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Influence of Buffer Gas and Vibration Temperature of Carbon Clusters on Fullerene Formation in a Carbon Plasma

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A new model of fullerene formation in carbon containing plasma is proposed. The model takes into account carbon cluster heating and cooling during transformations due to chemical bonds formation and destruction. In addition, the heating and cooling of carbon clusters by buffer gas is considered. The calculations give the qualitatively correct correlation between fullerene yields in helium and argon.

Keywords: Fullerenes, Buffer Gas, Low-Temperature Plasma, Modeling.

1. INTRODUCTION

In 1985, the discovery of buckminsterfullerene prompted a flurry of activity as scientists sought to characterize this new form of carbon and produce its bulk quantities. When bulk synthesis was achieved by Krätschmer et al.[1] in 1990, scientific investigation of fullerene intensified and diversified as various research groups produced a wide array of both endohedral and exohedral derivatives. Though there are many works devoted to the formation fullerenes and their derivatives in carbon containing plasma, the mechanism of their formation has not been fully clarified yet.[2,3]

Up to now majority of articles concerning the fullerene formation were devoted to the reactions of intermediate neutral carbon clusters and processes of their transformation. The most perspective models consider these precursor clusters as polycyclic rings,[4] smaller fullerenes of 30–40 atoms,[5] and non-classical fullerenes with heptagons.[6] Unless few exceptions,[7,8] the role of charges of clusters in the process of their coagulation was generally outside the research scope. In Ref. [7] it was demonstrated experimentally that formation of fullerenes in ionized carbon plasma is more efficient than the synthesis in neutral carbon vapor. Theoretically the reactions between charged and neutral carbon polycyclic structures were considered.[8] In addition, in all articles before the role of cluster inner temperature, which is connected with phonon excitation in the cluster (vibration temperature), was out of scope. But obviously that formation or destruction of chemical bonds in the cluster would strongly change this temperature because of high energy of C–C bond. So the cluster vibration temperature variation would change all processes of carbon clusters transformation during fullerenes formation. Also the role of buffer gas molecules in balancing of vibration and kinetic (connected with forward cluster movement) cluster temperatures was not taken into consideration.

In our previous articles,[9,10] it was proposed a new model of fullerene formation in carbon-buffer gas plasma. The model described evolution of different carbon cluster concentration C_k at their coagulation during fullerene formation. Instead of description of detailed transformation of precursor clusters into fullerenes, the model elucidated an important role of cluster charges, temperature, and electron concentration in plasma to the fullerene yield. All essential cluster parameters (electron affinity, ionization potentials, cross section) were calculated by averaging of these parameters for different clusters with fixed distribution derived from experiments.

The model considered an influence of carbon clusters charges on the cross section of cluster collisions. But again the heating/cooling processes of carbon clusters and buffer gas influence was out of the scope. Moreover, all carbon clusters were differed only by number of atoms, but not the number of dangling (radical) bonds in the cluster.

In this study, we present a new theoretical model of fullerene formation in carbon containing plasma. In this model unaccounted earlier factors are taking into account. First of all, in the model all carbon clusters are described by the reduced description scheme, firstly proposed in Refs. [11, 12]. In this scheme all carbon clusters are distinguished by both the number of cluster atoms n and number of free radical bonds l in the cluster, so

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concentration $C(n, l)$ of every kind of cluster in the plasma depend on n, l. As more stable form of small carbon clusters condensed from plasma are the clusters with sp or sp^2 hybridization (chains, rings, sections of grapheme planes, and their combinations), in the model we consider carbon atoms with 0, 1, or 2 radical bonds per atom only. At that fullerene molecules would not have radical bonds ($l = 0$); monocyclic clusters have one radical per atom ($l = n$); chain clusters have one radical bond per atom, except terminal atoms ($l = n + 2$). All other clusters (bi-, tricyclic, and unclosed fullerene shells) would contain intermediate number of radicals per atom. At this stage of model development we keep in mind the fullerenes C_{60} and C_{70} only because they are effectively obtained in experiments. Therefore in the calculations only the clusters with $n = 60$ and 70 could have zero number of radicals ($l = 0$).

