

Molecular dynamics simulations of the interaction of carbon nanotube and a carbon disulfide solvent

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ABSTRACT

An analysis of the molecular dynamics (MD) of the interaction between a carbon nanotube (CNT) and a carbon disulfide active solvent (CS₂) has been carried out. The aim of the present work is to estimate the dynamical and structural behavior of the CNT-CS₂ system at different relative atomic concentrations and under temperature changes. The structural radial distribution functions and the dynamical configurations have been built for a CNT interacting with a CS₂ solvent. A nontrivial observation for the CNT-CS₂ system is that the solvent carbon disulfide atoms make up a patterned (layered) formation around the carbon nanotube.

Keywords: Molecular Dynamics; Carbon Nanotube; Carbon Disulfide Solvent

1. INTRODUCTION

Among the organic materials, carbon Nanotubes (CNTs) are unique for their electrical and chemical properties. They are very interesting in terms of material research and electronic applications. Depending on their chemical structure, carbon nanotubes (CNTs) can be used as an alternative to organic or inorganic semiconductors as well as conductors. The chemical bonding of nanotubes is composed entirely of sp² bonds, similar to those of graphite. This bonding structure, which is stronger than the sp³ bonds found in diamonds, provides the molecules with their unique strength. Nanotubes naturally align themselves into "ropes" held together by van der Waals forces. The nature of the bonding of a nanotube is described by quantum chemistry—specifically, orbital hybridization. Solvents in which the CNTs can be solubilized include chlorobenzene, chloroform, methylene chloride, carbon disulfide, benzene, etc. The solubilities

of the carbon nanotubes in these solvents range from about 0.01 to 5.0 mg/ml [1-4].

The aim of the present paper is to simulate the dynamical and structural properties of a CNT interacting with a carbon disulfide (CS₂) solvent taking into account the Van der Waals forces only. For the CNT-CS₂ system, we simulate different relative CNT solvent concentrations and temperature scales. In the description of the physical properties of the CNT, we employ the Tersoff potential [5]. It is a special case of a density-dependent potential, which reproduces the properties of the covalent bonding in systems containing carbon, silicon, germanium, etc, and alloys of these elements. A special feature of the potential is that it allows bond breaking and associated changes in bond hybridization. The energy is modelled as a sum of pair-like interactions where, however, the coefficient of the attractive term in the pairlike potential (which plays the role of the bond order) depends on the local environment giving a many-body potential.

The Tersoff potential has 11 atomic and 2 bi-atomic parameters (see, formulas 1-9):

$$U_{ij} = f_C(r_{ij})[f_R(r_{ij}) - \gamma_{ij}f_A(r_{ij})], \quad (1)$$

where the potential parameters have the following forms:

$$f_R(r_{ij}) = A_{ij} \exp(-a_{ij}r_{ij}), \quad (2)$$

$$f_A(r_{ij}) = B_{ij} \exp(-b_{ij}r_{ij}), \quad (3)$$

$$f_C(r_{ij}) = \frac{1}{2} + \frac{1}{2} \cos[\pi(r_{ij} - R_{ij}) / (r_{ij} - S_{ij})], R_{ij} < r_{ij} < S_{ij}, \quad (4)$$

In (1) $f_R(r_{ij})$ and $f_A(r_{ij})$ mean repulsive and attractive, $f_C(r_{ij})$ —potential cutoff functions ($f_C(r_{ij}) = f_C(r_{ij}) = 1$ for $r_{ij} < R_{ij}$ and $f_C(r_{ij}) = 0$ for $r_{ij} > S_{ij}$).

It is worth noting that the main feature of the Tersoff potential is that the coefficients in (1) reflect many-body

nature of the interactions. The basic means of the coefficients is that the strength of each bond depends on the local environment and is lowered when the number of neighbors is relatively high. This dependence can accentuate or diminish the attractive force relative to the repulsive force, according to the environment, such that:

$$\gamma_{ij} = \chi_{ij} (1 + \beta_i L_{ij}^{\eta_i})^{-1/2\eta_i}, \quad (5)$$

$$L_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) \omega_{ik} g(\theta_{ijk}), \quad (6)$$

$$g(\theta_{ijk}) = 1 + c_i^2 / d_i^2 - c_i^2 / [d_i^2 + (h_i - \cos \theta_{ijk})^2], \quad (7)$$

$$a_{ij} = (a_i + a_j) / 2, \quad b_{ij} = (b_i + b_j) / 2, \quad (8)$$

$$A_{ij} = (A_i A_j)^{1/2}, \quad B_{ij} = (B_i B_j)^{1/2}, \quad A_{ij} = (A_i A_j)^{1/2}, \\ R_{ij} = (R_i R_j)^{1/2}, \quad S_{ij} = (S_i S_j)^{1/2}. \quad (9)$$

We have accepted the following values: $\chi_{ii} = 1$, $\chi_{ij} = \chi_{ji}$, $\omega_{ii} = 1$, $\omega_{ij} = \omega_{ji}$.

