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A simple method for estimating the size of nuclei on fractal surfaces

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ABSTRACT

Determining the size of nuclei on complex surfaces remains a big challenge in aspects of biological, material and chemical engineering. Here the author reported a simple method to estimate the size of the nuclei in contact with complex (fractal) surfaces. The established approach was based on the assumptions of contact area proportionality for determining nucleation density and the scaling congruence between nuclei and surfaces for identifying contact regimes. It showed three different regimes governing the equations for estimating the nucleation site density. Nuclei in the size large enough could eliminate the effect of fractal structure. Nuclei in the size small enough could lead to the independence of nucleation site density on fractal parameters. Only when nuclei match the fractal scales, the nucleation site density is associated with the fractal parameters and the size of the nuclei in a coupling pattern. The method was validated by the experimental data reported in the literature. The method may provide an effective way to estimate the size of nuclei on fractal surfaces, through which a number of promising applications in relative fields can be envisioned.

1. Introduction

One of the most important open questions in crystallization is the controls of nucleus size and structure by substrate geometry configurations with the auxiliary manipulations of nucleating rates [1–7]. While there have increasing experimental/computational methods for investigating homogeneous and heterogeneous nucleation, there are almost no equivalent developments for assessing the size of the nuclei in contact with complex surfaces structured, for example, in the pattern of self-similarity (fractal structure).

Determining the size of the nuclei on complex surfaces is always a big challenge in aspects of biological, material and chemical engineering. In the last decades, there have been developed many methods that can directly measure the size of nuclei. Gasser et al. [8] reported a real–space imaging technique by laser scanning confocal microscopy for identifying and observing both the nucleation and growth of crystalline regions directly. Yau and Vekilov [9] used direct atomic force microscopy to determine the raft-like shape of apoferritin crystals (quasi-planar nuclei) and estimate their size. Andersen et al. [10] applied *in-situ* powder X-ray diffraction with Rietveld refinement and whole powder pattern modeling to measure the size of maghemite nanocrystals. Nanev et al. [11] used a microscopy-based method to separate the nucleation and growth stages of the crystallization process for insulin crystals and assess their size. Those successfully used techniques, however, meet limitations by complex experimental constraints. For instance, when crystallization takes place in the pores of porous solids, the microscopy-based technique would fail to detect the nuclei. So, more frequently, the size of nuclei remains estimated approximately from (classic and advanced) thermodynamic analysis [12,13], the inverse analysis of experimental data that were not designed to measure the size [14], molecular simulations [7,15] and the combination of experiments and simulations [16]. Although most of the published methods for nuclei size determination might assess the size of nuclei successfully, there remains no perfect approach covering all the phase transition mechanisms and affecting factors, especially when nucleation occurs on fractal surfaces. Therefore, finding a simple way to determine the size of the nuclei heterogeneously nucleating on fractal surfaces is the main task of this study.

A fractal surface is structured in the pattern of self-similarity that repeats at every scale theoretically [17] or in limited scales practically [18–20]. Previous study by Stolyarova et al. [21] indicated that the number of nucleation seeds on a fragment with fractal structures significantly exceeds that on the one with flat surfaces, which can be reasonably due to a sufficient local molecular concentration for nucleation generated by the fractal structure. Furthermore, the nucleation–promoting effect may hold for any substrate with fractal structures. The authors further presented an explicit model to link nucleation density to fractal parameters. Although the model in Ref. [21] contained a nucleus-volume-related parameter, it remains requiring a clear and explicit model to elucidate the way in which the nucleation density is governed

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by the size of nuclei and the fractal parameters of surfaces. This, in turn, may help to establish a method to estimate the nuclei size once the nucleation density and fractal parameters are determined.

In what follows, we first presented a section to establish the relations between nucleation density and the size of the crystals that nucleate on fractal surfaces heterogeneously. We showed scale-depended regimes for calculating the contact areas between the nuclei and substrates. Those generated equations can be used to estimate the size of nuclei once nucleation density, fractal dimension and the up and low bounds of fractal regions were known. The simple method was tested by the data reported in the literature. The results may provide an effective way to estimate the size of nuclei on fractal surfaces.

