

1-1-2009

Diffusive growth of fullerenes and carbon nanotubes

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Abstract

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Keywords

carbon, diffusive, growth, fullerenes, nanotubes

Disciplines

Physical Sciences and Mathematics

Publication Details

Bunder, J. E. & Hill, J. M. (2009). Diffusive growth of fullerenes and carbon nanotubes. *Journal of Chemical Physics*, 131 (24), 244703-1-244703-5.

Diffusive growth of fullerenes and carbon nanotubes

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(Received 1 October 2009; accepted 4 December 2009; published online 22 December 2009)

The video of a growing fullerene within a carbon nanotube, initiated by a tungsten catalyst, provides a dramatic realization of a complex nanoscale process. While there may be many detailed models which can account for this growth, we propose one of the simplest possible models which is consistent with the major observed features of the growth process. In particular, we assume that the fullerene is immersed in a carbon vapor environment, and that the growth occurs as a consequence of the diffusion of the carbon vapor into the fullerene. Moreover, we assume that the classical diffusion equation applies in the region exterior to the fullerene and that a standard Stefan condition applies at the moving fullerene surface. We assume that the gaseous medium through which the carbon atoms diffuse is represented through the value of the diffusion coefficient D appearing in the classical diffusion equation. We also assume that the influence of the catalyst is felt through the value of the constant α appearing in the Stefan condition. Based on these assumptions, we derive simple similarity solutions for both spherical and ellipsoidal fullerenes which are entirely consistent with the observations. A corresponding analysis is provided for the longitudinal growth of a carbon nanotube. © 2009 American Institute of Physics. [doi:10.1063/1.3277673]

I. INTRODUCTION

The growth, or shrinkage, of fullerenes and carbon nanotubes (CNTs) within a carbon vapor environment has been directly observed in a number of experiments.^{1–3} The supplementary data of Ref. 2 include a video of a fullerene growing inside a CNT, initiated by a tungsten catalyst. This remarkable footage provides a fascinating and tantalizing insight into a nanoscale process.

Several theoretical explanations of the growth mechanism of fullerenes and CNT have been presented, many of which discuss a diffusion process.^{4–8} Our purpose here is to formulate the simplest possible diffusion model which might exhibit all the major observed features of the process. Unlike previous models of the diffusive growth of fullerenes, we are concerned with the carbon vapor concentration in the entire environment, rather than just on the surface of the fullerene. In particular, we assume that the fullerene is immersed in a carbon vapor environment, and that growth occurs as a consequence of carbon vapor diffusing into the fullerene. Furthermore, we assume that this process is governed by the classical diffusion equation and that the rate of growth of the fullerene surface takes the form of a standard Stefan moving boundary condition.⁹ Physically, this condition says that the rate of growth of the fullerene (i.e., the boundary velocity) is proportional to the flux of the carbon onto the surface. Although the proposed model is simple and it may well explain the major observed features of fullerene growth, there is a lack of detailed experimental data on the concentration of the carbon vapor around the fullerene, which is required for the model to be adequately tested.

We also develop a simple classical diffusion model to describe the longitudinal growth of a CNT. Like the fullerene

case, we assume that the CNT is in a carbon vapor environment which diffuses into the CNT. Although we assume that the diffusion process for the CNT is the same as that for the fullerene, the different geometries of the two situations naturally lead to quite different results.

We model the growth of a fullerene (or CNT) by assuming that this growth can be described by the diffusive adsorption of carbon atoms onto the surface of the fullerene. If $c(\mathbf{r}, t)$ is the carbon vapor concentration at position \mathbf{r} and time t in the environment surrounding the fullerene, then the differential equation that describes the classical diffusion process is

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} = D \nabla^2 c(\mathbf{r}, t), \quad (1)$$

where D is the diffusion coefficient which is assumed to be constant and ∇^2 is the usual three-dimensional Laplacian. The value of the constant diffusion coefficient D is dependent on the specifics of the fullerene environment. Generally, a growing fullerene is immersed in an inert gas, such as nitrogen or argon, and different gases will affect the diffusion properties of the carbon vapor. Other important parameters that might affect D include the temperature and pressure. We assume that the concentration inside the fullerene is zero, and that it has a constant value c_0 on the surface of the fullerene. Although the experimental fullerene growth takes place inside a CNT,² here we will make the assumption that the fullerene is in an infinite carbon vapor environment such that the concentration at an infinite distance from the fullerene is a constant c_∞ .

