

Stability and Shrinkage by Diffusion of Hollow Nanotubes

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Abstract. The shrinkage via the vacancy mechanism of a mono-atomic nanotube is described. Using Gibbs-Thomson boundary conditions an exact solution is obtained of the kinetic equation in quasi steady-state at the linear approximation. A collapse time as a function of the size of a nanotube is determined. Kinetic Monte Carlo simulation is used to test the analytical analysis.

Introduction

Recently Sun *et al.* [1] have developed a simple and generic approach to the large-scale synthesis of hollow nanostructures made of Au, Pt and Pd. The key step of this process is the redox reaction between a Ag template and the solution of the appropriate salt precursor. This approach has been successfully applied to prepare hollow nanostructures of noble metals with a range of different morphologies such as spheres, tubes, triangular rings, prisms and cubes. A quite different method for synthesizing hollow (binary) nanostructures that makes use of the Kirkendall effect has been demonstrated by Yin *et al.* [2]. It was shown that due to the larger diffusion rate of cobalt, the reaction of cobalt nanocrystals with oxygen, sulfur and selenium leads to the formation of hollow nanospheres of cobalt oxide, sulphide and selenide, respectively. An interdiffusion theory that describes the diffusion formation of hollow nanospheres as resulting from the precipitation of supersaturated vacancies has been sketched [3]. Such hollow nanostructures have considerable promise in a wide range of technological applications such as catalysis without competing side reactions, vehicles for drug delivery, containment of environmentally sensitive species and many others [1,2,4].

However, it has been noted [5,6] that hollow nanospheres should in fact be unstable in principle and, with time, they will tend to shrink into a solid nanosphere. This is because the resulting reduction in surface area should be energetically more advantageous. According to [5,6] the mechanism of shrinking can be considered as resulting from the vacancy flux from the inner surface to the external surface. The driving force for this flux is the difference between the vacancy concentrations c_v on the inner and external surfaces. In [7] using Gibbs-Thomson boundary conditions an exact solution was obtained of the kinetic equation of shrinking via the vacancy mechanism of a hollow mono-atomic nanosphere in quasi steady-state at the linear approximation. The collapse time as a function of the geometrical sizes of hollow nanospheres was determined. In this paper, we report on the first study of the shrinking kinetics by vacancy diffusion of a pure element nanotube.

Theory

For a nanotube with internal radius r_i and external radius r_e , the variation of vacancy composition near the surfaces with the number of vacancies in the void N_V^{void} is simply given by the Gibbs-Thomson equation:

$$c_V^\pm = c_V^0 \exp\left(\pm \frac{\partial \Delta G_s / \partial N_V^{\text{void}}}{kT}\right), \quad (1)$$

where c_V^0 is the equilibrium vacancy concentration near a planar surface, $\Delta G_s = 2\pi r H \gamma$ is the free energy of the cylindrical surface with a principal radius of curvature r ($r = r_i$ or $r = r_e$) and length H and γ is the surface energy per unit area. In the above formula, the curvature is taken as positive for the inner surface and negative for the external surface. Since for a cylindrical geometry we have that:

$$\frac{\partial \Delta G_s}{\partial N_V^{\text{void}}} = \frac{\partial \Delta G_s}{\partial r} \frac{\partial r}{\partial N_V^{\text{void}}} = \frac{\gamma \Omega}{r}, \quad (2)$$

Eq. 1 reduces to:

$$c_V^\pm = c_V^0 \exp\left(\frac{\beta}{\pm r}\right), \quad (3)$$

where $\beta = \gamma \Omega / kT$ and Ω is the atomic volume. In the following, we will assume that the equilibrium vacancy concentration c_V^{eq} in the volume of the system does not strongly differ from the equilibrium vacancy concentration near a planar surface ($c_V^0 \approx c_V^{\text{eq}}$) and, thereafter, we will use c_V^{eq} instead of c_V^0 . If the ratio $\beta/r \ll 1$, then, for the vacancy concentrations at the inner and the external surfaces of a nanotube a linear approximation in a similar way to a hollow nanosphere [5-7], can be used:

$$\begin{aligned} c_V^i = c_V(r_i) &= c_V^{\text{eq}} \left(1 + \frac{\beta}{r_i}\right), \\ c_V^e = c_V(r_e) &= c_V^{\text{eq}} \left(1 - \frac{\beta}{r_e}\right). \end{aligned} \quad (4)$$

A linear approximation (Eq. 4) is satisfactory (with a maximum error of 5%) when $r_i > 3\beta$.