This reduced scheme allows to distinct clusters of different shape and to trace the cluster transformation which usually reduce number of free radical bonds in the cluster during annealing. At that this scheme is quite simple to use it in intensive calculations of cluster kinetics.

At second, in the model all cluster concentrations $C(n, l)$ include now information about cluster vibration temperature T: $C(n, l) \rightarrow C(n, l, T)$. The variation of carbon cluster temperature is the result of new carbon bonds formation/destruction in clusters. The cluster kinetic temperature is considered to be equal to the plasma temperature.

At third, the model takes into account the influence of the buffer gas to all clusters temperature. If the buffer gas temperature is T_{gas}, all carbon clusters having temperature $T < T_{\text{gas}}$ would be heated and clusters with $T > T_{\text{gas}}$ would be cooled.

At last, allow non-stationary process of fullerenes formation, the model observe evolution of every cluster concentration C during time t, so the cluster concentrations are depend on the time: $C(n, l, T) \rightarrow C(n, l, T, t)$. At that cluster distribution in space considered to be uniform, so the concentrations $C(n, l, T, t)$ do not depend on space coordinates r.

According to the model, processes of clusters collision involve information about three cluster concentrations:

$$\sum_{n_1, l_1, T_1} \sum_{n_2, l_2, T_2} (C(n_1, l_1, T_1, t) + C(n_2, l_2, T_2, t) \\ \rightarrow C(n_1 + n_2, l_1 + l_2 - 2, T_3, t))$$

Solving of such dynamic equations for cluster concentration require long-duration calculations. So in the calculations we fixed the plasma temperature $T_{\text{gas}} = 3000$ K and electron concentration $n_{\text{e}} = 10^{17}$ m^{-3}, which were close to the plasma parameters during fullerene synthesis.

2. CALCULATION DETAILS

The model describe the process of fullerene formation in the carbon contained plasma which consist from the buffer gas and different carbon clusters with concentration $C(n, l, T, t)$. To trace dependence of fullerene synthesis on buffer gas sort, in the calculations we have used He and Ar. At that the plasma is considered in the thermal equilibrium. Because of a mass-spectrometric analysis[13] of clusters during the fullerene formation has shown that the quantity of even clusters was larger than that of odd clusters by some orders, we have took into account the even carbon clusters only. To model graphite evaporation from graphite electrodes or plates which is the source of carbon clusters in the plasma-chemical synthesis, at the beginning of the modeling ($t = 0$) the dimer molecules C_2 were lived only, so $C(n, l, T, t) \neq 0$ at $n = 2$, $l = 4$. Here it were used experimental facts, that fullerenes are formed from very small clusters.[14]

According to the model, the kinetic equations for all cluster concentrations $C(n, l, T, t)$ were integrated over the time t. The concentrations $C(n, l_n, T_n, t)$ (1) were changed due to several processes. The main process was the process of cluster coagulation: concentration of a cluster C_n increased in reactions of coagulation of smaller clusters $C_k + C_m \rightarrow C_n$ ($k + m = n$) and decreased in reactions of coagulation of this cluster with others $C_n + C_p \rightarrow C_{n+p}$ ($n + p \leq n_{\max}$). These processes were described by reaction constants $K_{k,m}^{l_k, l_m}$ and $K_{n,p}^{l_n, l_p}$, respectively.

The second process was the process of cluster structure transformation with rate constant $M_n^{l_n}$. We considered this transformation as step-by-step association/dissociation of inner cluster bonds with respective decreasing/increasing of radical number l in the cluster. The third process was the process of cluster heating/cooling by buffer gas atoms with rate constant $N_n^{l_n}$. At that the processes of cluster dissociation were not taken into account due to high activation energy of cluster break-down. So, the total set of dynamic equations for all cluster concentrations was:

$$\begin{aligned} &\frac{d}{dt} C(n, l_n, T_n, t) \\ &\quad = \sum_{\substack{k+m=n \\ l_k + l_m - 2 = l_n}} K_{k,m}^{l_k, l_m} C(k, l_k, T_k, t) C(m, l_m, T_m, t) \\ &\quad - \sum_{n+p \leq 120} K_{n,p}^{l_n, l_p} C(n, l_n, T_n, t) C(p, l_p, T_p, t) \\ &\quad - M_n^{l_n} C(n, l_n - 2, T_n^+, t) - N_n^{l_n} C(n, l_n, T_n^*, t) \end{aligned} \qquad (1)$$