The carbon disulfide (CS₂) solvent has a comparatively high solubility (~7.9 mg/ml). Several earlier papers considered interaction between the CS₂ solvent and a fullerene (C₆₀) solution [6-12]. The C₆₀-CS₂ system belongs to a class of solutions where a peak in the temperature dependence of solubility is observed ($T_{\max} \sim 280$ K). The structural features of the fullerene in a solution, as well as the fullerene-solvent (C₆₀-CS₂) interaction mechanism have been investigated in detail in [6-12] by different methods (small-angle neutron scattering (SANS) and others). As was noted in [12], the characteristic size of the CS₂ molecule (~0.3 nm) is comparable to that of the C₆₀ fullerene (~1 nm); so, any interface organization of the CS₂ molecules different from that in bulk must result in a significant difference between the interface and bulk molecular density of the solvent, and, hence, affect the visible size of the fullerene.

2. MATERIALS AND METHODS

We performed the molecular dynamics (MD) simulation of several CNT-CS₂ model systems. The MD simulation was based on the DL_POLY general-purpose code [13-15]. The MD cell is orthorhombic and square in the XY plane (30.7 × 30.7 × 41.7). The integration algorithm is an NPT Berendsen 'ensemble'.

The CNT (carbon nanotube) consists of 800 carbon atoms in a nanotube of 41.7 angstrom in length (see **Figure 1**). For the CNT, we used the Tersoff potential parameters of the DL_POLY software database [13-14]:

$$A = 1393.6, \quad a = 3.4879, \quad B = 346.74, \quad b = 2.2119, \\ R = 1.8, \quad S = 2.1, \\ \beta = 1.5724 \times 10^{-7}, \quad \eta = 0.72751, \quad c = 38049, \quad d = 4.3484, \quad h = -0.57058.$$

The CS₂ molecules were treated as rigid with the bond length of 1.55 angstrom between carbon and sulfide atoms (**Figure 2**). Throughout the computation, only the Lennard-Jones (LJ) interactions were taken into account. The number of the CS₂ solvent molecules was varied, so we simulated CNT-solvent model systems of different relative atomic concentrations: $x = 0.2, 0.4, \dots, 1.0$ (**Figure 3**). The LJ potential was also used for the CNT-solvent interactions; the potential and parameters are shown in **Table 1**, where C denotes the CNT carbon

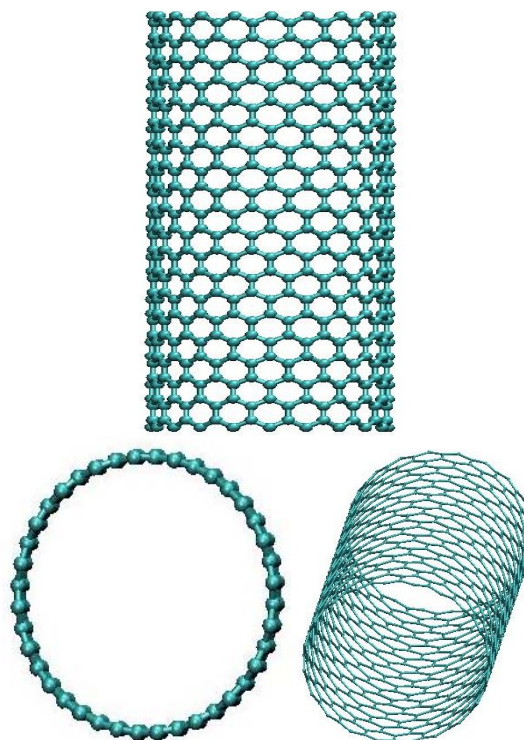


Figure 1. Structural presentations of the carbon nanotube (CNT) (top and bottom).

Table 1. Potential parameters of the CNT-CS₂ model.

Atomic pair	Potential	Functional form	Parameters	ϵ , eV	σ , Å
C-C _s	Lj	$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$	ϵ, σ	0.0044	3.35
C-S	Lj	...	ϵ, σ	0.0082	3.44
S-S	Lj	...	ϵ, σ	0.0153	3.52

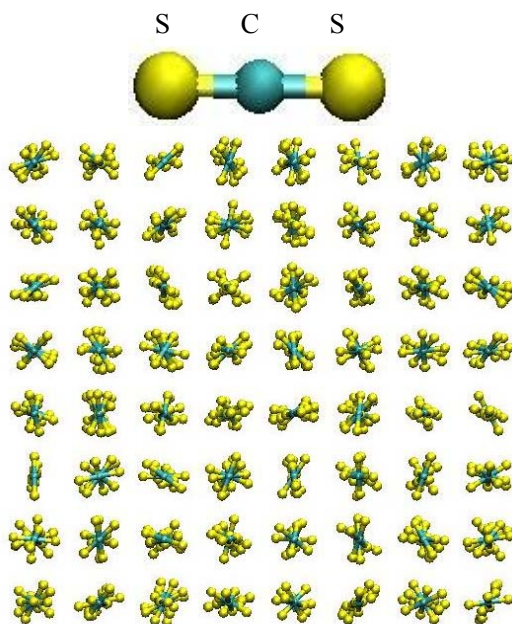


Figure 2. Structural presentations of the CS₂ solvent (top and bottom).