The diffusion equation in cylindrical coordinates (considering the area far from the ends of the nanotube and therefore the assumption of cylindrical symmetry is valid) for the steady-state approximation of the vacancy concentration is [8]:

$$\frac{\partial}{\partial r} \left(r \frac{\partial c_V}{\partial r} \right) = 0. \quad (5)$$

With the boundary conditions of Eq. 4 this has the following solution:

$$c_V(r) = c_V^{\text{eq}} \left[1 + \beta \frac{r_e \ln(r_e) + r_i \ln(r_i) - (r_e + r_i) \ln(r)}{r_e r_i \ln(r_e / r_i)} \right]. \quad (6)$$

Then, according to Fick's first law, the vacancy flux J_V from the void to the shell across the inner surface is simply given by:

$$\Omega J_V(r_i) = -D_V \frac{\partial c_V}{\partial r} \Big|_{r=r_i}, \quad (7)$$

where D_V is the diffusion coefficient of the vacancies. D_V is related to the measurable tracer diffusion coefficient by $D^* = c_V^{\text{eq}} D_V f_0$ where f_0 is the geometric tracer correlation factor for the lattice. The radius r_i of the inner surface varies with time as:

$$\frac{dr_i}{dt} = -\Omega J_V(r_i) = -c_V^{\text{eq}} D_V \beta \frac{r_e + r_i}{r_i^2 r_e \ln(r_e / r_i)}. \quad (8)$$

The external radius of the nanotube r_e changes can be found from the condition of conservation of matter:

$$r_f^2 = r_e^2 - r_i^2 = \text{const}. \quad (9)$$

In order to obtain the analytical (closed form) solution of Eqs. 8 and 9, we introduce new non-dimensional variables and, making use of Eq. 9, we relate them to the old variables:

$$\varepsilon = \frac{r_i}{r_e}, \quad \tau = \frac{6c_V^{\text{eq}} D_V t \beta}{r_f^3}, \quad r_i = \frac{\varepsilon r_f}{(1 - \varepsilon^2)^{1/2}}, \quad r_e = \frac{r_f}{(1 - \varepsilon^2)^{1/2}}. \quad (10)$$

Then Eq. 8 can be rewritten as:

$$\frac{d\varepsilon}{d\tau} = \frac{1}{6} \frac{(1 - \varepsilon^2)^{5/2}}{\varepsilon^2} \frac{1 + \varepsilon}{\ln(\varepsilon)}. \quad (11)$$

This equation can be readily solved analytically to give the solution (where we defined $\delta = \varepsilon / \varepsilon_0$ and $\varepsilon_0 = r_{i0} / r_{e0}$ is the ratio of the inner r_{i0} and the external r_{e0} radii of the nanotube at the initial time $t = 0$):

$$\begin{aligned} \frac{5}{4} \tau(\delta) = & \ln \left[\frac{1 + (1 - \varepsilon_0^2 \delta^2)^{\frac{1}{2}}}{1 + (1 - \varepsilon_0^2)^{\frac{1}{2}}} \right] + \arcsin(\varepsilon_0 \delta) - \arcsin(\varepsilon_0) + \varphi_1(\varepsilon_0) - \varphi_1(\varepsilon_0 \delta) + \\ & + [\varphi_2(\varepsilon_0 \delta) - 1] \ln(\delta) + [\varphi_2(\varepsilon_0 \delta) - \varphi_2(\varepsilon_0)] \ln(\varepsilon_0), \end{aligned} \quad (12)$$

where

$$\varphi_1(x) = \frac{1 + 3x + x^2}{2(1 - x^2)^{\frac{1}{2}}(1 + x)}, \quad (13)$$

$$\varphi_2(x) = \frac{2 + 2x - 3x^2 + 2x^3 + 2x^4}{2(1 - x^2)^{\frac{3}{2}}(1 + x)}, \quad (14)$$