From the classical collision theory used for description of the process of two cluster (C_k, C_m) coagulation: $C(k, l_k, T_k, t) + C(m, l_m, T_m, t) \rightarrow C(k + m, l_k + l_m - 2, T_{km}, t)$ one can get the reaction constant $K_{k,m}^{l_k, l_m}$ which is equal $K_{k,m}^{l_k, l_m} = \sigma_{k,m}^{l_k, l_m} P_{k,m} \text{v}_{k,m} P_{\text{bond}}$; where $\text{v}_{k,m} = \sqrt{8T/\pi\mu_{k,m}}$ is the average relative velocity of both clusters, $\mu_{km} = m_k m_m/(m_k + m_m)$ is the reduced mass of C_k and C_m; $\sigma_{k,m}^{l_k, l_m} = \sigma_{k,m}^{l_k, l_m}(q_k, q_m)$ is the cross-section of two cluster collision depending on the cluster charges q_k, q_m. We assume here that the cross-section $\sigma_{k,m}^{l_k, l_m} = \pi r_b^2 l_k l_m$ of two cluster coagulation is proportional to the numbers of free radical bonds l_k è l_m in the both clusters.

It means that both clusters can be associated together in the places of dangling radical bonds only. r_b here is the affected zone of single free radical bond influence. In all calculations $r_b = 1.7$ Å have been used. After coagulation the number of radical bonds in joined cluster was equal $l = l_k + l_m - 2$. Further decreasing of l would be happened at subsequent internal transformation of the cluster. At that just after coagulation the joined cluster temperature is $T_{k+m} = (kT_k + mT_m)/(k+m)$, where k and m are the number of atoms in clusters C_k and C_m.

Energy barrier E_a for both clusters association lead to modification of the rate of coagulation on Arrenius factor $P_{\text{bond}} = e^{-E_a/T_{\text{gas}}}$, where T_{gas} is the plasma temperature. Due to extreme complexity of E_a calculations for all clusters, it was used an average value $E_a = 2.0$ eV, received from Ref. [15].

According to the collision theory of charged particles, if the clusters C_k and C_m have charges q_k and q_m respectively, the cross-section of the cluster collisions $\sigma_{k,m}^{l_k,l_m}$ is multiplied on factor $P_{k,m}$:

$$P_{k,m} = \sum_{q_k=-2}^{+1} \sum_{q_m=-2}^{+1} \left(1 - \frac{q_k q_m \cdot p_k p_m}{\varepsilon_{\text{kin}}(r_k + r_m)}\right)$$

Here $r_k + r_m$ is the sum of the effective radiuses of both clusters which determine the minimal possible distance between them; ε_{kin} is the average relative kinetic energy of both cluster movement; $p_k(q_k)$ and $p_m(q_m)$—the probabilities of both cluster to have the charges q_k and q_m. These probabilities are defined for every cluster C_k by Saha equations:[16]

$$\frac{p_k(q+1)\cdot n_{\text{e}}}{p_k(q)} = 2\left(\frac{m_{\text{e}} k_B T_{\text{gas}}}{2\pi\hbar^2}\right)^{3/2} \frac{Z_k^{q+1}}{Z_k^q} \exp(-IP_k^q/k_B T_{\text{gas}}),$$
$$q = -2, -1, 0, +1$$

where IP_k^q is the ionization potential of cluster C_k^q, having a charge q; $Z_k^q(T_{\text{gas}})$ is the electronic statistical sum for the cluster C_k with charge q at temperature T_{gas}, n_{e} is the electron concentration in plasma.

In our calculations we have used charges $q_k = \{-2, -1, 0, 1\}$ for all clusters, because ionization potentials and electron affinities for all clusters with other charges are very large, so the probability of their existence in the plasma is negligible. The IP_k^q values for every cluster C_k have been calculated as the differences between binding energies $E_k(q_k)$ of this cluster having different charges q_k.

