf. Pentagons in SWNC apex are analogues of single-wall C-nanotube (SWNT) (CNT) tip topology; Classes of positive-curvature CNCs [3–5] /Clar theory [6–10] were analyzed. Ends of SWNTs predicted electronic states topology. Classes of positive-curvature CNCs [3–5] /Clar theory apex are analogues of single-wall C-nanotube (SWNT) (CNT) (NT) tip, where geometrical requirement for seamless connection accounted by cone wall model of wrapped GR sheets, SWNCs with discrete opening angles θ = 19º, 39º, 60º, 85º and 113º in pyrolytic C were explained by cone wall model of wrapped GR sheets, pentagons in SWNC suggest pentagon role that, introduced into nanographene (GR) allowed curved-structures nucleation/growth of 60º for semi-conductors. CNCs/electronics. C_{diamond} by alternating B/N provided BN-cubic [26]. BN-hexagonal (h) resembles C_{graphite} since fused planar six-membered B_{N} rings; however, interlayer B–N exist. BN nanotubes were visualized [27–29]. BN-h was proposed [30]. Other layered materials are: WS_{2}, etc. [42–46]. Pyrolytic nano-B_{x}C_{y}N_{z} shows C/BN domains; compound provides materials useful as nanocomposites (NCs)/semiconductor devices enhanced towards oxidation [47–49]. CNTs are inert/difficult to integrate into NCs/electronics.

C-NanoBuds* (NT-BUDs, fullerene-functionalized SWNTs) were synthesized [50]; all are semiconductors [51]. GR sparked potential to be ingredient of devices (e.g., single molecule gas sensors, ballistic transistors, spintronic) [52]. It was called mother of all graphitic forms because it can be wrapped into fullerenes, rolled into CNTs and stacked into graphite [53]. It consists of hexagonal arrangement of C-atoms in two-dimensional (2D) honeycomb crystals. It differs from most conventional 3D materials. Basic GR is semimetal/zero-gap semiconductor. Zigzag-edges nature imposes localization of electron density with maximum at the border C-atoms, leading to formation of flat conduction/valence bands near Fermi level. Localization states are spin polarized and in case of ordering electron spin along zigzag edges, GR is established in anti/ferromagnetic phase. The former breaks GR sublattice symmetry that changes its band structure and opens a gap. GR/CNTs show third-order nonlinerity. Electronic properties of semiconductor monolayers are better than the bulk,
spawning efforts to create functionalized monolayers of other bonded crystal structures. Higher carrier mobility is achieved via ultra-thin topologies but terminating monolayers with ligands for specific applications, ultra-thin materials are made more sensitive than the bulk for sensors. Solvent selection was analyzed [54–56]. Coronado group examined multifunctional hybrid nanocomposites based on CNTs/chemically modified GR [57–59]. Other 2D materials were analyzed [60–66]. Some GR-fullerene nanobuds (GR-BUDs) [67] are CNTs/chemically modified GR [57–59]. Other 2D materials were group examined multifunctional hybrid nanocomposites based on Sc/GR clusters [79] cluster models, Sc/GR clusters columnlet shape. Gibbs energy is to perform a comparative study of fullerene, SWNT/NT-BUD and columnlet models are examined. Based on droplet/bundlet models, class of phenomena accompanying solution behaviour is analyzed [69–74] SWNT and other 2D materials were analyzed [60–66]. Some GR-fullerene nanobuds (GR-BUDs) [67] are coronado applications, ultra thin materials are made more sensitive than the thin materials are made more sensitive than the Torrens.