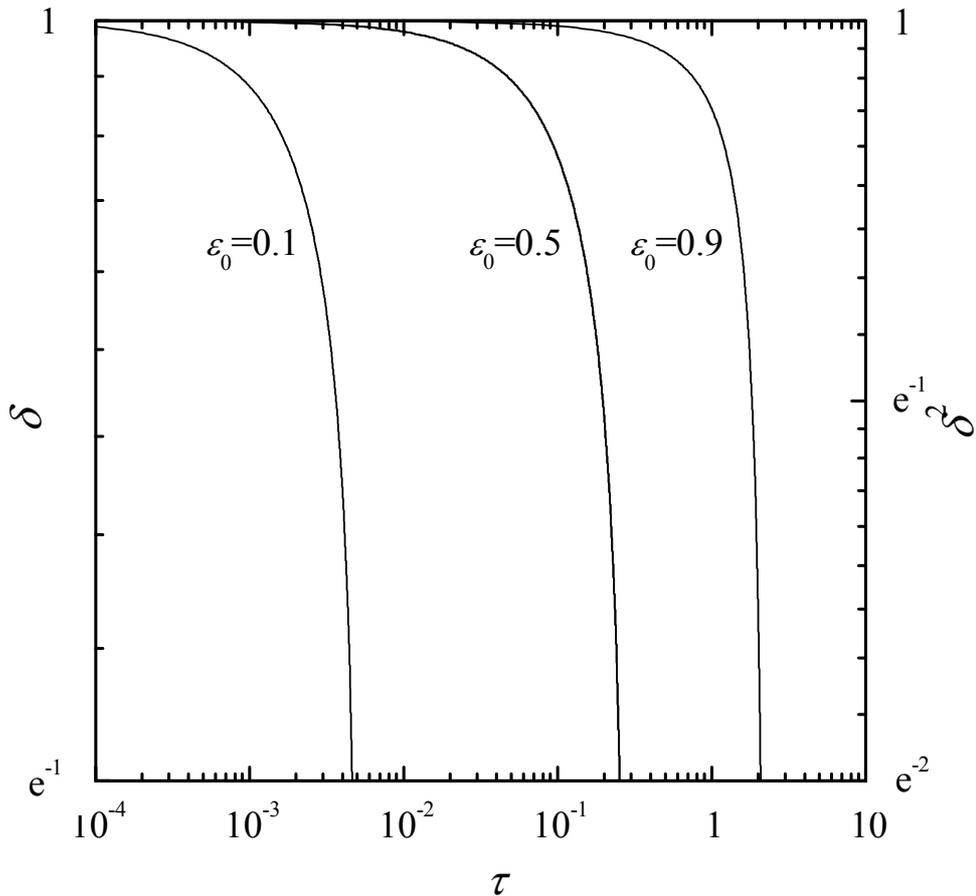


Figure 1. Shrinking kinetics of a pure element nanotube having initial ratios of inner and external radii $\varepsilon_0 = r_{i0}/r_{e0}$ equal to 0.1, 0.5 and 0.9. The normalized size parameter and dimensionless time are $\delta = \varepsilon/\varepsilon_0$ and $\tau = 6c_v^{\text{eq}} D_v t \beta / r_f^3$ respectively.