In all calculations the E_k values were calculated using VASP package.[16,17] This package allows one to make *ab initio* calculations basing on the plane wave decomposition and the Vanderbilt type pseudopotentials[18] in the framework of DFT approach.

The values of IP_k^q were calculated for clusters C_2, C_4, C_8, C_{10}, C_{14}, C_{18}, C_{20}, C_{40}, C_{60}, C_{70}, and C_{80} of different shapes with different number of free radicals. By analogy with our previous work,[9] we used the cluster shapes consisted of hexagons or pentagons and hexagons only. If there were used some isomers of a cluster C_k, we calculated the average values of IP_k^q for this k. After that, the values of IP_k^q were interpolated for all $k \in \{2-120\}$.

For the processes of inner cluster transformation the constant M_n^l, could be calculated in the way similar with association processes:

$$M_n^l = \nu_{\text{phon}} \exp(-E_{\text{bar}}/k_B T_{n,l})$$

Here $T_{n,l}$ is the vibration cluster temperature, which is defined from the energy of cluster phonon vibrations. Because of difficulty of all phonon frequency calculations for all clusters, we used the average value $\nu_{\text{phon}} = 10^{11}$ s^{-1} for all clusters $C(n, l, T, t)$. This value was calculated by averaging of phonon frequencies for set of different carbon clusters.

The processes of cluster heating or cooling take place if the cluster vibration temperature $T_{n,l}$ differ from the buffer gas temperature T_{gas} (plasma temperature). Because of complexity of such cluster cooling/heating rate calculation, we applied a simple approach for such calculations. This approach used that an average velocities v_{gas} of buffer gas molecules at $T_{\text{gas}} \approx 3000$ K are $v_{\text{gas}} \approx 5 \cdot 10^3$ m/sec and interaction radius between gas molecule and carbon cluster is $\sim$1 Å. At that it is easy to estimate that time of both particle interaction $\tau_{\text{int}} \leq \nu_{\text{phon}}^{-1}$. So the collision of buffer gas molecule and carbon cluster can be considered as elastic interaction, so formulas for the particle momentum change during elastic impact are applicable.

Also we estimated the probabilities of inelastic processes of cooling/heating with involving of ionized or exited states of buffer gas atoms (He, Ar). The values of these probabilities are proportional to Arrenius-type factor $p \sim \exp(-E/k_B T_{\text{gas}})$ where E is ionization potential IP or first excitation energy E^* of the buffer gas atom. For argon and helium these values are: $IP_{\text{Ar}} = 15.8$ eV, $E^*_{\text{Ar}} \sim 10$ eV, $IP_{\text{He}} = 24.6$ eV, $E^*_{\text{He}} \sim 14$ eV correspondently. Even for the lowest of these energies $p \sim 10^{-15}$ at $T_{\text{gas}} = 3000$ K, so at temperature under consideration accounting of buffer gas ions or excited states can be omitted.

Assuming that energy of all phonon modes is distributed with equal probability among all cluster C_N atoms, it is easy to find average kinetic energy of every atom in the cluster: $\bar{\varepsilon}_{\text{kin}} \approx \frac{3N-6}{4} kT_{\text{nl}}$. Here the numerator is equal to the number of phonon modes in cluster, the denominator is account of energy of kinetic energy contribution (1/2) to the total energy of one phonon mode $(1/2 \cdot k_B T_{n,l})$. Because of spatial and cluster shape averaging, the normal to the cluster surface velocity of any carbon atom in average would be equal $\bar{\nu}_{\text{normal}} \approx \sqrt{2\bar{\varepsilon}_{\text{kin}}/3m_{\text{c}}}$, where m_{c} is carbon atom mass. Taking into consideration preceding formulas, it is easy to calculate the average part of kinetic energy which is passed between buffer gas molecule ($\bar{\varepsilon}_{\text{kin, gas}} \approx \frac{1}{2} kT_{\text{gas}}$) and a nearest to that molecule cluster carbon atom at their interaction. After that it easy calculate an average change of the cluster vibration temperature due to the collisions with buffer gas molecules. This change of cluster temperature $\tilde{f}(n, T_{n,l}, T_{\text{gas}})$ during

