Fullerenes, Nanotubes, and Carbon Nanostructures, 14: 481–488, 2006

ISSN 1536-383X print/1536-4046 online
DOI: 10.1080/15363830600666365

Fullerene Cluster Formation in Carbon Disulfide and Toluene

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Abstract: A kinetic theory of cluster formation and growth in fullerene solutions is developed. Two basic models for cluster evolution are analyzed and qualitatively compared with experimental data. The data for carbon disulfide and toluene are used. For oversaturated solutions it is shown, that the liquid drop model cannot appropriately describe the observed kinetics of cluster growth. Thus, an additional limiting term that will stabilize the cluster growth in the solution is needed. This leads to the model of limited growth that does qualitatively agree with experimental data.

Keywords: Fullerene, cluster, kinetics, solutions

INTRODUCTION

In recent time, interest to fullerene solutions has considerably grown mainly due to their much promising medical and biological applications. Investigating any fullerene solution one encounters the problem of describing cluster formation and growth. There exist a lot of experiments which show

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different aspects of this problem (for brief review see, e.g., (1, 2)). Current theoretical description restricts itself to chemical thermodynamics (1) or simplest phenomenological models (2). In this work, we have made an attempt of developing a stage-by-stage description of the kinetics of cluster growth in fullerene solutions. For this purpose, kinetic equations of the nucleation theory (3, 4) were used. We start with the basic liquid drop model to check, whether we can describe the experimental data in frame of metastability of cluster state. From the numerically calculated evolution of mean cluster size with time, we obtain, that the time of existence of a metastable state in the systems studied (solutions of C_{60} in carbon disulfide (CS_2) and toluene ($C_6H_5CH_3$)) is much less, than the times observed in experiments. The limited growth model, containing an additional stabilizing term, proves to be an appropriate development of the previous model.

INITIAL EQUATIONS AND APPROXIMATIONS

Our aim is to obtain the evolution of the cluster size distribution function $f(n,t)$ with time. Function $f(n,t)$ represents the bulk concentration of fullerene clusters consisting of n monomers (further–«cluster of size n») at the moment t. We suppose that fullerenes inside the cluster are densely packed and cluster form is quasispherical, independent of its size (the aggregation number n). It is also assumed that the formation and growth of clusters is only possible by means of aggregation or emission of monomers.

Based on these assumptions, we may write the following equation (3):

$$\frac{\partial f(n,t)}{\partial t} = w^{(+)}_{n-1,n} f(n-1,t) + w^{(-)}_{n+1,n} f(n+1,t) - w^{(+)}_{n,n+1} f(n,t) - w^{(-)}_{n,n-1} f(n,t) \tag{1}$$

Here $w^{(+)}_{n-1,n}$ is the probability of a single C_{60} molecule to aggregate to a fullerene cluster of the size $(n-1)$, and $w^{(-)}_{n,n-1}$ is the probability of a fullerene cluster to loose a single monomer. The initial and boundary conditions are determined by the initial concentration of free monomers, c_0, in the solution. We suppose, that the concentration of fullerenes in the solution does not change with time:

$$f(n,t=0) = \begin{cases} 0, & n > 1 \\ c_0, & n = 1 \end{cases} \qquad \sum_{n=1}^{\infty} n f(n,t) = c_0 \tag{2}$$

Changes in the free energy of the system ΔG due to the formation of an n or $(n-1)$ size cluster are determined by the monomer aggregation to monomer emission probability ratio:

$$\frac{w_{n-1,n}^{(+)}}{w_{n,n-1}^{(-)}} = \exp\left\{-\frac{\Delta G(n) - \Delta G(n-1)}{k_B T}\right\} \tag{3}$$

The probability $w_{n-1,n}^{(+)}$ depends on the kinetics of cluster growth. As a rule, two regimes of growth are considered: diffusion- and kinetic-limited aggregation. In DLA-regime, the time of monomer aggregation to the surface of the fullerene cluster is negligibly small compared to the particle drift time towards the aggregate and $w_{n-1,n}^{(+)}$ is then:

$$w_{n,n+1}^{(+)} = 4\pi Dc\left(\frac{3w_s}{4\pi}\right)^{1/3} n^{1/3} \tag{4}$$

where D is the diffusion coefficient, c is the concentration of free monomers in solution at the given moment of time, w_s is the excluded volume of the C_{60} molecule.