Since the linear approximation of the Gibbs-Thomson boundary conditions (Eq. 4) is satisfactory only at the beginning from $r_i > 3\beta$ (as mentioned above), the lowest value of δ given by Eq. 12 cannot be equal to zero. It should obey the following condition: $\delta > \varepsilon_0^{-1} [1 + (r_f/3\beta)^2]^{1/2}$. Therefore, it is reasonable to define a collapse time as the time during which the magnitude of δ will decrease e times, namely: $\tau_c = \tau(\delta = e^{-1})$. Hence, Eq. 12 can be applied to find the collapse time only for a nanotube with geometrical parameters obeying the following condition: $\varepsilon_0 > e [1 + (r_f/3\beta)^2]^{1/2}$. It should be noted that ε^2 is the ratio of the number of virtual lattice sites within the void to the total number of lattice sites inside the whole of the nanotube, i.e.:

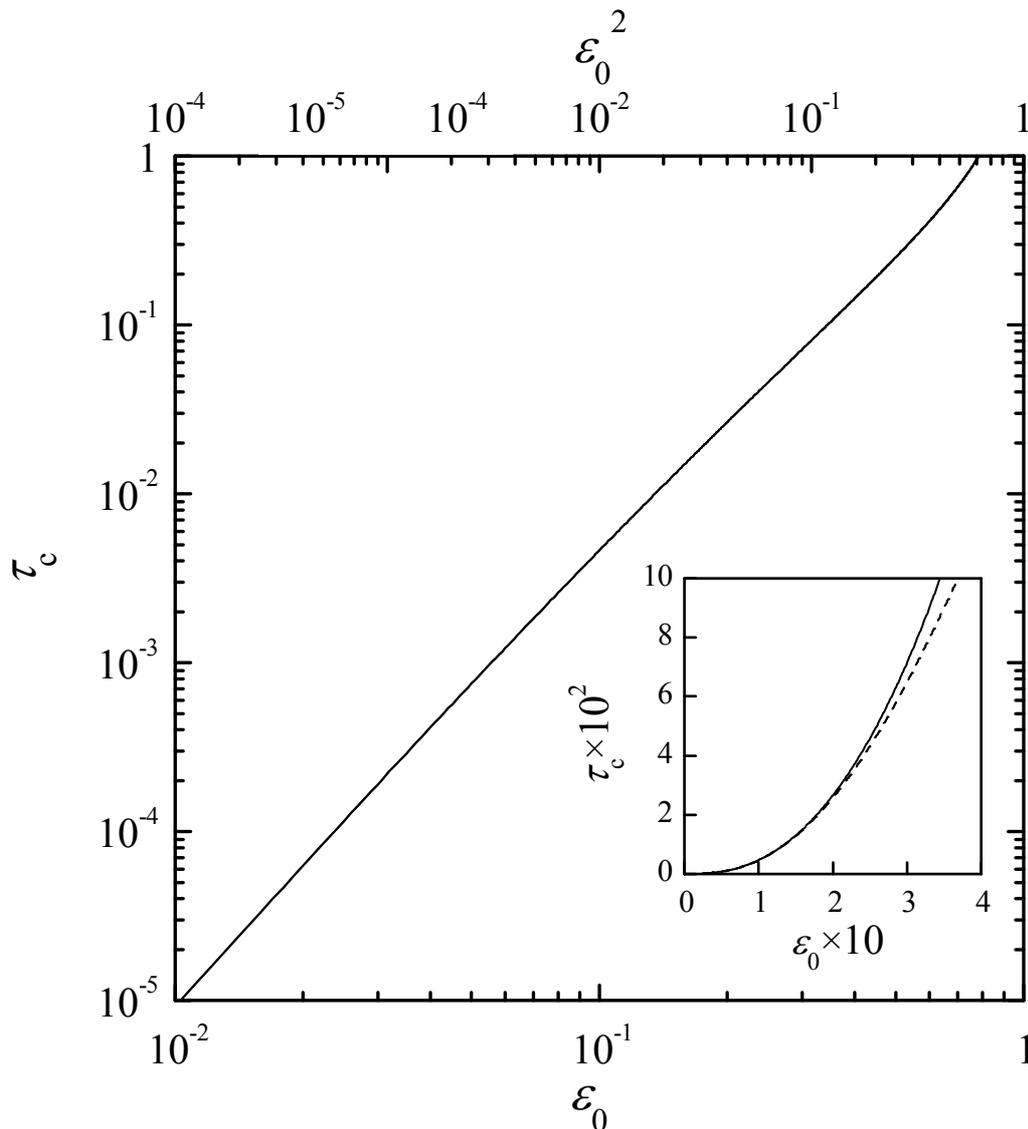


Figure 2. The dimensionless collapse time $\tau_c = \tau(e^{-1})$ as a function of the dimensionless size parameter $\varepsilon_0 = r_{i0}/r_{e0}$ of a nanotube at $t = 0$. The inset show the asymptotic approximation (dashed line) of the exact solution (solid line) Eq. 12 for the case $\varepsilon_0 \rightarrow 0$ Eq. 16.

$$\varepsilon^2 = \frac{r_i^2}{r_e^2} = \frac{N_V^{\text{void}}}{N + N_V^{\text{shell}} + N_V^{\text{void}}}, \quad (15)$$

where N is the numbers of atoms and N_V^{shell} is the numbers of vacancies within the shell of the nanotube respectively and N_V^{void} is the number of vacancies in the void of the nanotube.

The course of the shrinking kinetics by vacancies of a pure element nanotube can be visualized with the aid of Fig. 1. This shows a plot of the normalized size parameter δ (or δ^2) versus the dimensionless time τ for three initial ratios of inner and external radii ε_0 , these being 0.1, 0.5 and 0.9. It is evident that shrinking is delayed with an increase of ε_0 (with constant r_f). The dependence of the collapse time $\tau_c = \tau(e^{-1})$ on the initial ratio of the inner and external radii ε_0 is plotted in Fig. 2.