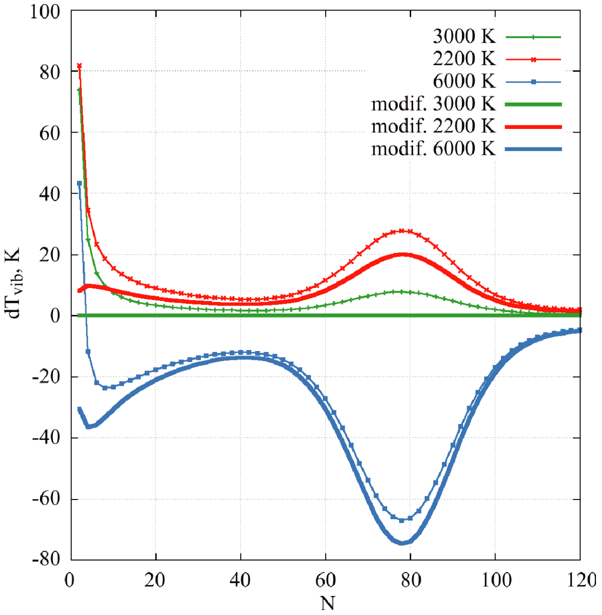

Fig. 1. Dependence of the rate of cluster vibration temperature change on number of atoms N in it due to collisions with He atoms for different cluster temperatures. The original (thin lines with markers) and corrected (thick lines) dependences are shown. dT_{vib} is average change of vibration temperature during one time step $\Delta t = 10^{-9}$ s.

one time step (10^{-9} s) is shown in Figure 1. In the Figure 1 one can see (thin lines with markers) that even this simple model quite good describe the cooling/heating processes, what means that any cluster having the vibration temperature higher (colder) than the plasma (buffer gas) temperature would be cooled (heated) at collisions. For more exact accordance, function $\tilde{f}(n, T_{n,l}, T_{\mathrm{gas}})$ was modified as: $f(n, T_{n,l}, T_{\mathrm{gas}}) = \tilde{f}(n, T_{n,l}, T_{\mathrm{gas}}) - \tilde{f}(n, T_{\mathrm{gas}}, T_{\mathrm{gas}})$. This function is shown in the Figure 1 by thick lines for $T_{\mathrm{gas}} =$ 3000 K.

While as we have defined response rate for all processes of cluster concentration modification, the dynamical equations for all cluster concentrations have been integrated over time. *I* the calculations for integration over the time step $\Delta t = 10^{-9}$ s and the total time duration $t_{\mathrm{final}} = 2 \cdot 10^{-4}$ s were used.

3. RESULTS AND DISCUSSION

In the Figure 2 the change of the cluster distribution $C(N, t) = \sum_{l,T} C(N, l, T, t)$ integrated over radicals and vibration temperatures is shown. One can see the narrow peaks of C_{60} and C_{70} concentration growth. The growth of C_{60} and C_{70} clusters concentration occurs due to presence of C_{60} and C_{70} fullerenes which have no radicals ($l = 0$). These peaks are explained by absence of free radicals in fullerene molecules which suppress further reactions of fullerene coagulation with other clusters. All other clusters having free radicals are coagulated into bigger clusters (with final $N = 100$–120 atoms in our calculations) which form soot particles in experiments of fullerene synthesis. In our calculations we associate the growth of big clusters with $N = 100$–120 with soot particles too.

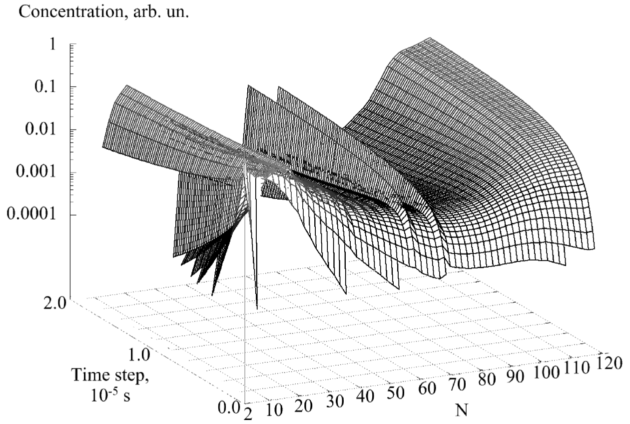

Fig. 2. Change of the integrated cluster distribution $C(N, t)$ during the time. N is the number of atoms in carbon cluster.