where

\[ G_n = G_n - G_2 \]  

where \( G_1 \) and \( G_2 \) are responsible for contribution to Gibbs energy of molecules placed inside volume and on surface of cluster, respectively, and correspond to formation energies \( A_n \) and \( -B \). The chemical potential \( \mu_n \) of a cluster of size \( n \) is:

\[ \mu_n = G_n - T \ln C_n \]  

where \( T \) is absolute temperature and \( C_n \) concentration of \( n \)-sized cluster. With (1) it results:

\[ \mu_n = G_n - G_2 - T \ln C_n \]  

where \( G_1 \) and \( G_2 \) are expressed in temperature units. In saturated sheet solution, cluster-size distribution function is determined via equilibrium condition linking clusters of specified size with solid phase, which corresponds to equality between chemical potentials for sheets incorporated into clusters of any size and crystal, resulting in the expression for the distribution function in a saturated solution:

\[ \mathcal{f}(n) = g_n \exp \left( \frac{-(A_n + B)}{T} \right) \]  

where \( A \) is equilibrium difference between sheet interaction energies with its surroundings in solid phase and cluster volume, \( B \), similarly on cluster surface and \( g_n \) statistical weight of \( n \)-sized cluster. One neglects \( g_n(n,T) \) dependencies in comparison with exponential (4), which normalization:

\[ \sum_{n=1}^{\infty} \mathcal{f}(n)n = C \]  

requires \( A > 0 \), and \( C \) is solubility in relative units. As \( n \gg 1 \), normalization (5) results:

\[ C = \frac{\bar{G}_n}{T} \int_{n=1}^{\infty} n \exp \left( \frac{-(A_n + B)}{T} \right) dn \]

where \( \bar{G}_n \) is cluster statistical weight averaged over \( n \) that makes major contribution to integral (6) and \( C_n \) sheet molar fraction. The \( A, B \) and \( C_n \) were taken from \( C_60 \) in hexane/toluene/CS2 (\( A = 320K, B = 970K, C_60 = 5 \times 10^{-4} \)). Correction takes into account packing efficiencies of \( C_60 \)/sheet:

\[ A' = \frac{A}{\eta_{ph}} \quad \text{and} \quad B' = \frac{B}{\eta_{ph}}(\text{sheet})^n \quad \eta_{ph} = \frac{\eta_{cyl}}{\eta_{sph}} \]

where \( \eta_{cyl} \) are spheres (face-centred cubic, FCC) and cylinder packing efficiencies, respectively. Distribution-function dependences on concentration/temperature lead to sheet thermodynamic/kinetic parameters. For unsaturated solution, distribution function is obtained by clusters equilibrium condition. From Eq. (4) distribution function vs. concentration is:

\[ \mathcal{f}_n(C) = \lambda^m \exp \left( \frac{-(A_n + B)}{T} \right) \]  

where \( \lambda \) depends on concentration and is determined by normalization condition:

\[ C = C_0 \int_{n=1}^{\infty} n \lambda^m \exp \left( \frac{-(A_n + B)}{T} \right) dn \]  

where \( C_0 \) defines absolute concentration: \( C_0 = 10^{-4} \text{ mol·L}^{-1} \) is found requiring saturation in Eq. (9). The formation energy of \( n \)-sized cluster results:

\[ E_n = \mu(An - B) \]  

Using the distribution function one obtains the heat of solution per mole of dissolved sheet:

\[ H = \sum_{n=1}^{\infty} E_n \mathcal{f}_n(C) \frac{N_d}{N_d} \]

where \( N_d \) is the Avogadro number and \( \lambda \) depends on solution total concentration by normalization condition (9). The solute diffusion coefficient results:

\[ D = \frac{D_0}{T} n \int_{x=1}^{\infty} n \lambda^m \exp \left( \frac{-(A_n + B)}{T} \right) dn \]