It has often been observed that the growth of fullerenes or CNT requires some catalyst to be present in the carbon vapor. Numerous catalysts have been used to grow fullerenes and CNT, and while most catalysts are metals, for example, tungsten and iron,^{2,10} semiconductor catalysts are also

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possible.¹¹ In contrast, a catalyst is not necessary for the shrinkage of a fullerene which can be achieved through a number of methods, including thermal evaporation. In order to initiate fullerene growth, a certain concentration of catalyst particles may be required near the fullerene surface. We assume that these catalytic effects are described by a Stefan boundary condition that involves a parameter α , which is catalyst dependent and defines the adsorption of carbon atoms onto the moving boundary per unit volume. Although we are only concerned with the diffusion of carbon atoms, there may in reality be some diffusion of the catalyst particles onto the fullerene surface. Generally, it is found that the synthesized fullerene or nanotube contains residual catalyst contamination, although recent experiments have made some progress in growing pure, high quality nanotubes.¹² While it is possible to take into account the diffusion of the catalyst by generalizing Eq. (1), we shall assume that catalyst diffusion is a small effect which does not have a large impact on the general diffusion properties of the carbon vapor.

II. GROWTH OF A FULLERENE

Experimental studies have shown that a fullerene tends to remain approximately spherical when growing,² as this is the most energetically favorable geometry, and therefore we can assume that the solution is spherically symmetric and that the surface of the fullerene is defined by a sphere of radius $r=R(t)$, where $R(t)$ is an unknown function of time. In this case, Eq. (1) becomes

$$\frac{\partial c(r,t)}{\partial t} = D \left(\frac{\partial^2 c(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial c(r,t)}{\partial r} \right), \quad (2)$$

where the value of the constant diffusion coefficient D depends on the gaseous environment about the fullerene through which the carbon atoms diffuse. We assume that the carbon vapor concentration c_0 at the surface of the fullerene is constant and so obtain the moving boundary condition

$$c(R(t), t) = c_0. \quad (3)$$

Consider the infinitesimal volume contained between two successive fullerene surfaces. This volume will adsorb a certain number of carbon atoms which will be incorporated into the fullerene surface. We define the number of carbon atoms adsorbed per unit volume as α , a constant which is catalyst dependent and has the same units as the concentration $c(r, t)$. If the surface of the fullerene is growing with velocity $v=dR(t)/dt$, then the total number of carbon atoms which are added to the fullerene per unit time, per unit surface area is αv , the diffusive flux. This must equal the diffusion onto the fullerene surface $D \partial c(R(t), t) / \partial r$, assuming Fick's first law. Thus, we obtain the Stefan condition

$$D \frac{\partial c(R(t), t)}{\partial r} = \alpha \frac{dR(t)}{dt} \quad (4)$$

and we note that α is generally known as the Stefan number and is, in this context, dependent on the particular catalyst under consideration.

In choosing the moving boundary conditions (3) and (4), we have made some assumptions. Generally, the concentra-

tion at $r=R(t)$ will not remain constant, but $c(R(t), t)=c_0$ is a reasonable approximation if we are only interested in small time intervals. The Stefan condition is also an approximation as it does not take into account the lattice structure of the fullerene. The lattice structure implies that there is a particular relationship between the increase in fullerene surface area and the increase in the number of carbon atoms in the fullerene; specifically, the increase in surface area should always be proportional to the number of new atoms in the fullerene so that the surface density remains constant. The Stefan condition (4) does not take this constraint into account so the assumed constant density of carbon atoms on the fullerene surface may not be realistic. However, on solving the given differential equation with the stated boundary conditions, the correct proportional relationship between the surface area of the fullerene $4\pi R(t)^2$ and the number of atoms in the fullerene is obtained, indicating that the given Stefan condition (4) is reasonable. In the Appendix, we discuss some alternative moving boundary conditions which admit the same similarity variable (5) and therefore the same moving boundary $R(t)$ as that examined below.