The second fact leading to fullerene accumulation is a very low probability of bond break in fullerenes in comparison with other clusters, having radicals. Fullerene molecules have compact and stable geometrical structure. Therefore after bond breaking between two atoms due to geometry steadiness then atoms immediately form the bond again, i.e., the time of radical existence in fullerene is smaller than average time between collisions of this molecule with other carbon clusters. So radical formation in fullerenes is negligible in the model.

Because of low yield of higher fullerenes (C_{76}, C_{80}, C_{82}, etc.) in experiments we neglect such molecules which have no radicals ($l = 0$) in the current stage of the model. But such molecules having radicals are taken into account. Despite of this approximation the calculation results show the basic features of fullerene formation process.

In Figure 3 the cluster distribution $C(N, T) = \sum_l C(N, l, T, t_{\mathrm{final}})$ integrated over radical number at the last time step t_{final} is shown. One can see that the concentration of small clusters is the big yet. The distributions along cluster temperature for every N have a quite smeared

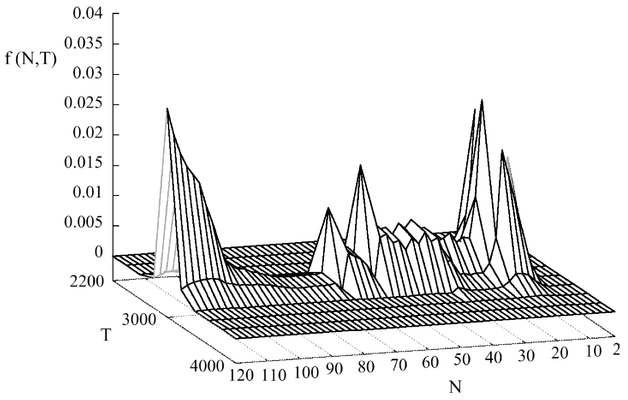

Fig. 3. Integrated over the radical number cluster distribution $C(N, T)$ at the last time point. N is the number of atoms in carbon cluster. T is vibration temperature of the cluster.

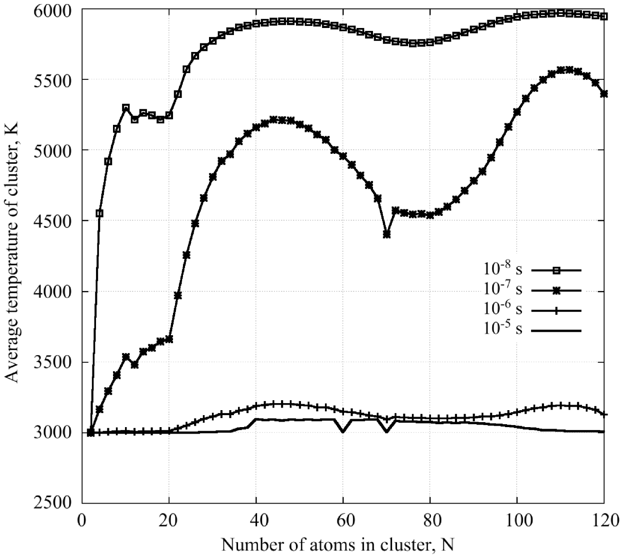

Fig. 4. Average cluster temperatures at different time moments in helium. $T_{gas} = 3000$ K.

peak near the gas temperature $T_{gas} = 3000$ K. It proves that any model of fullerene formation should take into account significant temperature variation of clusters.

In the Figure 4 dependences of cluster average temperatures on number of atoms in it are shown for different time moments in helium. At the beginning of coagulation carbon clusters are heated by the formation of new chemical bonds. Here their cooling rate by buffer gas occur rather quickly. At the time of $10^{-6} - 10^{-5}$ s all average temperatures become close to the gas temperature. The peculiarities at $N = 60$, 70 arise because of fullerenes accumulation. Fullerenes have no free radicals therefore they can only be cooled by buffer gas and can not be heated by forming new bonds.