where \( D_0 \) is the diffusion coefficient of a unit that was taken equal to that of \( C_60 \) in toluene \( D_0 = 10^{-8} \text{ m}^2 \text{s}^{-1} \). Eqs. (1)–(12) are modelled in a home-built program available from authors. A droplet cluster model
of C₆₀ is proposed following modified Eqs. (1')–(12'):
\[ G_n = G_n - G_c n^{3/2} \]  
(1')
\[ \mu_n = G_n - G_c n^{3/2} + T \ln C_n \]  
(3')
\[ f(n) = g_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(4')
\[ C = \frac{1}{g_n} \sum_{n=1}^{\infty} \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(6')
\[ f_n(C) = \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(8')
\[ C = \frac{1}{\lambda_n} \sum_{n=1}^{\infty} \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(9')
\[ E_n = n(\lambda_n - B n^{3/2}) \]  
(10')
\[ H = \sum_{n=1}^{\infty} E_n f_n(C) \times N_n = \sum_{n=1}^{\infty} n(\lambda_n - B n^{3/2}) \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(11')
\[ D = D_0 \int_{n=1}^{\infty} \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \frac{dn}{n^2} \]  
(12')

A **bundlet** cluster model of SWNT and NT-BUD is proposed following customized Eqs. (1'')–(12''):

\[ G_n = G_n - G_c n^{3/2} \]  
(1'')
\[ \mu_n = G_n - G_c n^{3/2} + T \ln C_n \]  
(3'')
\[ f(n) = g_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(4'')
\[ C = \frac{1}{g_n} \sum_{n=1}^{\infty} \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(6'')
\[ f_n(C) = \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(8'')
\[ C = \frac{1}{\lambda_n} \sum_{n=1}^{\infty} \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(9'')
\[ E_n = n(\lambda_n - B n^{3/2}) \]  
(10'')
\[ H = \sum_{n=1}^{\infty} E_n f_n(C) \times N_n = \sum_{n=1}^{\infty} n(\lambda_n - B n^{3/2}) \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \]  
(11'')
\[ D = D_0 \int_{n=1}^{\infty} \lambda_n \exp \left( \frac{-A_n + B n^{3/2}}{T} \right) \frac{dn}{n^2} \]  
(12'')
marked for SWNT/NT-BUD and even GR/GR-BUD, in agreement with lesser numbers of units in clusters (Figure 1). At $T = 260K$ from $C_{np}$ (droplet) to SWNT, NT-BUD (bundlet), GR and GR-BUD (columnlet) the solubility (Figure 2) decreases to 3%, 2%, 0.3% and 0.1% of $C_{np}$, respectively.

The cluster distribution function by size in $CS_2$, calculated for saturation concentration at solvent temperature $T = 298.15K$ (cf. Figure 3), shows that on going from $C_{np}$ (droplet) to SWNT (bundlet) the maximum aggregate size decays from $n_{max} \approx 8$ to $\approx 2$ and spreading is narrowed, in agreement with lesser number of units in clusters (Figure 1). The dispersal of NT-BUDs (bundlet) is somewhat enlarged to wider bundles with respect to SWNT. The dissemination of GRs (columnlet) is strongly narrowed in concordance with the fewest units ($n_{max} \approx 1$). The scattering of GR-BUDs (columnlet) is rather increased to longer stacks with regard to GR.

The concentration dependence for the heat of solution in toluene, benzene and $CS_2$ calculated at solvent temperature $T = 298.15K$ (cf. Figure 4) shows that for $C_{np}$ (droplet), on going from $C < 0.1\%$ of saturated ($<n> = 1$) to $C = 15\%$ ($<n> = 7$) the heat of solution decays by 73%. In turn, for SWNT (bundlet) the heat of solution rises by 54% in the same range in agreement with a lesser number of units in clusters (Figs. 1 and 3). Moreover, in NT-BUD (bundlet), GR and GR-BUD (columnlet) the heat of solution increases by 98%, 392% and 680%, respectively. The discrepancy between experimental data for the heat of solution of fullerenes, CNT/NT-BUDs and GR/GR-BUDs is ascribed to the sharp concentration dependence for the heat of solution.