2. Estimating method

A heterogeneously nucleating process is often very complex especially when nuclei form on a rough surface with, for instance, fractal structures. By tracking a number of representative nuclei with definable "macro" properties from the parent phase (e.g., solutions, gases and melts), this process can be identified qualitatively and/or characterized quantitatively. However, the roughness of substrate may make it difficult to determine the contact area – one of the most important parameters for evaluating the nucleation density and the size of nuclei. Several assumptions were made in this study to obtain a simple and tough estimate. Firstly, a general assumption of spherical-cap shaped nuclei was adopted regardless of the geometry and surface properties of the contact substrate. This provides a practical way to calculate the contact areas between the spherical-cap shaped nuclei and the substrate with complex structure, and to link the size of the contact areas to the real size of the nuclei. Secondly, a Wenzel type contact between the nuclei and rough substrate was retained. This says that the areas of the contact surfaces are completely covered by the nuclei without empty voids involved. And this regime has been reported to account for the boiling and wetting behaviors on fractal hierarchical surfaces [22,23]. The debates of the relevant issues (e.g., the available range and physical limitation of the Wenzel model) have been discussed in depth in the literature [24,25]. Thirdly, it retained the constraints employed extensively in the literature (e.g., [26–28]), that is, the application of macroscopic thermodynamic properties to very small nuclei (groups of molecules) is acceptable. This allows to eliminate the complexity raised by the changes of scale-related properties. This scheme has been used to expose the effect of size and curvature on the characteristics of heterogeneous nucleation on rough surfaces [26], although the deviations of the thermodynamic properties by scaling effect may be relatively large because the thermodynamic inequilibrium (e.g., supercooling or supersaturation) for nucleation is generally innegligible.

Under the premises mentioned above, now we focused on the regimes by which a nucleus is in contact with a substrate. Let R stand for the radius of the spherical-caped nucleus, d the size of the contact area, θ the contact angle between the nucleus (phase 2) agglomerated from the parent phase (phase 1) and the substrate (phase 3), L_x the scale for observing, and L_u and L_i the up and low bounds of the fractal region respectively; see Fig. 1. For a smooth surface, the contact area of the embryo on the surface, a perfect circle, depends only on the diameter, d, without the scaling effect; see Fig. 1(a). The area, S_e, can be expressed as,

$$S_{e1} = \frac{\pi}{4} d^2 = \pi R^2 \cos^2\theta, \quad D = 2 \tag{1}$$

The perfect contact between the spherical-cap shaped nucleus and substrate allows to link the area to the size of the nucleus with the help of the contact angle as shown in Eq. (1).

For a fractal surface, the contact area, remaining a circle roughly, depends on its size, the fractal dimension, and the up and low bounds of fractal region. Three different regimes of the contact area between the nucleus and fractal substrate can be identified as illustrated in Fig. 1(b)–(d).

If a large embryo forms on the fractal surface with a small up bound of fractal region, $d > L_u$, the contact area of the single nucleus over the fractal substrate, S_e, is larger than that over the smooth surface by a factor $(L_u/L)^{(D-2)}$, with L the minimum scale of measurement.

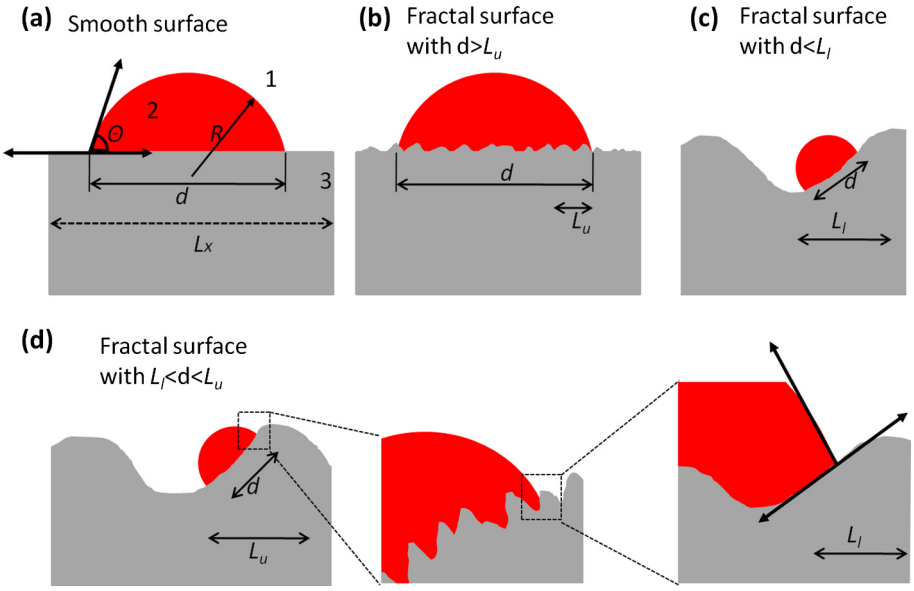

Fig. 1. Schematic illustration of heterogeneous nucleation on different surfaces: (a) nuclei are in contact with smooth surface and there is no scaling effect on the contacted area; (b) nuclei are in contact with fractal surface with the size of the contacted area significantly larger than the up bound of the fractal region, $d > L_u$; (c) nuclei are in contact with fractal surface with the size of the contacted area significantly smaller than the low bound of the fractal region, $d < L_l$; and (d) nuclei are in contact with fractal surface with the size of the contacted area between the low and up bounds of the fractal region, $L_l < d < L_u$. In this illustration, phase 1 represents the parent phase (liquid or gas), phase 2 denotes the nuclei or crystals and phase 3 is the substrate with smooth or rough surfaces.