In the Figure 5 the full distribution of C_{60} clusters over the cluster temperature T_{vib} and the number of radicals is shown at the final time step. The concentration of fullerene C_{60} with no radicals ($L = 0$) having vibration temperature T_{vib} equal to gas temperature ($T_{vib} = 3000$ K) prevails over other concentrations by order because of its stability. During the processes of carbon coagulation the C_{60} clusters with high number of radicals (monocyclic rings etc.) are formed from smaller clusters. They have average T_{vib} near the T_{gas} because they have the most intensive interaction with buffer gas due to their relatively big cross section. During decreasing of radical number in the cluster its vibration temperature is increased due to formation of new chemical bonds. Therefore the most of C_{60} clusters with $L \leq 30$ have high vibration temperatures (about 6000 K). But substantial part of all fullerene molecules C_{60} (with $L = 0$) have the average T_{vib} equal to T_{gas} again because it is cooled by buffer gas only and does not heated due to new bonds formation.

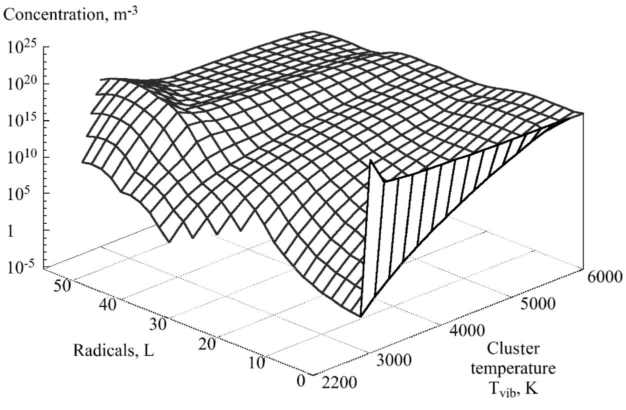

Fig. 5. Distribution of C_{60} cluster distribution $C(60, L, T, t_{final})$ over the radical number L and the cluster temperature T_{vib} at the last time point. $T_{gas} = 3000$ K.

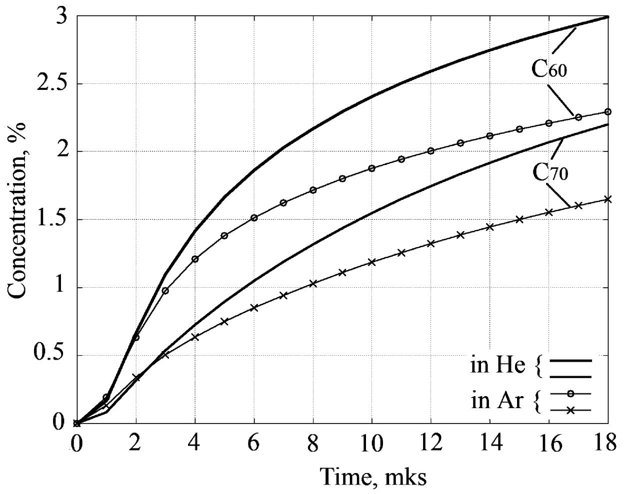

Fig. 6. Change of the C_{60} and C_{70} fullerene concentration in argon and helium during the time.

The Figure 6 shows the main result of calculations. The curves show the fullerenes C_{60} and C_{70} growth in different buffer gases. The total fullerene concentration in helium (5.2%) is about 30% higher than in argon (4.0%). This result is in qualitatively coincidence with experimental data. The difference in fullerene yield in argon and helium is lower than in experiments. It can be explained by variations of plasma parameters in space and in time in experiment conditions, which were not included in the model. Due to these variations the mass and heat transfer in the plasma can play an important role. But in the suggested model the processes of heat conductivity do not keep in mind because in the model the cluster distribution depends on time but it is uniform in space.

However, the model shows that the mass of buffer gas molecules plays the essential role in the carbon clusters cooling/heating processes. Here obtained results qualitatively coincide with experimental data. Further development of the model with taking into account cluster dissociation and higher fullerenes detailed consideration can give more exact difference between fullerenes yield in argon and helium and more reliable C_{60}:C_{70}:$C_{N>70}$ ratio.

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