In the temperature dependence for the heat of solution in toluene, benzene and $CS_2$ calculated for saturation concentration (cf. Figure 5) $C_{np}$ results are plotted for $T > 260K$ after FCC/SC transition. For $C_{np}$ (droplet) on going from $T = 260K$ to $T = 400K$ the heat of solution rises 2.7kJ·mol$^{-1}$. The heat of solution of SWNT (bundlet) increases 10.4kJ·mol$^{-1}$ in the same range and becomes endergonic. For NT-BUD (bundlet) the heat of solution augments 11.3kJ·mol$^{-1}$ similarly endergonic. Moreover, GR and GR-BUD (columnlet) heats of solution enlarge 82 and 76kJ·mol$^{-1}$, respectively, likewise endergonic.
The diffusion coefficient vs. concentration in toluene at $T = 298.15K$ (cf. Figure. 6) shows that cluster formation, close to saturation, decreases the diffusion coefficients by 56%, 69%, 73%, 95% and 97% for $C_{60}$ (droplet), SWNT, NT-BUD (bundlet), GR and GR-BUD (columnlet), respectively, compared with ($C_{60}$)$_0$. Diffusion coefficients of SWNT, NT-BUD, GR and GR-BUD decay by 29%, 37%, 88% and 93% contrasted with ($C_{60}$)$_0$ in agreement with lesser number of units in clusters.

**Discussion**

For a long time and, because of the fact that some theoretical works established that the long-range crystalline order was impossible in a strictly 2D material, GR was considered as only a reference structure that is found in the origin of other type of stable structures with which one is more familiarized, e.g., CNTs, fullerenes or simply C$_{graphite}$ itself [82]. Not by the fact that it was considered as a hypothetical material, it left of being in the mind of some researchers. The first and practically unique intuitions of obtaining GR were based on chemical exfoliation where C$_{graphite}$ adequately intercalated, could present considerably separated GR sheets. The compound so formed resulted, however, of scarce interest.

From purely geometrical considerations the columnlet (GR/GR-BUD), bundlet (SWNT/NT-BUD) and droplet (fullerene) cluster models predict different behaviours. (1) Spheres (droplet) pack in three dimensions (3D), while cylinders (bundlet) do equivalently to circles in 2D and sheets (columnlet) stack against 1D. The $C_{60}$ clusters can be greater than SWNT/NT-BUD bundles than GR/GR-BUD stacks, because of $C_{60}$ > SWNT/NT-BUD > GR/GR-BUD additional curvatures and dimensions. (2) The co-ordination numbers are: CN$_{droplet}$ = 12, CN$_{cylinder}$ = 6 and CN$_{column}$ = 2. As surface affects energy [Eqs. (10), (10') and (10'')] on changing the number of atoms the clusters should present discontinuities in areas and stability, especially about the corresponding co-ordination numbers. Consequently a discontinuity is expected between closed (C$_{60}$)$_{13}$ and open (C$_{60}$)$_{14}$ (droplet); the same happens between stopped up SWNT/NT-BUD$_3$ and ajar SWNT/NT-BUD$_7$ (bundlet), and connecting congested GR/GR-BUD$_2$ and unlocked GR/GR-BUD$_1$ (columnlet), which different sizes are in concordance with $C_{60}$ > SWNT/NT-BUD > GR/GR-BUD extra curvatures and dimensions. (3) Smaller clusters are of the least consideration in columnlet, bundlet and droplet models because all three approaches are valid when n >> 1 unit. (4) It has not escaped our notice that aggregates near (C$_{60}$)$_{13}$, SWNT/NT-BUD, and GR/GR-BUD$_2$ could be representative of the droplet, bundlet and columnlet models, respectively, with different sizes in agreement with $C_{60}$ > SWNT/NT-BUD > GR/GR-BUD added curvatures and dimensions. However, all our calculations were performed with the whole size distribution. (5) Because spherical (2D-curved) $C_{60}$ is more reactive than cylindrical (1D-bended) SWNTs than sheet (straight) GR, a greater dispersion in the results of $C_{60}$ cluster size (n = 13) is expected, with regard to lesser reactive SWNTs that are waited more uniform in SWNT$_n$ (n ~ 7) and least reactive GR$_n$ that are anticipated more consistent in GR$_n$ (n = 3). In addition $C_{60}$ is more soluble than SWNTs than GR in organic solvents. (6) The GR is strongly influenced by the materials it comes into contact with, whether solid, liquid or gas. (7) Strictly 2D (single layer) GR is rarely pristine since it contains a number of impurities, C or foreign ad-atoms, vacancies, etc., and the finite crystalline size and support-related-effects, e.g., conformity, wrinkles, etc. For a group of potential applications the presence of those defects provides interesting properties related to the spin phenomena, for advanced nanoelectronics and to make possible the attachment of specific molecules. (8) In the investigation at the atomic scale of the impact that atomic defects have on the structural, electronic and magnetic properties of GR layers grown on different materials the pure bidimensionality of GR gives to these defects a critical role. (9) The study of the coupling of GR with its local environment is absolutely critical to be able to integrate it in tomorrow’s electronic devices. (10) The atomically thin single-crystal membranes offer ample scope for fundamental research and new technologies, whereas the observed corrugations in the third dimension may provide subtle reasons for the stability of 2D crystals.