To solve Eq. (2) with the moving boundary conditions (3) and (4), we assume a similarity solution where the solution is taken to be a function of the single similarity variable,

$$\xi(r, t) = r/\sqrt{Dt + \beta}, \quad (5)$$

for some constant β . On defining $c(r, t)=C(\xi(r, t))$, the diffusion problem in terms of ξ becomes

$$\frac{d^2 C(\xi)}{d\xi^2} + \left(\frac{2}{\xi} + \frac{\xi}{2} \right) \frac{dC(\xi)}{d\xi} = 0, \quad (6)$$

$$C(\xi_R) = c_0, \quad \frac{dC(\xi_R)}{d\xi} = \alpha \xi_R / 2,$$

where $\xi_R=\xi(R(t), t)$ is the value of $\xi(r, t)$ on the fullerene surface, which is assumed to be constant. This assumption implies that the moving boundary $R(t)$ is given explicitly by $R(t)=\xi_R \sqrt{Dt + \beta}$. The solution to the above differential equation is

$$C(\xi) = c_0 + \frac{\alpha \xi_R^3}{2} \int_{\xi_R}^{\xi} \eta^{-2} e^{(\xi_R^2 - \eta^2)/4} d\eta. \quad (7)$$

We define the dimensionless difference between the carbon concentration outside the fullerene and on the fullerene surface as $\Delta c(r, t)=[c(r, t)-c_0]/\alpha$. In order to compare the difference in carbon concentration at the fullerene surface and at infinity, we define $\lim_{r \rightarrow \infty} \Delta c(r, t)=[c_\infty - c_0]/\alpha = \Delta c_\infty(\xi_R)$. It can be shown that

$$\Delta c_\infty(\xi_R) = \frac{\xi_R^2}{2} - \frac{\sqrt{\pi} \xi_R^3 e^{\xi_R^2/4}}{4} \operatorname{erfc}(\xi_R/2), \quad (8)$$

where $\operatorname{erfc}(x)$ is the complementary error function. This equation is plotted in Fig. 1. Clearly, our assumptions that the concentration at infinity is constant and that ξ_R is constant are in agreement. If we know $\Delta c_\infty(\xi_R)$, then ξ_R can be determined numerically. Given the asymptotic expansion of $\operatorname{erfc}(x)$ at large x ,

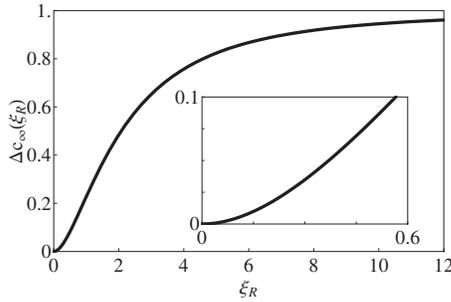


FIG. 1. A plot of Eq. (8), the difference between the carbon concentration at infinity and the carbon concentration on the fullerene surface c_0 as a function of ξ_R and in units of α . The inset is the same plot, but for small ξ_R .

$$\operatorname{erfc}(x) = \frac{e^{-x^2}}{x\sqrt{\pi}} \sum_{n=0}^{\infty} (-1)^n \frac{(2n)!}{n!(2x)^{2n}}, \quad (9)$$

it can be shown that when $\xi_R \rightarrow \infty$, we have $\Delta c_{\infty}(\xi_R) = 1$.