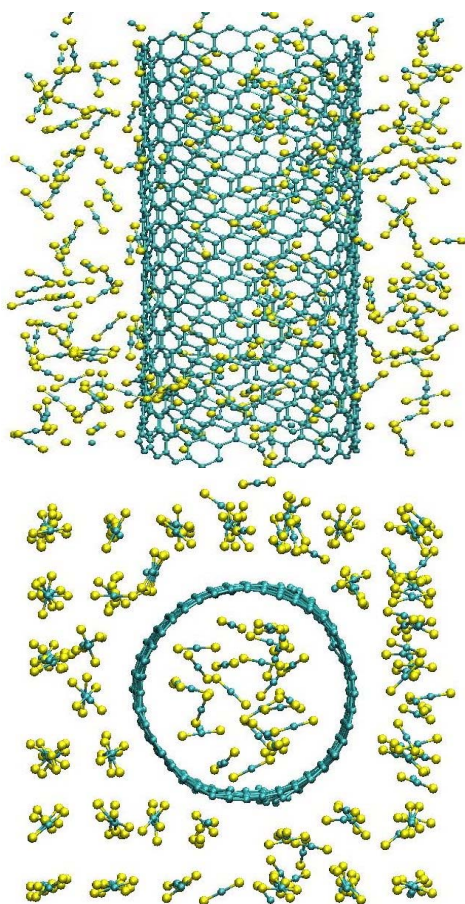


Figure 3. Structural presentations of the CNT-CS₂ system (top and bottom).

atoms and C_s—the carbon atoms of the CS₂ solvent.

3. RESULTS AND DISCUSSIONS

The dynamics of the interaction between the CNT (carbon nanotube) and the CS₂ solvent has been studied at different ratios of the CNT-solvent atomic concentrations:

$$x = \frac{N_s}{N_{CNT}}$$

where N_s is the number of the solvent atoms and N_{CNT} is the number of the CNT atoms. We have simulated five CNT-CS₂ systems with $x = 0.2, 0.4, 0.6, 0.8$ and 1 . We call the systems with $x = 0.2$ and $x = 1$ low- and high-density systems, respectively. The CNT consists of 800 carbon (C) atoms. Further, we denote the carbon atoms of the CS₂ solvent as C_s.

3.1. Structural RDFs for the CNT-Solvent Atomic Pairs

In **Figure 4**, we present the behavior of the radial

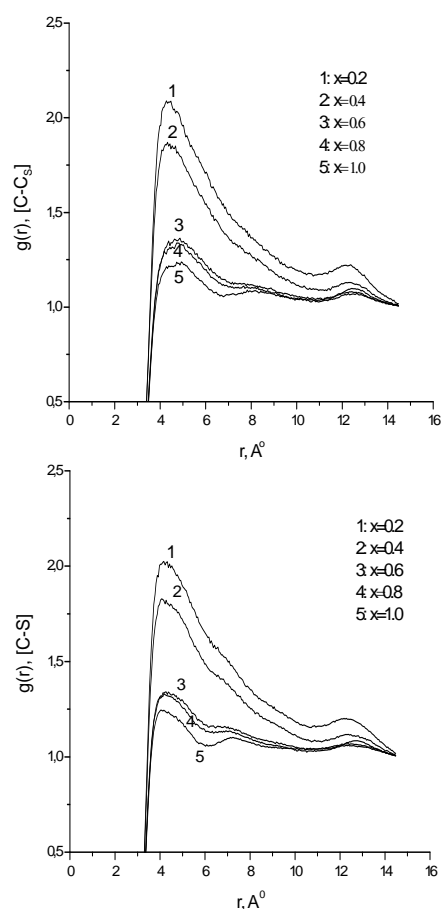


Figure 4. Structural RDFs for the atomic pairs C-Cs and C-S at different ratios of the CNT-solvent atomic concentration x .

distribution function (RDF) for the CNT-solvent atomic pairs C-C_s and C-S at different values of x . It can be seen that the RDF of the CNT-CS₂ system at $x > 0.4$ obeys a similar law. For all values of x , we have clearly observed two peaks in the RDF graphs. However, for $x > 0.4$, **Figure 4** shows an additional small RDF peak between the first two ones. This behavior of the RDF points to a structural rearrangement of the CNT-CS₂ system, which is going from the low density phase ($x = 0.2$) into the high density phase ($x = 1$). The additional (third) peak in the RDF curve has also been observed on the temperature dependence (part III below).