Finally, let us consider the asymptotic behavior of the collapse time τ_c of the nanotube at $\varepsilon_0 \rightarrow 0$. We expand every function in Eq. 12 into a Taylor series. Thus we get relationship:

$$\tau_c = -2\varepsilon_0^3 \ln(\varepsilon_0) + O(\varepsilon_0^3), \quad (16)$$

which is satisfied over a rather wide range of ε_0 values (see Fig. 2, inset).

Kinetic Monte Carlo simulations

Monte Carlo (MC) calculations were performed on a f.c.c. lattice $44a \times 44a \times 16a$ (a is the lattice parameter) with periodic boundary conditions. The initial nanotube with $\varepsilon_0 = 0.5$ consisted of 38 656 atoms and had an inner radius $r_{i0} = 8a$, external radius $r_{e0} = 16a$ and a linear size $H = 16a$. The axis of the nanotube was oriented along the [001] direction (z -direction) and had $X_{\text{axis}} = Y_{\text{axis}} = 22a$ spacings. The rest of the sites on the lattice were vacant. Therefore, periodic boundary conditions only along the z -direction were imposed. No initial vacancies were introduced inside the shell itself of the nanotube. We consider nearest neighbor pair interactions. The reduced pair interaction energy $\phi/kT = -1.2$ was chosen using the expression [7]:

$$-\frac{6\phi}{kT} \approx \frac{1}{1 - 2c_V^{\text{eq}}} \ln\left(\frac{1 - c_V^{\text{eq}}}{c_V^{\text{eq}}}\right) \quad (17)$$

to provide on the one hand reasonable calculation speed and, on the other, an equilibrium vacancy concentration $c_V^{\text{eq}} \approx 7.54 \times 10^{-4}$ close to the vacancy concentration at the melting temperature T_m .