Any spherically symmetric problem of the form given in Eq. (2) can be solved using Eq. (5), and this form of ξ is chosen here because it provides one of the simplest possible solutions of the classical diffusion equation (1) consistent with the moving boundary conditions in Eqs. (3) and (4). However, simplicity is not the only reason why we choose Eq. (5) for our solution. Our main reason for choosing this form of ξ is that it can be justified from the known geometry of a growing fullerene. The relationship between the number of carbon atoms N and the average radius R of the fullerene can be approximated by $R = b\sqrt{N}$, where $b = 0.045$ nm.¹³ Therefore, if a fullerene initially has radius R_0 and N_0 atoms, and if this fullerene grows at a constant rate of δN carbon atoms/s, the radius as a function of time is

$$R(t) = \sqrt{b^2 t \delta N + R_0^2}, \quad (10)$$

which is of the same form as $R(t) = \xi_R \sqrt{Dt + \beta}$, obtained from Eq. (5). Thus, we can show that $\xi_R^2 = b^2 \delta N / D$ and $\beta = R_0^2 / \xi_R^2$, which provides some justification to our previous claim that ξ_R is constant.

Using data from Ref. 2, we can take $\delta N = 0.5$ atoms/s and $R_0 = 0.412$ nm. The diffusion coefficient is unknown so we choose $D = 1 \times 10^8$ nm²/s. With these parameters, we can determine $\Delta c(r, t)$, which is plotted in Fig. 2. As $b^2 \delta N \ll D$ in this case, ξ_R is rather small and, as can be seen from Fig. 1, we would either expect very little variation in the carbon concentration outside the fullerene or a rather large value of

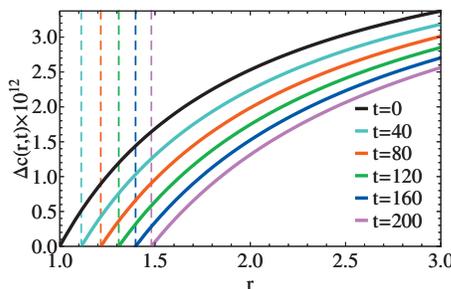


FIG. 2. The relative concentration $\Delta c(r, t)$ about a fullerene at several different time steps. The dashed lines are where $r = R(t)$, with the time t corresponding to the solid lines of the same color. The distance r is in units of R_0 .

α . In cases where the concentration varies by a negligible amount within the environment and can, for experimental purposes, be considered constant, estimating ξ_R may not be possible. However, the gradient of $\Delta c(r, t)$ is strongly dependent on D , with smaller values of D resulting in larger gradients, although the general shape of the curves in Fig. 2 remains much the same. Therefore, a variation in concentration may be easier to measure when D is relatively small. From Fig. 2, it appears as if the radius of the fullerene grows linearly with time, in contradiction to Eq. (10). However, this seemingly linear behavior is consistent with Eq. (10) and arises because $b^2 t \delta N \ll R_0^2$ over the time period t being considered here.

One can modify the above equations to take account shrinking fullerenes simply by setting $t \rightarrow -t$. In this case, we choose $\xi(r, t) = r / \sqrt{\beta - Dt}$ and $R(t) = \xi_R \sqrt{\beta - Dt} = \sqrt{R_0^2 - b^2 t \delta N}$, but the solution for the carbon concentration given in Eq. (7) remains the same. For example, a C_{1300} , $R_0 = 1.62$ nm, fullerene has been observed to shrink at a constant rate of $\delta N = 1.3$ atoms/s.¹ One should note that in this experiment, it was observed that the shape of larger fullerenes is polyhedral rather than spherical, and only fullerenes smaller than C_{330} , $R = 0.82$ nm, tend to be spherical.

For polyhedral fullerenes, it is more accurate to consider an ellipsoidal model rather than a spherical model. In this case, it is again possible to assume a single similarity solution for the solution of Eq. (1). First, we define for $\mathbf{r} = (x, y, z)$

$$\mathbf{R} = \mathbf{r} / \sqrt{Dt + \beta}, \quad (11)$$

which is analogous to Eq. (5), and these new coordinates $\mathbf{R} = (X, Y, Z)$ can be mapped to the ellipsoidal coordinates $\xi_{1,2,3}(\mathbf{r}, t)$. It can be shown that only one of these coordinates, $\xi_1(\mathbf{r}, t)$, is relevant to ellipsoids, and therefore it is this coordinate which is chosen for the similarity solution.¹⁴ In particular, one can write