3.2. Structural RDFs for the Solvent-Solvent Atomic Pairs

In **Figure 5** and **6**, the radial distribution functions (RDFs) are presented for the solvent-solvent atomic pairs (C_s-C_s, C_s-S, and S-S) at different values of x . It is seen that the RDFs of the solvent atoms differ from each other by their first peaks only; the secondary peaks for all solvent-solvent atomic pairs (CS₂-CS₂) are similar. The RDF for the S-S atoms has a comparably large first

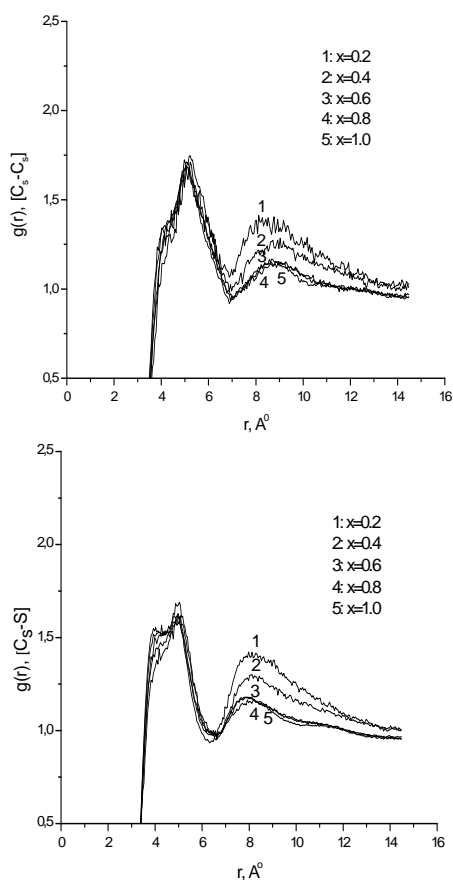


Figure 5. Structural RDF for the atomic pairs C_s-C_s and C_s-S at different ratios of the CNT—solvent atomic concentration x .

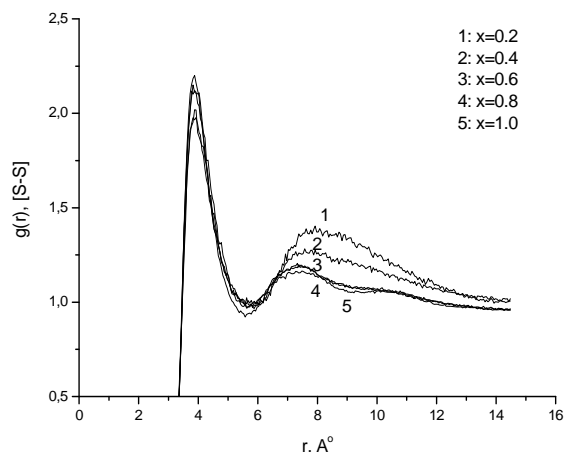


Figure 6. Structural RDF for the atomic pair S-S at different ratios of the CNT—solvent atomic concentration x .

peak (**Figure 6**). This indicates that in the solvent media, the atomic pair S-S has a relatively high ordering in comparison with the C_s-C_s one. The RDF first peak for the C_s-S atomic pair (**Figure 5**, right) is low as compared with S-S ones. We attribute such behavior to an influence of CNT's carbon (C) atoms on the CNT—solvent interaction process and ordering.

3.3. MD-Simulated Structural CNT-CS₂ Configurations

We have compared the MD structural configurations of the CNT-CS₂ system for the low-density ($x = 0.2$) and high-density ($x = 1$) phases. In **Figure 7**, MD-simulated snapshots are presented for $x = 0.2$. **Figure 7** shows the side and top views (left and right, respectively) of the CNT-CS₂ system; the snapshots correspond to the moments of $t = 0$ (top), 10 ps (middle), and 80 ps (bottom). It is seen that starting from arbitrarily distributed positions at the initial ($t = 0$) state, the solvent (CS₂) atoms become more structured in the later states of the dynamics around and inside the CNT.

The CS₂ structuring behavior around the CNT has also been observed during temperature variation in the CNT-CS₂ system. In **Figure 8**, the RDF curves are displayed for the low density phase ($x = 0.2$) depending on temperature: $T = 200$ K (1), $T = 250$ K (2), and $T = 300$ K (3). **Figure 8** shows the RDF results for CNT-solvent atomic pairs C-C_s (left) and C-S (right). The RDFs in **Figure 8** show some RDF changes (only for the first peaks).

Figure 9 shows RDF curves for the solvent-solvent atomic pairs C_s-C_s (left) and C_s-S (right). A visible change in the RDF graph is seen for the atomic pair C_s-S. During the temperature variation, we observe changes for C_s-S both in the first and secondary peaks.