We chose the Metropolis MC algorithm for its transparency and to provide a clear relationship between MC steps per atom (MCSA) n and real time t . For this case, the relation evidently is $t = n/\Gamma_0$, where $\Gamma_0 = 12\nu_0$ and ν_0 is the effective attempt frequency. Then it

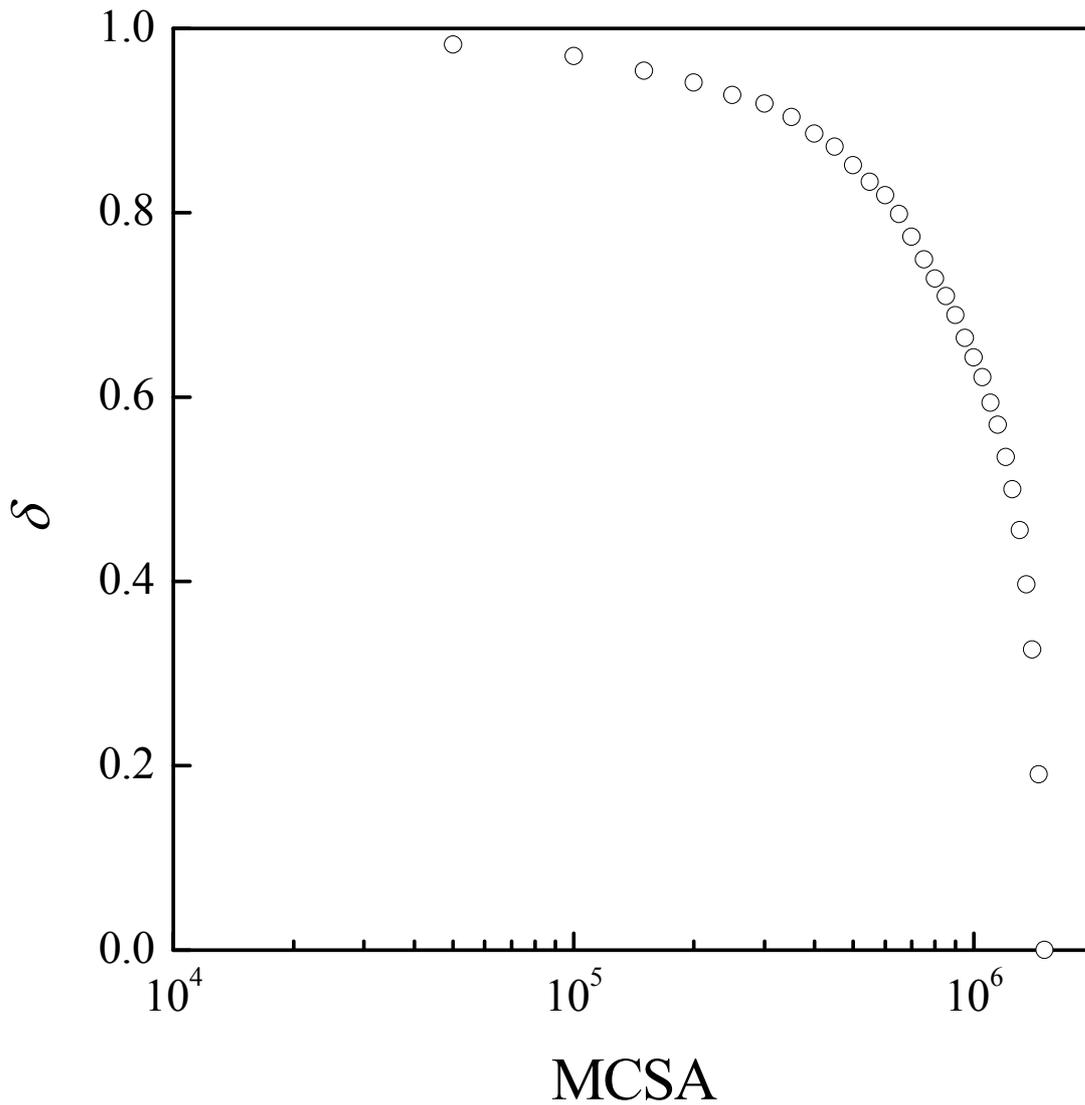


Figure 3. MC simulation of the shrinking kinetics of a pure element nanotube with $\varepsilon_0 = 0.5$ and $\phi/kT = -1.2$. The normalized size parameter is $\delta = \varepsilon/\varepsilon_0$.

follows immediately that $D_V t = a^2 n/12$ (for this model $D_V = a^2 \nu_0$). Thus, if Eq.12 is valid then using it for the τ calculation on the basis of measurements of N_V^{shell} and N_V^{void} during MC simulations and, next, determination of ε (or δ) with aid of Eq. 15, it follows from Eq. 10 that we should get a linear dependence of τ versus n .

