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THE SHAPE OF A NUCLEUS GROWING ON THE STRONGLY CURVED SURFACE OF A NANOFIBER

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Abstract. The equilibrium shape of a critical nucleus has a strong impact on important parameters of nucleation theory, such as the nucleation rate. While on a flat substrate the growing nucleus has the shape of a spherical cap, the shape of a nucleus on the strongly curved surface of a nanofiber is more complex. In the present paper, we propose a simple model for estimating the deviation of the shape of the critical nucleus from spherical. It is shown that the nucleus extends more in the direction of the axis of the nanofiber than in the perpendicular direction, and the deviation from a spherical shape is stronger in the case of well wettable surfaces.

Keywords: nanofiber, nucleation, equilibrium shape.

1. Introduction

In recent years, nanotechnology has found a constantly growing range of applications in civil engineering. Nano-capsules filled with gel and placed in the volume of concrete can provide a self-healing ability for the material; submicron optical fibers mixed with Portland cement have enabled the creation of translucent concrete; carbon nanotubes improve the mechanical durability of concrete; titanium dioxide nanoparticles break down organic pollutants; zinc oxide nanoparticles improve the resistance of concrete to water, etc. [1,2]. One of such possible applications of nanotechnology in civil engineering is protection of buildings from aggressive influence of the environment. Many deteriorative phenomena start at the surface of a building material and slowly find their way into the volume, which makes protection of the surface a very important task [3]. However, nanoparticles tend to attract each other and to coagulate, which usually makes it a non-trivial task to cover the surface of a building material.

In recent times, nanotextiles have been proposed as a potential way to solve this problem. Nanotextiles by themselves have a number of useful properties, which make them a promising candidate for protective layers. Their small thickness make them very flexible and nearly transparent, which is important, for example, for protection of historical building, which often have strongly curved architectonic elements. Because a nanotextile is a porous material, the air can relatively freely pass through it. This porosity and extremely small radius of curvature of nanofibers lead to very high surface-to-volume ratio for this type of a material in comparison with usual protective materials like plasters. It means that nanotextiles interact with the environment stronger than usual materials. Moreover, if we manage to distribute nanoparticles with desired properties uniformly over the surface of a nanotextile, the resulting textile will combine good properties of both types of nanomaterial. For example, silver nanoparticles are known to have strong bactericide effect. The nanotextile imbued with silver nanoparticles and attached to the surface of construction material will inhibit a growth of molds and significantly improve the longevity of building. Taking into account huge amount of money paid every year for restoration of surface of civil constructions every factor which can reduce the rate of required treatment will lead to appreciable savings.

One possible way to achieve a uniform distribution of nanoparticles on the surface of a nanotextile is by a nucleation process. The nanotextile is placed in a chamber filled with a medium in a metastable state. Due to the subsequent nucleation and growth process, nanoparticles are formed on the surface of the nanotextile. Since the nucleation process is stochastic, a generally uniform distribution of nanoparticles over the surface can be expected. A better understanding of the nucleation process on a highly curved nanotextile surface will also be valuable in applications outside civil engineering. For example, technology involving this process has been suggested for improving the efficiency of semiconductor devices [4].

2. Heterogeneous nucleation

From the thermodynamical point of view, the formation of nuclei on the surface of a nanofiber is controlled by an excess of Gibbs free energy. In a metastable medium, atoms have higher free energy than in the form of a cluster. The expression for the change of free energy during this transition consists of two terms: the volume term, and the surface term. The volume