$$X^2/(\xi_1^2 - a^2) + Y^2/(\xi_1^2 - b^2) + Z^2/\xi_1^2 = 1, \quad (12)$$

which describes an ellipsoid in the \mathbf{R} coordinate space with axes $\sqrt{\xi_1^2 - a^2}$, $\sqrt{\xi_1^2 - b^2}$ and ξ_1 . If $\mathbf{r}_S(t)$ defines the surface of the fullerene in Cartesian coordinates at time t and we define $\xi_1(\mathbf{r}_S(t), t) = \xi_S$, which we will assume to be constant, then the axes of the ellipsoidal fullerene are

$$A(t) = \sqrt{(\xi_S^2 - a^2)(Dt + \beta)}, \quad (13)$$

$$B(t) = \sqrt{(\xi_S^2 - b^2)(Dt + \beta)}, \quad C(t) = \xi_S \sqrt{Dt + \beta}.$$

These three axes may be related to experimental data, as was done for the radius $R(t)$ of the spherical fullerene.

In terms of ξ_1 , $c(\mathbf{r}, t) = C(\xi_1(\mathbf{r}, t))$ and Eq. (1) is¹⁴

$$\frac{d}{d\xi_1} \left(f(\xi_1) \frac{dC(\xi_1)}{d\xi_1} \right) + \frac{\xi_1}{2} f(\xi_1) \frac{dC(\xi_1)}{d\xi_1} = 0, \quad (14)$$

where $f(\xi_1) = \sqrt{(\xi_1^2 - a^2)(\xi_1^2 - b^2)}$. As in the spherical case, the carbon vapor concentration is assumed to be constant on the fullerene surface, $C(\xi_S) = c_0$. The Stefan condition in Cartesian coordinates is

$$D \frac{\partial c(\mathbf{r}_S(t), t)}{\partial \mathbf{r}} = \alpha \frac{d\mathbf{r}_S(t)}{dt} \quad (15)$$

and in terms of ξ_1 it becomes

$$\frac{dC(\xi_S)}{d\xi_1} = \alpha \xi_S / 2. \quad (16)$$

The solution of Eq. (14) satisfying the above conditions is

$$C(\xi_1) = c_0 + \frac{\alpha \xi_S f(\xi_S)}{2} \int_{\xi_S}^{\xi_1} f(\eta)^{-1} e^{(\xi_S^2 - \eta^2)/4} d\eta. \quad (17)$$

When $a=b=0$, this ellipsoid solution reduces to the spherical solution given in Eq. (7) and the axes given in Eq. (13) reduce to the spherical radius $R(t) = \xi_R \sqrt{Dt + \beta}$.

III. LONGITUDINAL GROWTH OF A CNT

The linear growth of CNT is quite different from fullerenes in that CNT tend to remain open at one end during the growth process, which enables inner walls of multiwalled CNT to grow with the outer wall, and they tend to predominantly grow in length rather than radius. Therefore, for a CNT, we use cylindrical coordinates and as a first approximation we ignore all angular and radial components so that Eq. (1) becomes

$$\frac{\partial c(z, t)}{\partial t} = D \frac{\partial^2 c(z, t)}{\partial z^2}. \quad (18)$$

In addition, we have the boundary condition that the carbon concentration is constant on the growth surface, $c(L(t), t) = c_0$, where $z=L(t)$ is the length of the CNT. For this geometry, the Stefan condition is

$$D \frac{\partial c(L(t), t)}{\partial z} = \alpha \frac{dL(t)}{dt}. \quad (19)$$

For a more precise model, we might also consider radial effects, but because the growth in the radius of the nanotube is extremely small, we assume that it has a negligible effect on the concentration. Just like before, we assume that the concentration is a function of a single similarity variable.