In the case of KLA-regime, when the time of incorporation of a monomer to the aggregate is larger that the time of particle diffusion towards the aggregate surface, the following equation can be obtained:

$$w_{n,n+1}^{(+)} = 4\pi D^{(*)} c a_m \left(\frac{w_s}{w_m}\right)^{2/3} n^{2/3} \tag{5}$$

where $D^{(*)}$ is the diffusion coefficient characterizing the aggregation rate of particles to the aggregate. Index m stands for the parameters of the aggregate.

In general, both processes of transport of the segregating particles to the cluster surface as well as the rate of incorporation may be of importance for the rate of cluster formation and growth. As the result, we obtain an intermediate regime (DLA + KLA), and the probability $w_{n-1,n}^{(+)}$ is described by the following equation:

$$w_{n,n+1}^{(+)} = 4\pi D^{(*)} c\left(\frac{3w_s}{4\pi}\right)^{1/3} n^{1/3}\left\{\frac{(a_s/a_m)n^{1/3}}{1 + [(D^{(*)}/D)(a_s/a_m)]n^{1/3}}\right\} \tag{6}$$

Substituting (3), (6) into (1) we obtain the system of kinetic equations that describe the system considered. For more details, consider (3, 4).

Obtained kinetic equations we can solve numerically and as a result obtain the evolution of the main parameters characterizing the cluster state–mean cluster size and concentration of clusters in the solution. The behavior of this parameters depends on type of the model we use. Different models result in different expressions for work of cluster formation ΔG(n).

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LIQUID DROP MODEL

In liquid drop model, the expression for the work of cluster formation consists of the bulk term $-n\Delta\mu$ and the surface term $\alpha_2 n^{2/3}$:

$$\Delta G(n) = -n\Delta\mu + \alpha_2 n^{2/3} \quad \alpha_2 = 4\pi\sigma\left(\frac{3w_s}{4\pi}\right)^{2/3}$$
$$\Delta\mu = k_B T \ln\left(\frac{c}{c_{eq}^{(\infty)}}\right) \tag{7}$$

where σ is the surface tension on the cluster-surrounding phase interface, $\Delta\mu$ is the difference between the chemical potential of the monomer in a free state in the solution and the chemical potential of the monomer in the cluster, $c_{eq}^{(\infty)}$ is the concentration of segregating particles in the solution necessary for equilibrium coexistence of the solution with a solid phase at a planar interface.

In this case, the growth of a cluster in the solution is governed by the competition between its surface and bulk energy.

In an unsaturated solution ($c_0/c_{eq}^{\infty} < 1$), a stable cluster size distribution establishes in $\Delta t \sim 10^{-6}$ sec [4]. Figure 1 shows the dependence of mean cluster size $<n>$ on the value of the initial concentration of C_{60} for the

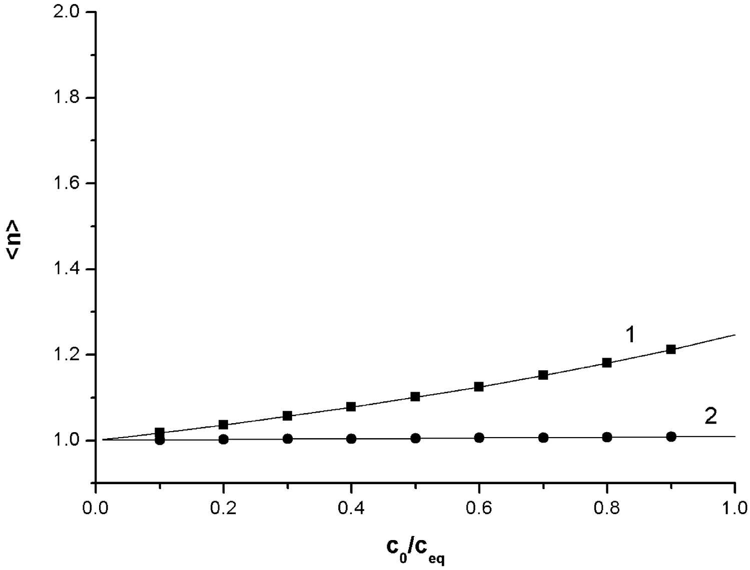

Figure 1. The dependence of $<n>$ on the concentration of C_{60} in unsaturated solution. Solid curves–analytical calculation. Points–numerical calculation; $1 - \alpha_2/k_BT = 3$ (toluene); $2 - \alpha_2/k_BT = 8$ (carbon disulfide).