In Fig. 3, the changes of the normalized size parameter δ are shown during MC simulation of the shrinking kinetics of a f.c.c. nanotube. As can be seen from Fig. 4, τ calculated from this data according to Eq. 12 depends linearly from n . Thus the results of the analysis above of the shrinking kinetics of a nanotube are in complete accord with the kinetic MC simulation of this process. Linear fitting of the data (Fig. 4) allows the determination of the parameter β (see Eq. 10). Taking into account that for the nanotubes studied $r_i = 8\sqrt{3}a$, we will have that $\beta \approx 1.296a$ using the linear fitting only for the points satisfying the condition $r_i > 3\beta$ (see Fig. 4). The parameter β directly relates to the surface energy per unit area γ . It should be noted for our purposes, since any nanotube has inner and external surfaces, and each of them has a set of different facets, γ is considered to be the mean of some effective surface energy per unit area averaged over all facets of both surfaces of

the nanotube (the influence of the external one will be stronger due to its larger area) during shrinkage. Therefore, knowing the parameter β allows the determination of the crystallographic surface with the surface energy per unit area equivalent or close to the averaged surface energy per unit area of internal and external surfaces of nanotube during the shrinkage.

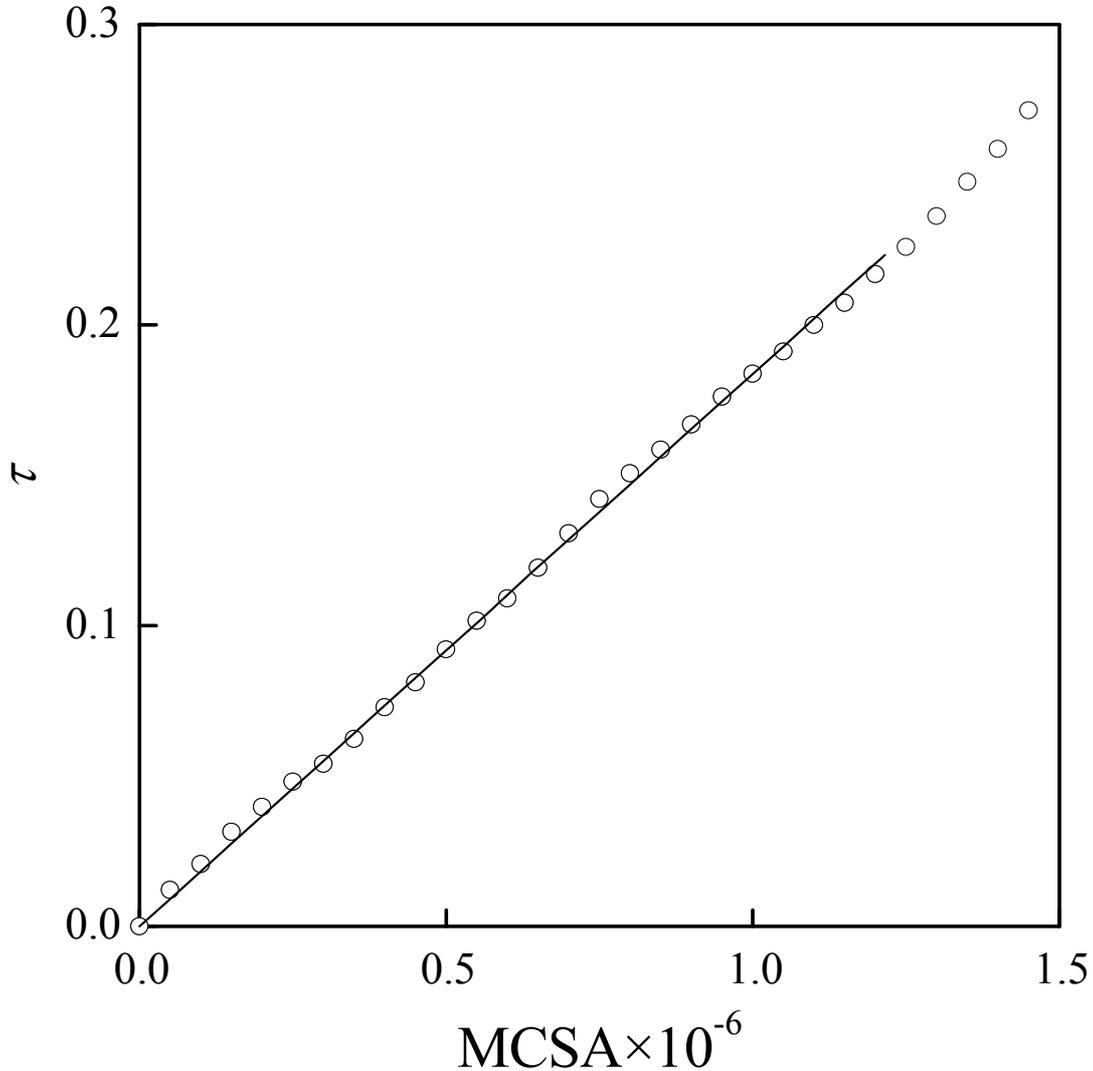


Figure 4. Test of Eq. 12 on the basis of the results of MC simulation shrinking kinetics of a pure element nanotube with $\varepsilon_0 = 0.5$ and $\phi/kT = -1.2$ (see Fig. 3).

The simplicity of the model used in the MC simulation allows the writing of expressions for the surface energy per unit area $\gamma = -3\phi/s$ (s is the area per atom) considering that each surface atom has 6 bonds on average. Then, using the relation $s = -3\Omega\phi/\beta kT$ we can calculate the area per atom and next, compare with the ones for crystallographic surfaces. Taking into account that for the f.c.c. lattice the volume per