As seen in the RDF graph in **Figure 10**, the atomic

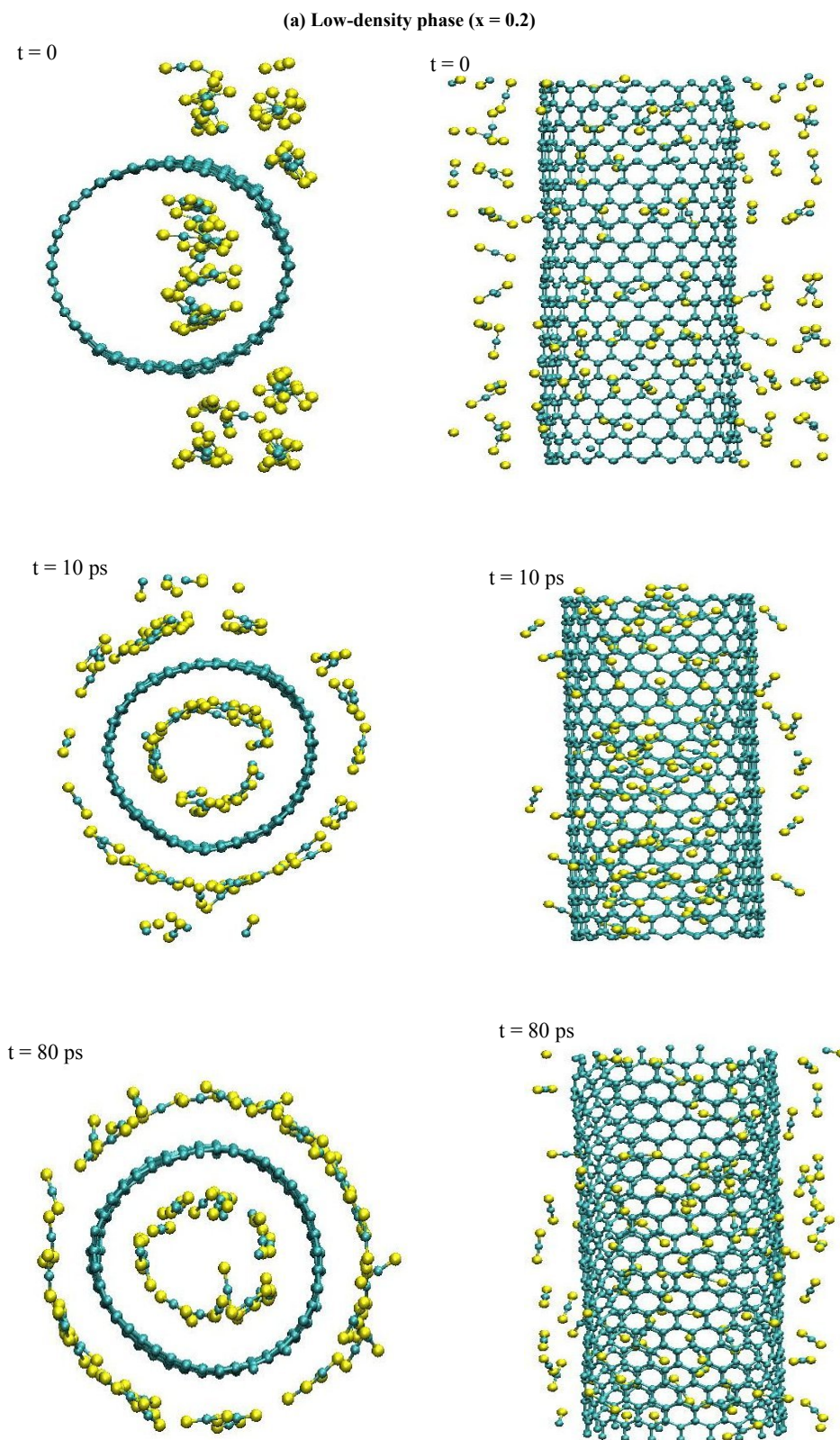


Figure 7. Snapshots of the CNT—solvent configurations at a low density (relative atomic concentration $x = 0.2$).

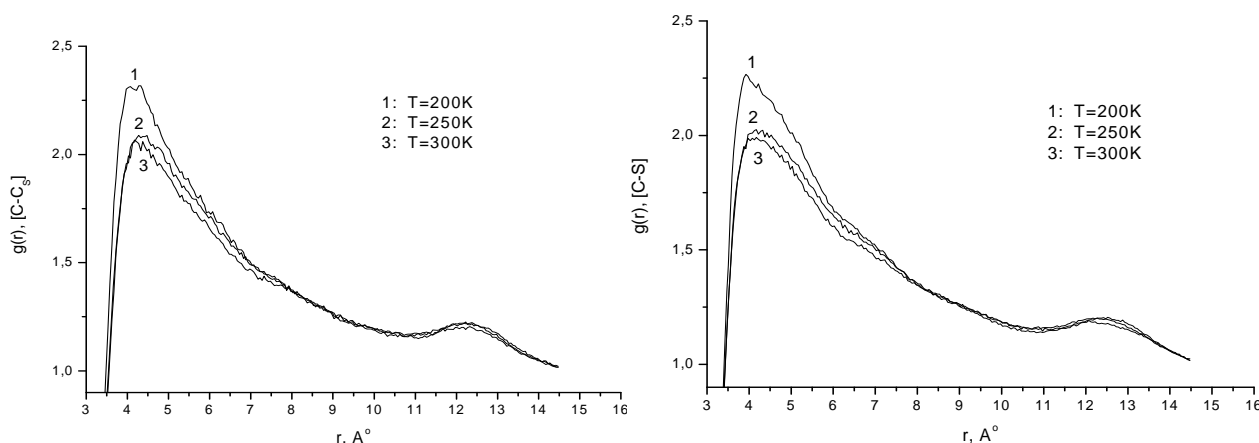


Figure 8. Structural RDFs for the atomic pairs C-Cs and C-S at $x = 0.2$ with temperature.