The microscopic dimensional considerations above present macroscopic effects. In a linear chain, for a linear model the square fluctuation is proportional to the distance because the amplitude of the fluctuation rises with the squared remoteness. It is because of this circumstance that one should attribute the origin of the qualitative distinction that exists between the solid and liquid states. In a liquid, the coherence is conserved at only long distances while naturally the neighbouring atoms preferably form the arrangements of minimal energy. In the 1D case, the difference between solid and liquid will be only quantitative and instead of a well-determined fusion point there will be a continuum passing.

**Conclusions**

From the discussion of the present results the following conclusions can be drawn.

1. The nanoworld structural diversity is a consequence of its quantum nature. Several criteria reduced the analysis to a manageable number of magnitudes, viz. closeness, curvature, dimension and efficiency. Our non-computationally intensive approach, i.e., object clustering plus property prediction, assessed reliability. Type, dimensions and producer selection of fullerenes, nanotubes and graphenes must be chosen to ensure the transfer of methods developed between laboratories. Our interaction energy parameters for nanobuds are taken from $C_{60}$. For nanotube bud an $C_{60}$/tube intermediate behaviour was expected. However, nanotube-bud properties result closer to tubes. Thinner nanotube-bud bundles appear less stable but wider ones are more stable than tube packages.

2. Association energy parameters of nanographene are obtained from $C_{60}$. A nanotube-bud behaviour or further was expected. For C$_{graphene}$ nanobud an $C_{60}$/C$_{graphene}$ in-between behaviour was anticipated. Notwithstanding, nanobud features appear closer to C$_{graphene}$. Shorter nanobud stacks result less stable but longer ones appear more stable than C$_{graphene}$ columns. The solubility decays with temperature result smaller for C$_{graphene}$/bud than nanotube/bud than $C_{60}$, in agreement with lesser numbers of units in clusters. The discrepancy between experimental data for the heat of solution of fullerenes, nanotubes, graphenes and their buds is ascribed to the sharp concentration dependence for the heat of solution. The
diffusion coefficient drops with temperature result greater for $C_{graphene}$/bud than nanotube/bud than $C_{opt}$, corresponding to lesser number of units in aggregates.

3. Some systems are dominated by the isolated pentagon rule, some others are not. Further work will explore similar nanostructures nature: generalization to systems more complex; e.g., a way of bypassing weak homonuclear bonding exists in closed $B_N$, involving replacement of 5-membered by 4-ring $B_N$, with heteroatom alternation, $BN$/AlN tubes/heterojunctions, silicene, germanene and carbine. The C-nanostructures are more controllable while heterostructures present richer behaviour, especially for transition-metal compounds, showing lubricant and electronic uses.

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References