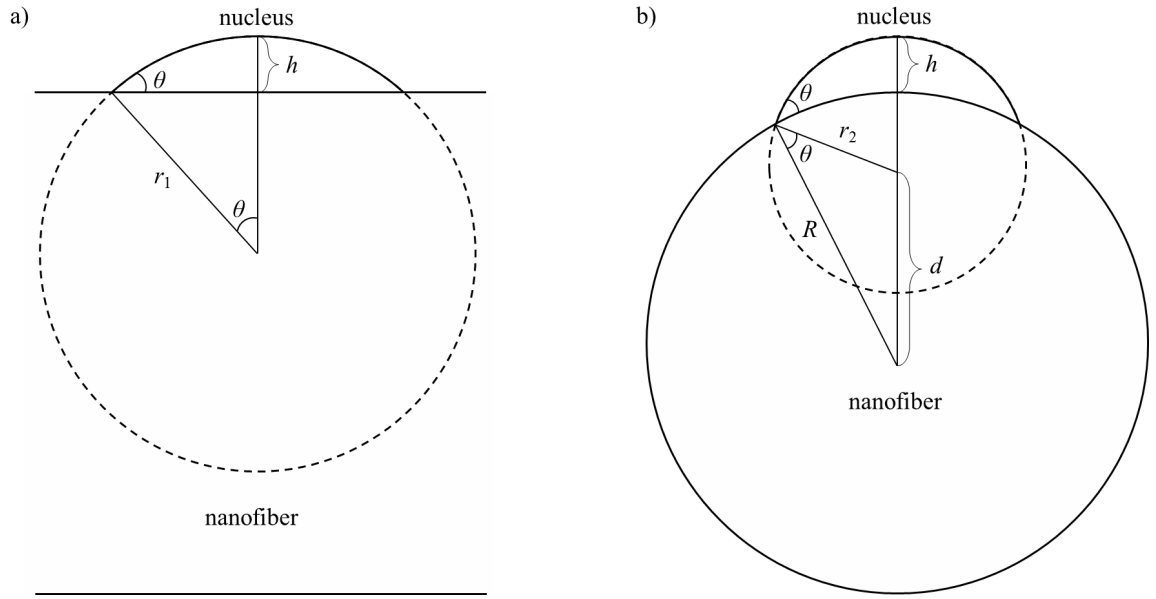

FIGURE 1. Cross-sections of the nucleus on the nanofiber: a) parallel to the nanofiber axis; b) perpendicular to the nanofiber axis.

term expresses the general tendency of a metastable phase to become stable. This term makes a negative contribution to the total free energy of the cluster. The surface term is positive, because the atoms on the interface have relatively high free energy. Thus, the change in the total free energy of n atoms during their transition from the metastable phase into a nucleus can be written as follows:

$$\Delta G = -n\Delta\mu + \gamma\sigma n^{2/3}, \tag{1}$$

where $\Delta\mu$ is the difference of the chemical potentials of the initial metastable phase and the cluste, σ represents the average excess surface energy, and γ stands for the so-called shape factor. The growing nucleus is in contact with the ambient metastable phase and the supporting nanofiber. Both areas of contact are proportional to $n^{2/3}$, and the specific proportionality coefficient leads to the shape factor γ.

Equation (1) represents the energy barrier that the growing nuclei have to overcome, because for small n the surface term in (1) prevails. The critical nucleus is in non-stable equilibrium with the environment, and its size can be found to be

$$n = \left(\frac{2\gamma\sigma}{3\Delta\mu}\right)^3. \tag{2}$$

The nucleation rate, i.e. the number of overcritical nuclei appearing in the system per unit volume per unit time, is proportional to the exponent of the free energy of a critical nucleus:

$$I \sim \exp(-\Delta G_c). \tag{3}$$

It can be seen from the above formulas that the nucleation rate depends on the specific shape of the critical nucleus, represented by its shape factor γ. In order to describe the nucleation process on the surface of nanofibers one needs to know the shape of the corresponding nuclei [5,6].

In the standard theory of heterogeneous nucleation it is assumed that the characteristic radius of curvature of the substrate is much larger than the radius of the nucleus. This assumption leads to the conclusion that growing nuclei have the shape of a spherical cap. However, this assumption is not valid for heterogeneous nucleation on a nanotextile.

3. Equilibrium shape of a nucleus

The equilibrium shape of a nucleus on an arbitrary surface can be obtained by minimizing its free energy under the condition of constant volume. The application of this principle to the line of contact of the nucleus with the substrate leads to the well-known Young-Laplace equation for contact angle θ:

$$\sigma_{sa} - \sigma_{sn} - \sigma_{na}\cos\theta = 0, \tag{4}$$

where $\sigma_s a$ stands for the surface tension between substrate and ambient phase, σ_{sn} stands for the surface tension between substrate and nucleus, and σ_{na} stands for the surface tension between nucleus and ambient phase.

From (4) it follows that contact angle θ is constant along the whole line of contact of the nucleus with the nanofiber. Consequently, the equilibrium shape of a nucleus on the cylindrical surface of a nanofiber cannot be a spherical cap, because the contact angle on the intersection of a sphere with a cylinder varies along the contact line.

Some research has been done on the equilibrium shape of droplets on fibers [7,8]. In these papers it is usually assumed that the droplet already has a

macroscopic size. However, for applications in nucleation theory one needs to consider very small droplets smaller in size than or comparable in size with the radius of the nanofiber. In the present paper, we propose a simple theoretical model allowing the shape factor of very small nuclei to be estimated.

While the nucleus as a whole cannot be considered as a spherical cap, one can assume that its cross-sections by planes parallel and perpendicular to the axis of nanofiber may be well approximated by circular arcs. However, these arcs have a different diameter and their centers do not coincide.