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solutions C_{60}/CS_2 and $C_{60}/C_6H_5CH_3$. As we can see, the value of $<n>$ is always close to one in case of an unsaturated solution. This means, that the major part of the fullerene concentration is in the form of free monomers.

If solution is oversaturated ($c_0/c_{eq}^{\infty} > 1$), then there exist one possibility to observe clusters in frame of this model–the metastable state of solution. The time evolution of $<n>$ in this case goes in several stages. There exists a certain stage (called the stage of independent growth), at which mean cluster size in solution stays constant. This is a metastable state of the system. If the time period of stage of independent growth is large enough, then we may expect that the value of mean cluster size observed in the experiments may be its value at that stage.

For two solutions studied, carbon disulfide and toluene, the time evolution of mean cluster size $<n>$ is presented on Figure 2. As we see from the figure, for both solutions, the time length of the stage of independent growth ($\sim 10^{-3}$ sec) is too short in comparison with experimental time.

Therefore, we can conclude, that for the oversaturated solutions, the liquid drop model cannot appropriately describe the processes of cluster formation and growth in the solutions. A certain development of the model is needed. One of the possible ways is to modify the expression for the work of cluster formation ΔG(n) in a way to stabilize the growth of clusters at a certain stage.

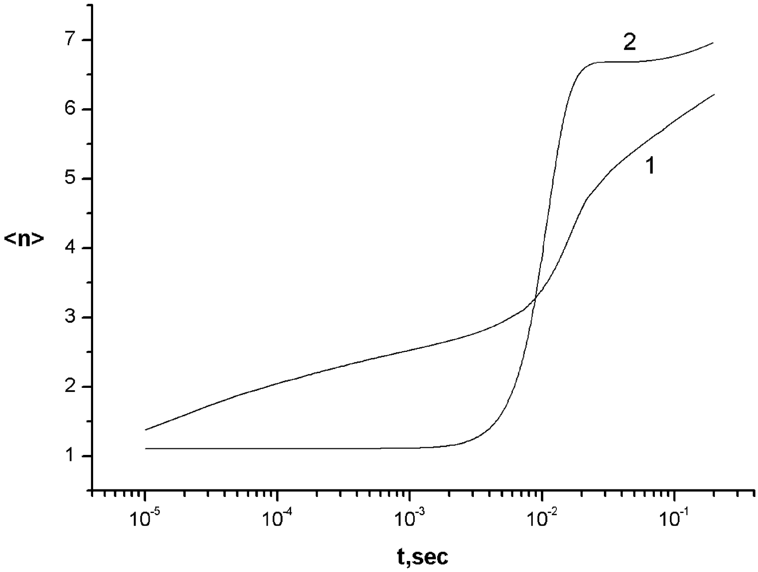

Figure 2. The dependence of $<n>$ on the concentration of C_{60} in oversaturated solution. 1 – $\alpha_2/k_BT = 3$ (toluene); 2 – $\alpha_2/k_BT = 8$ (carbon disulfide).

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LIMITED GROWTH MODEL

To stabilize cluster growth, we must add an additional term of the type kn^{β} into the expression for ΔG(n):

$$\frac{\Delta G(n)}{k_B T} = -n \ln \frac{c_0(t')}{c_{eq}^{\infty}} + \frac{\alpha_2}{k_B T} n^{2/3} + \frac{k}{k_B T} n^{\beta} \tag{8}$$

For this model, the unsaturated solution behaves similar to the liquid drop model (Figure 2). In the case of an oversaturated solution, the modified expression for ΔG(n) leads to the change in the behavior of the system.

Figure 3 reflects the difference between two models. As we can see, in case of the liquid drop model, the clusters, that have passed the energetic barrier at small sizes, “fall” into an infinite “pit” i.e., start to grow to arbitrary large sizes. The resulting stable state of the system in this case is one large cluster (representing solid phase) in equilibrium with concentration of $c_{eq}^{(\infty)}$ monomers and small clusters. As we have shown in the previous chapter, this kind of behavior leads to results that cannot appropriately describe experimental data.

On the other hand, in case of the limited growth model the stabilizing term changes the behavior of the system qualitatively making a certain size energetically favorable for all the clusters that have passed the energetic barrier. Thus, large clusters tend to reach that size and stay there in a stable state. This very state may be observed in the experiments.