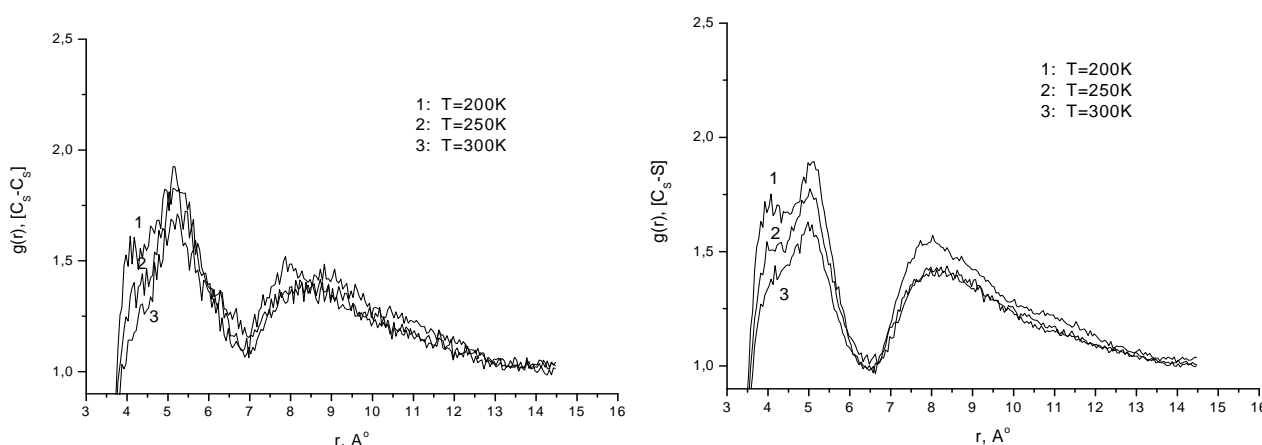


Figure 9. Structural RDF for the atomic pairs Cs-Cs and Cs-S at $x = 0.2$ with temperature.

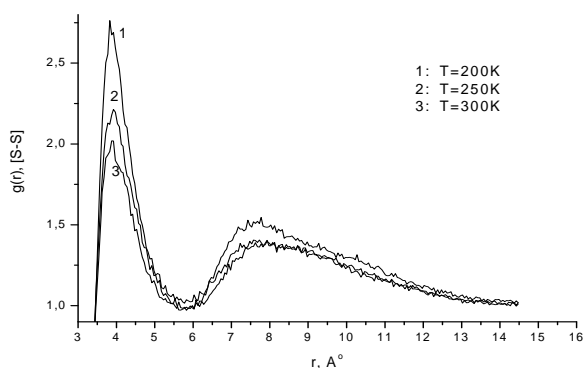


Figure 10. The structural RDF for the atomic pair S-S at $x = 0.2$ with temperature.

pair S-S has a relatively high ordering in the solvent media. Also, the RDF for the S-S pair shows a strong temperature dependence. We see that the amplitude of the first peak decreases twice as the temperature increases from $T = 200$ K to 300 K.

In **Figure 11**, the MD snapshots are presented for the high density phase ($x = 1$).

Comparing these results with those of the low density phase ($x = 0.2$, **Figure 7**), we observe a similar structural formation of the CS_2 solvent atoms around the CNT. However, the RDFs of the high-density phase are strongly specific against the low-density phase RDFs. A comparison of **Figures 12-14** with **Figures 8-10** is straightforward.

3.4. Patterned Structure Formation in the CNT- CS_2 System

One of the nontrivial observations for the CNT- CS_2 system is that the solvent carbon disulfide atoms make up a patterned (layered) formation around the carbon nanotube. In **Figure 15**, we present a CNT- CS_2 resultant structure where the atomic distributions are compared in three regions (marked by the circles 1, 2, and 3). It is seen that in regions 1 and 2, the solvent CS_2 atoms have to be configured similarly to CNT's shape. The solvent atoms inside and outside the CNT are regularly distributed within the spheres of the same radii off the CNT. In contrast, for region 3 we observe an