atom is $\Omega = a^3/4$, we have that $s \approx 0.694a^2$. This value is close to $0.707a^2$ – the value of the area per atom for $\{110\}$ crystallographic planes. Thus, the averaged surface energy per unit area of the external surface (its contribution in the averaging of γ is dominant) of such a nanotube during shrinking is close to γ of the $\{110\}$ crystallographic surface. It is well known from both experimental data and molecular dynamics (MD) simulations using the embedded-atom method that the $\{110\}$ surface inclines to the reconstructions with increasing atomic density (see, for example, [9-12] and references therein). Therefore, we can anticipate that the reconstruction processes will occur in areas of high energy facets on the external surface of such nanotubes both in

real experiments and in MD simulations by the embedded-atom method. Furthermore, we should note that the reconstruction of the external surface has already been observed during the MD simulation of hollow nanospheres with similar geometrical parameters [13]. In principle, such reconstruction can noticeably affect the kinetics of the shrinkage nanotube described above. Therefore, further progress in the investigations of the stability of nanotubes should probably be guided by the MD method.

Summary

The shrinkage via the vacancy mechanism of a pure element nanotube has been described. Using Gibbs-Thomson boundary conditions an exact solution has been obtained of the kinetic equation in quasi steady-state at the linear approximation. The collapse time as a function of the geometrical sizes of nanotubes has been determined. Kinetic MC simulation of the shrinkage of nanotube was performed: it completely confirmed the predictions of the analytical model. However, it has been shown on the basis of this simulation that under real conditions reconstruction of the external surface can occur. This reconstruction could not be taken into account either in the theoretical analysis or kinetic MC simulation.

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