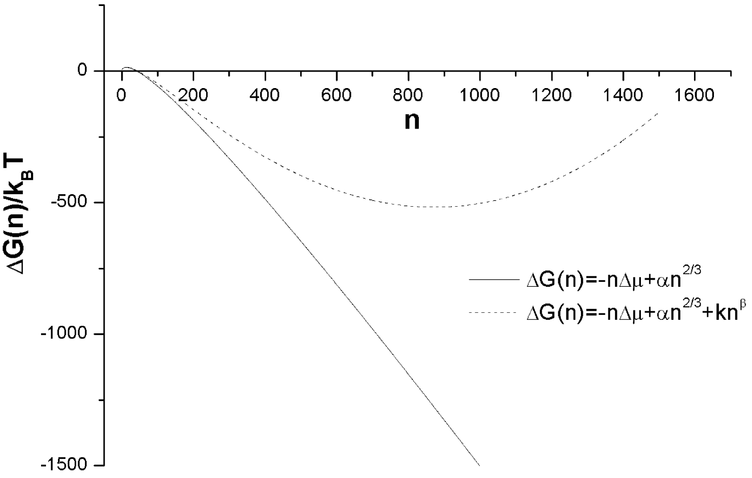

Figure 3. The ΔG(n) curves for the liquid drop model and the limited aggregation model.

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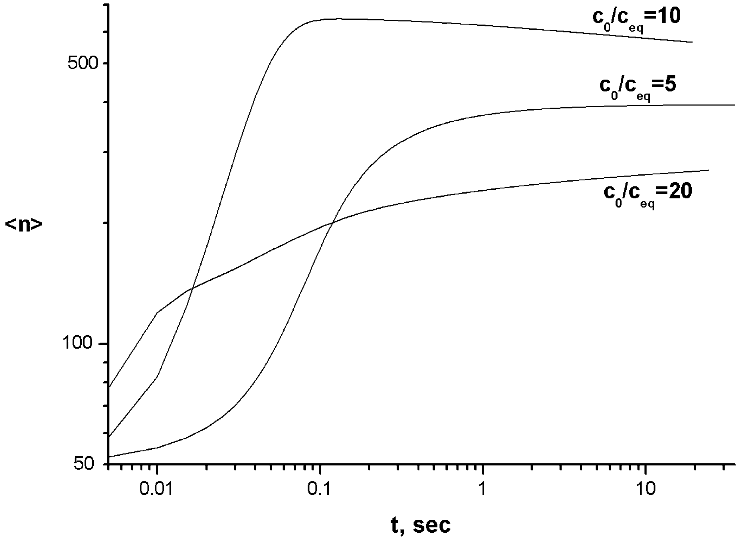

Figure 4. The variation of the mean cluster size with time for solutions with $\alpha_2/k_BT = 8$, $k/k_B T = 10^{-3}$ for the different initial concentrations.

We can analytically estimate the values of the stable cluster size and the concentration of clusters of that size (4):

$$N = (c - c_{eq}^{\infty})\left(\frac{\alpha_2}{3k(\beta - 1)}\right)^{-3/3\beta-2} \qquad n_\alpha = \left(\frac{\alpha_2}{3k(\beta - 1)}\right)^{3/3\beta-2} \tag{9}$$

Here n_α is the estimate of the preferred size of the clusters and N is the concentration of clusters of size n_α.

The evolution of mean cluster size with time is presented on Figure 4. It is seen that at the beginning of evolution there establishes some cluster size which, in further, is slowly changing to that determined by equation (9). Time period of stabilizing of cluster size is long enough and thus can explain evolution of mean cluster size, observed in different experiments.

CONCLUSIONS

In the present work in the frame of nucleation theory the kinetics of fullerene behavior in solutions have been studied. The evolution of mean cluster size with time has been calculated from the numerical solutions of system of kinetic equations with parameters from experimental data for carbon disulfide and toluene.

First, the liquid drop model was studied, consisting of a surface and bulk terms in the expression for work of cluster formation ΔG(n). For unsaturated solution, we obtain that the preferential state of C_{60} in the solution is the free monomer state. For oversaturated solution, clusters start to form and grow. The possibility of existence of a metastable cluster concentration was studied. We obtain, that the time length of existence of such state in this case is less than 10^{-3} sec.

The limited growth model, containing an additional stabilizing term in the expression for $\Delta G(n)$, proves to be an appropriate development of the liquid drop model. In this case, for oversaturated solutions we obtain the behavior that qualitatively describes the observed kinetics of C_{60} dissolution.

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