We denote the thickness of the nucleus (i.e., the maximum distance of its surface from the surface of the nanofiber) as h, the radius of a nanofiber as R, and the radii of the circular arcs in parallel and perpendicular cross-sections as r_1 and r_2 (see Figure 1). Then

$$h = r_1(1 - \cos\theta) \tag{5}$$

and

$$h = d + r_2 - R, \tag{6}$$

where d is the distance between the axis of the nanofiber and the center of the circular arc in perpendicular cross-section:

$$d^2 = r_2^2 + R^2 - 2r_2R\cos\theta. \tag{7}$$

From (6) and (7), we obtain the expression for the radius of curvature of the surface of the nucleus in the plane perpendicular to the nanofiber axis:

$$r_2 = \frac{h^2 + 2hR}{2(h + R - R\cos\theta)}. \tag{8}$$

The deviation of the shape of the nucleus from spherical can be estimated by the ratio of its radii of curvature r_1 and r_2:

$$\frac{r_1}{r_2} = \frac{2(x + 1 - \cos\theta)}{(x + 2)(1 - \cos\theta)}, \tag{9}$$

where $x = h/R$ is the dimensionless thickness of the nucleus. In Figure 2, the dependence of ratio (9) on dimensionless thickness x is shown for different values of the contact angle. It is clear that the more wettable the surface of the nanofiber is, the larger is the deviation of the shape of the nucleus from a spherical cap.

4. Conclusion

It follows from (9) that the growing nucleus is always more extended in the direction parallel to the nanofiber axis than in the perpendicular direction (r_1/r_2 is always greater than 1). For a well-wettable surface ($\theta \approx 0$, $\cos\theta \approx 1$) this effect is stronger, because the area of contact of the nucleus with the fiber is larger and the nucleus better "feels" the deviation of the surface of the fiber from the flat surface.

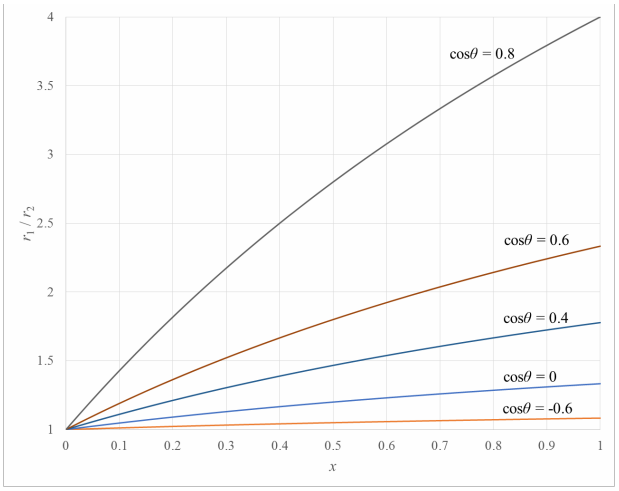

Figure 2. Deviation of the equilibrium nucleus shape from spherical as a function of nucleus relative thickness x; r_1 is the radius of curvature in the plane parallel to the axis of the nanofiber; r_2 is the radius of curvature in the plane perpendicular to the axis of the nanofiber; θ is a contact angle.

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References

[1] Lee J., Mahendra S., Alvarez P., Nanomaterials in the Construction Industry: A Review of their Applications and Environmental Health and Safety Considerations, ACS Nano, Vol. 4, Issue 7, 2010, p. 3580.

[2] Olar R., Nanomaterials and Nanotechnologies for Civil Engineering, Buletinul Institutului Politehnic Din IASI, Vol. LIV, Issue 4, 2011.

[3] Vodák F. et al. Effect of γ-irradiation on strength of concrete for nuclear-safety structures, Cement and Concrete Res. 35, 2005, p. 1447.

[4] Vaněček M. et al, Steady-state transport under non-equilibrium conditions in undoped and phosphorus doped a-Si:H at very low temperature, Journal of Non-Crystalline Solids, Vol. 90, Issue 1-3, 1987, p. 183.

[5] Demo P., Kožíšek Z., Šášik R., Analytical approach to time lag in binary nucleation, Phys. Rev. E 59, 1999, p. 5124.

[6] Demo P., Sveshnikov A., Hošková Š., Ladman D., Tichá P., Physical and chemical aspects of the nucleation of cement-based materials, Acta Polytechnica 52, 2012, p. 15.

[7] Haloi P. et al, Stability and Surface Free Energy Analysis of a Liquid Drop on a Horizontal Cylindrical Wire Using FEM Simulation, IJRET, Vol. 03, Issue 03, 2014, p. 332.

[8] Wu X., Dzenis Y. A., Droplet on a Fiber: Geometrical Shape and Contact Angle, Acta Mech., Vol. 185, 2006, p. 215.