It has been observed experimentally that CNT often grows at a constant rate³ and so the length $L(t)$ can be written as

$$L(t) = vt + L_0 \quad (20)$$

for some constant velocity v and initial tube length $L_0 > 0$.¹⁵ For example, in Ref. 3, a CNT was shown to grow at the constant rate of $v=500$ nm/s until it reached a length of about 0.7 mm. With Eq. (20) in mind, we define the similarity variable,

$$\xi(z, t) = (\beta z - Dt) / \beta^2, \quad (21)$$

so that $\xi(L(t), t) = \xi_L = L_0 / \beta$ and $\beta = D/v$. Substituting Eq. (21) into the differential Eq. (18) and solving for the given boundary conditions, $c(L(t), t) = c_0$ and Eq. (19), yields the solution

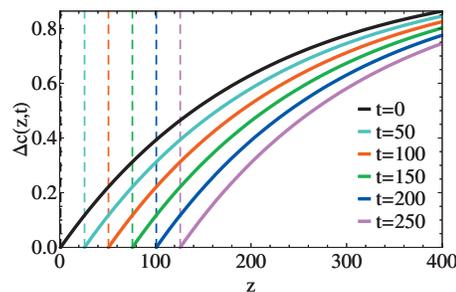


FIG. 3. The relative concentration $\Delta c(z, t)$ about a CNT at several different time steps with $D=1 \times 10^8$ nm²/s, $v=500$ nm/s, and $L_0=1$ μ m. The dashed lines are where $z=L(t)$, with the time t corresponding to the solid lines of the same color. The distance z is in units of L_0 .

$$C(\xi) = c_0 + \alpha - \alpha e^{\xi_L - \xi}, \quad (22)$$

where $c(z, t) = C(\xi(z, t))$. This simple solution is well known in the classical diffusion literature as Langford's constant velocity solution.¹⁶ Note that we cannot set $L_0=0$ as this gives $\xi_L=0$. Furthermore, $L_0=0$ would not make sense in this model as we do not describe how a CNT begins to grow, but rather how it continues to grow once growth has begun. As in the fullerene case, we again observe that the solution assumes a constant concentration at infinity which we can define as c_∞ . In Fig. 3, we plot an example of the dimensionless difference in carbon concentration $\Delta c(z, t) = [c(z, t) - c_0] / \alpha$. As in the fullerene case, the value of D is not easy to determine, and makes a substantial difference to the relative concentration. Unlike the fullerene case, however, we find that even for relatively large values of D , the concentration gradient is large enough to be measurable.

IV. CONCLUSIONS

We have shown how a classical diffusion model and a Stefan condition may be used to describe the diffusive growth of fullerenes and CNT in a carbon vapor environment. For both problems, we have assumed that the classical diffusion equation and the stated moving boundary conditions admit a similarity solution, so that the partial differential equation reduces to an ordinary differential equation, and the carbon concentration far from the growth region is necessarily assumed to be a constant. For the fullerene model, five parameters are involved, namely, the concentrations of the carbon vapor at infinity c_∞ and at the fullerene surface c_0 , the Stefan constant α , the diffusion coefficient D , and the rate of carbon adsorption onto the fullerene surface δN . However, the solution may be uniquely defined by any four of these parameters since $\xi_R^2 = b^2 \delta N / D$ and ξ_R may also be determined from Eq. (8). In the CNT model, four parameters are required, c_0 , α , D , and the velocity of the growth v . Certain parameters, such as δN , for fullerenes, or v , for CNT, are relatively easily determined from experiments, while others, such as D and α are quite difficult to determine. Experimental data are required in order to confirm the validity of the models proposed here. In particular, actual values are required for the carbon vapor concentration in the growth environment. For example, if we knew the carbon concentra-

tions c_0 and c_∞ in the fullerene environment, as well as D and α , we would be able to make an estimate of the rate of carbon adsorption into the fullerene δN .