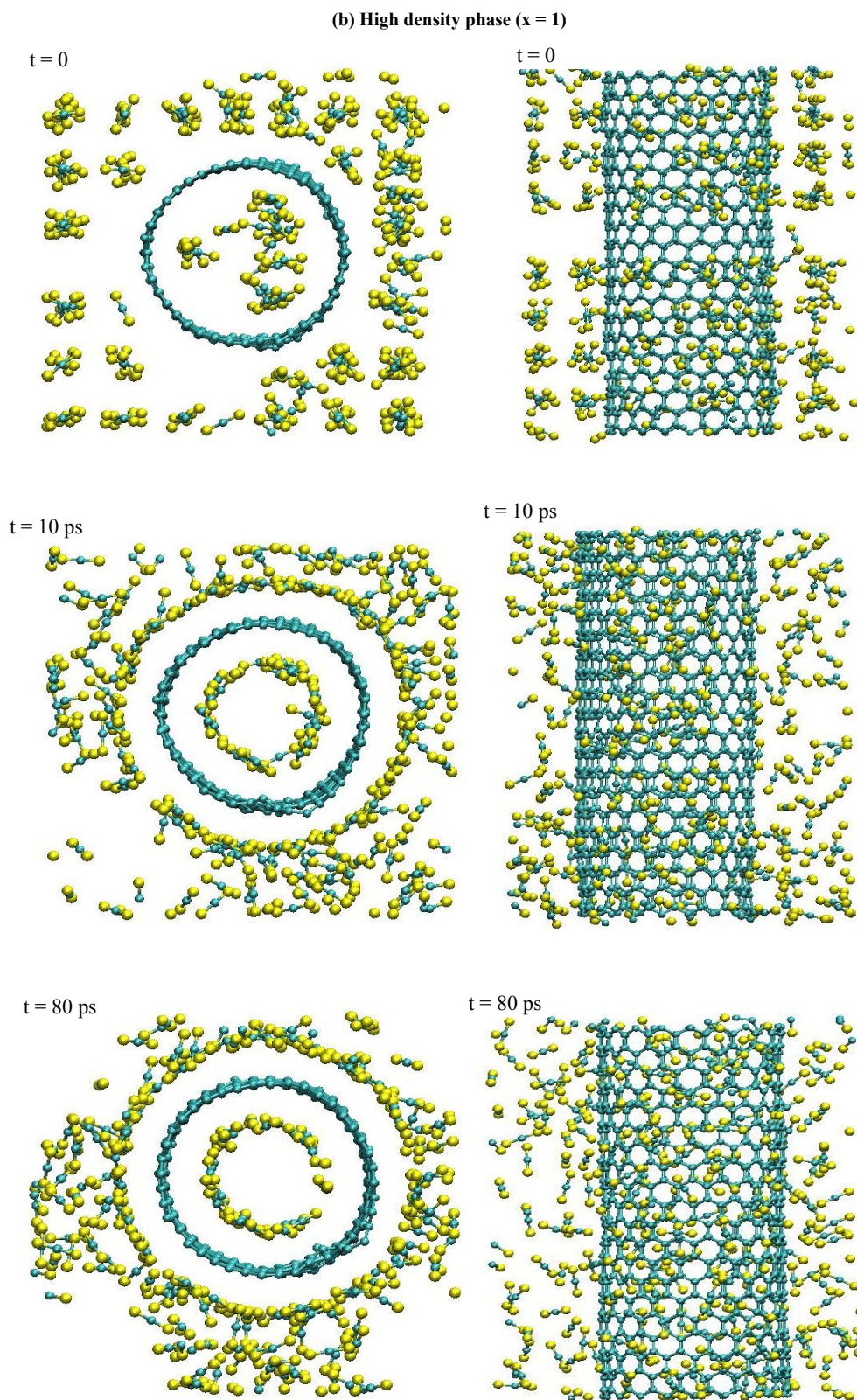


Figure 11. Snapshots of the CNT—solvent configurations at a high density (relative atomic concentration $x = 1$).

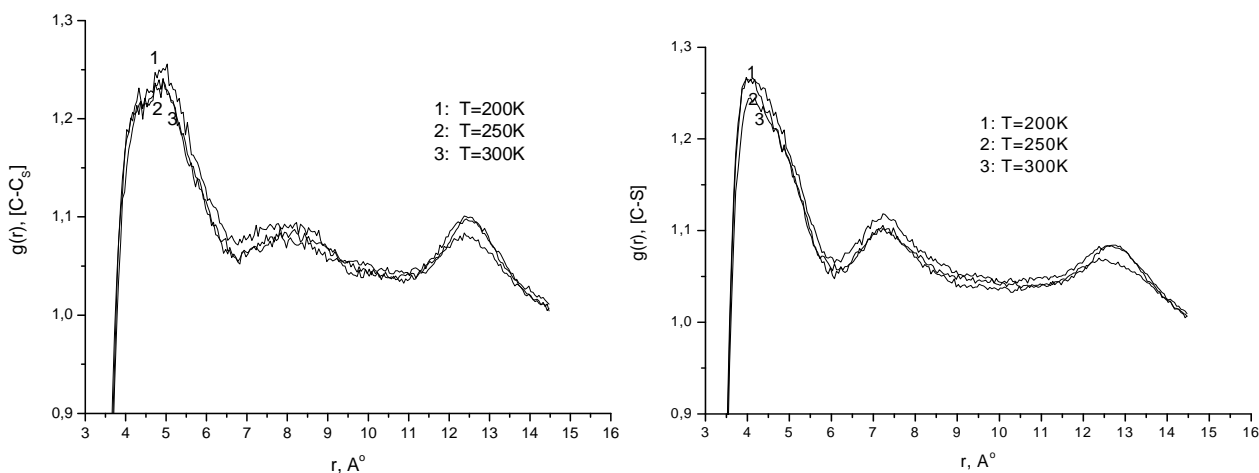


Figure 12. Structural RDFs for the atomic pairs C-Cs and C-S at $x = 1$ with temperature.