In reality, the actual physics of the problem might be far more complicated, such as a nonconstant c_0 or α . However, in the absence of detailed information, we have proposed the simplest possible models arising from the classical diffusion equation and the simplest similarity solutions which are appropriate for the given problem. Our purpose here is to identify the major issues for the model so that secondary effects can be incorporated at a later stage. Our assumptions are entirely consistent with the observed facts concerning fullerene and CNT growth over time and give a clear relationship between the rate of growth and the carbon vapor concentration. The model predicts that for a certain difference in the carbon vapor concentration at the surface of the fullerene or CNT to the background environment, i.e., $\Delta c(w, t)$ where $w=r, z$ for fullerenes and CNT, respectively, one can determine ξ_w where $W=R, L$ and, given the initial conditions of the fullerene or CNT, one can then predict the rate of growth, provided that one also knows the diffusion coefficient. Alternatively, one may be able to experimentally determine the rate of growth and from this determine the profile of the carbon vapor environment outside the fullerene or CNT.

ACKNOWLEDGMENTS

This work was partially undertaken while J.M.H. visited CEMES, CNRS at Toulouse. The hospitality of Wolfgang Bacsa and Marc Monthieux is gratefully acknowledged. We also acknowledge the support of the Australian Research Council through the Discovery Project scheme and thank Jeff Dwyne for illuminating discussions.

APPENDIX: GENERALIZED MOVING BOUNDARY CONDITIONS

It has been found experimentally that the radius of a growing spherical fullerene is of the form $R(t) = \xi_R \sqrt{Dt + \beta}$. Therefore, we require that any realistic solution of Eq. (2) is in agreement with this form of $R(t)$. In addition, we assume that there is a simple similarity solution, as we are looking for the major influences on the fullerene growth rather than the finer details. The choice of similarity solution depends not only on Eq. (2) but also on the moving boundary conditions (3) and (4). The model presented in Sec. II assumes some of the simplest possible moving boundary conditions. Specifically, it is assumed that the concentration is constant at the fullerene surface and that the diffusive flux onto the fullerene surface can be described by a standard Stefan condition. This model may be viewed as an initial step in the investigation of the diffusive growth of fullerenes. In this appendix, we will not detail physical arguments for certain boundary conditions, but will simply show that there are alternative moving boundary conditions to those given in Sec. II which still provide the experimentally verifiable result $R(t) = \xi_R \sqrt{Dt + \beta}$ and which may possibly provide a more accurate description of diffusive fullerene growth.

We consider the alternative moving boundary conditions

$$c(R(t), t) = c_0 R^m, \quad (A1)$$

$$D \frac{\partial c(R(t), t)}{\partial r} = \alpha R(t)^m \frac{dR(t)}{dt},$$

for some parameter m . For $m=0$, these reduce to the boundary condition and the Stefan condition used in Sec. II. A solution of Eq. (2) with the above boundary conditions is of the form

$$c(r, t) = r^m \xi^{-(m+1)} \phi(-\xi^2/4), \quad (A2)$$

where we have assumed the same similarity variable as before, $\xi(r, t) = r/\sqrt{Dt + \beta}$ and $\xi(R, t) = \xi_R$ so that $R(t) = \xi_R \sqrt{Dt + \beta}$, as required. The function $\phi(x)$ can be shown to satisfy the confluent hypergeometric differential equation

$$x\phi''(x) + (c-x)\phi'(x) - a\phi(x) = 0, \quad (A3)$$

with $c=1/2$ and $a=-(m+1)/2$. On taking the moving boundary condition (A1) into account, the solution for $\phi(x)$ is given by

$$\phi(x) = \xi_R^{m+1} [AM(a, c, x) + BU(a, c, x)], \quad (A4)$$

where $M(a, c, x)$ and $U(a, c, x)$ are the confluent hypergeometric functions of the first and second kinds,¹⁷ respectively, and the constants A and B are

$$A = -[(\alpha + 2c_0/\xi_R^2)U(a, c, x_R) + c_0U'(a, c, x_R)]/F, \quad (A5)$$

$$B = [(\alpha + 2c_0/\xi_R^2)M(a, c, x_R) + c_0M'(a, c, x_R)]/F,$$

with $x_R = -\xi_R^2/4$ and F is defined by

$$F = M'(a, c, x_R)U(a, c, x_R) - M(a, c, x_R)U'(a, c, x_R). \quad (A6)$$

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