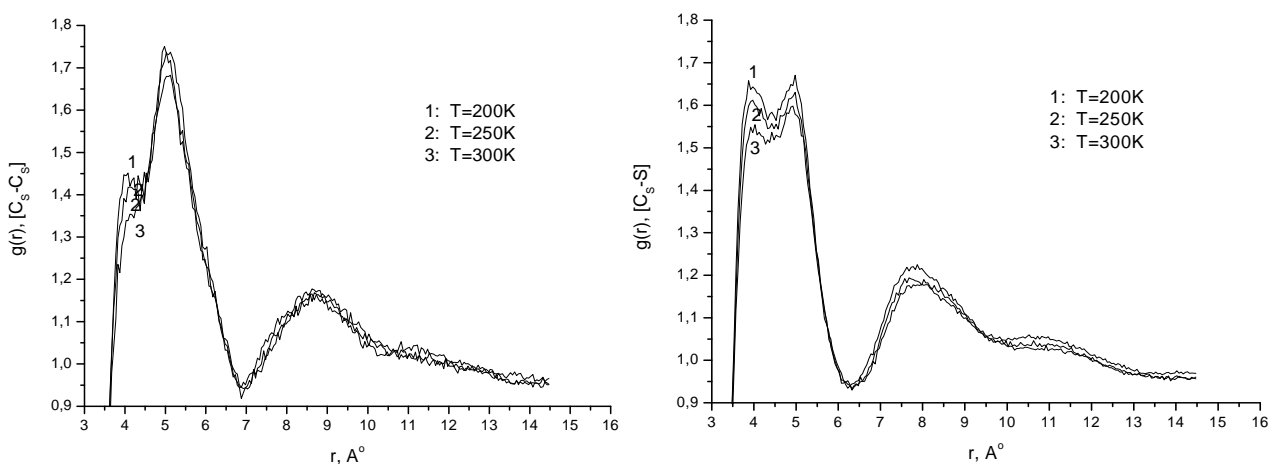


Figure 13. Structural RDFs for the atomic pairs Cs-Cs and Cs-S at $x = 1$ with temperature.

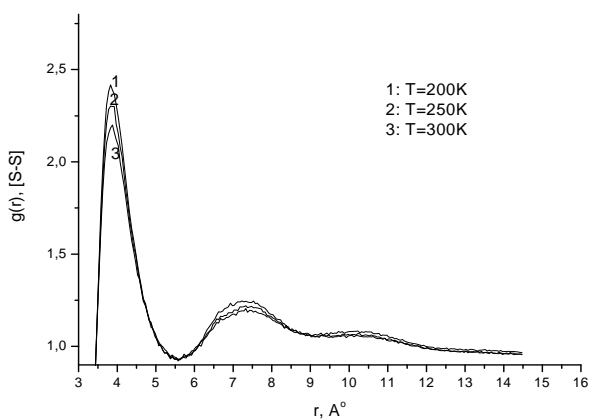


Figure 14. Structural RDF for the atomic pair S-S at $x = 1$ with temperature.

irregular structure of the same atoms that results from solvent-solvent interaction. It should be noted that **Figure 15** shows an important example of a graphene-

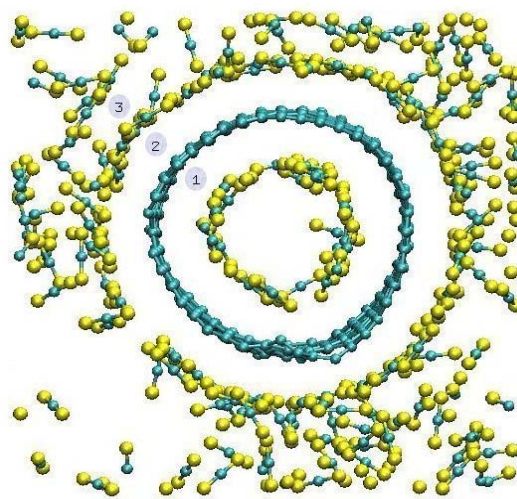


Figure 15. The CNT-CS2 atomic distributions for three regions shown as circles 1, 2, and 3.

like (patterned, layered) behavior. Such formations are of great importance for the applications and technological uses of the CNT-CS₂ systems [1-12].

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