

Last time**Homogeneous Nucleation: Simple Model**

Steady-State Nucleation Rate

Nucleation Incubation Time

Further Considerations of Nucleation in Solids

The simple theory of nucleation that was developed above contained several assumptions that are inappropriate for nucleation of a solid nucleus in a solid matrix. The assumption of constant and isotropic surface tension is incompatible with many experimental observations in solids. When the nucleating phase has a different volume or shape than the matrix material that it replaces, elastic energy must be considered as part of the volumetric contribution to nucleation.

The interfacial contribution to the nucleation barrier dominates at small nucleus sizes and volumetric contributions dominate at large nucleus sizes. The competition between these contributions can produce a complicated sequence of states for a developing phase—at small nuclei, the system may select a state that minimizes surface energy at the expense of elastic contributions; at larger sizes, interfacial structure can change with concomitant increases in interfacial energy if such a change decreases the excess energy through the volumetric contributions. The sequence of states may include changes in interfacial structure that relax elastic energy or even phase changes in the nuclei if less stable phases have smaller interfacial energies.

Role of Interface Structure on Interfacial Energy

When the nucleating phase has a crystal structure that is the same as its parent phase but differ only in composition or stress-free strain (e.g., they might have different molar volume), a small nucleus can assume non-equilibrium compositions or strains that minimize energy by satisfying interfacial bonds at the expense of volumetric chemical or elastic energy.

Typically for solid-state nucleation, elastic energy considerations dominate at small particle sizes and the interfacial energy can be reduced significantly by adopting a *coherent* structure. As the particle grows, elastic energy can be reduced by the introduction of misfit dislocations into the interface. Such interface dislocations transform a coherent into a semi-coherent interface at the expense of increased interfacial energy.

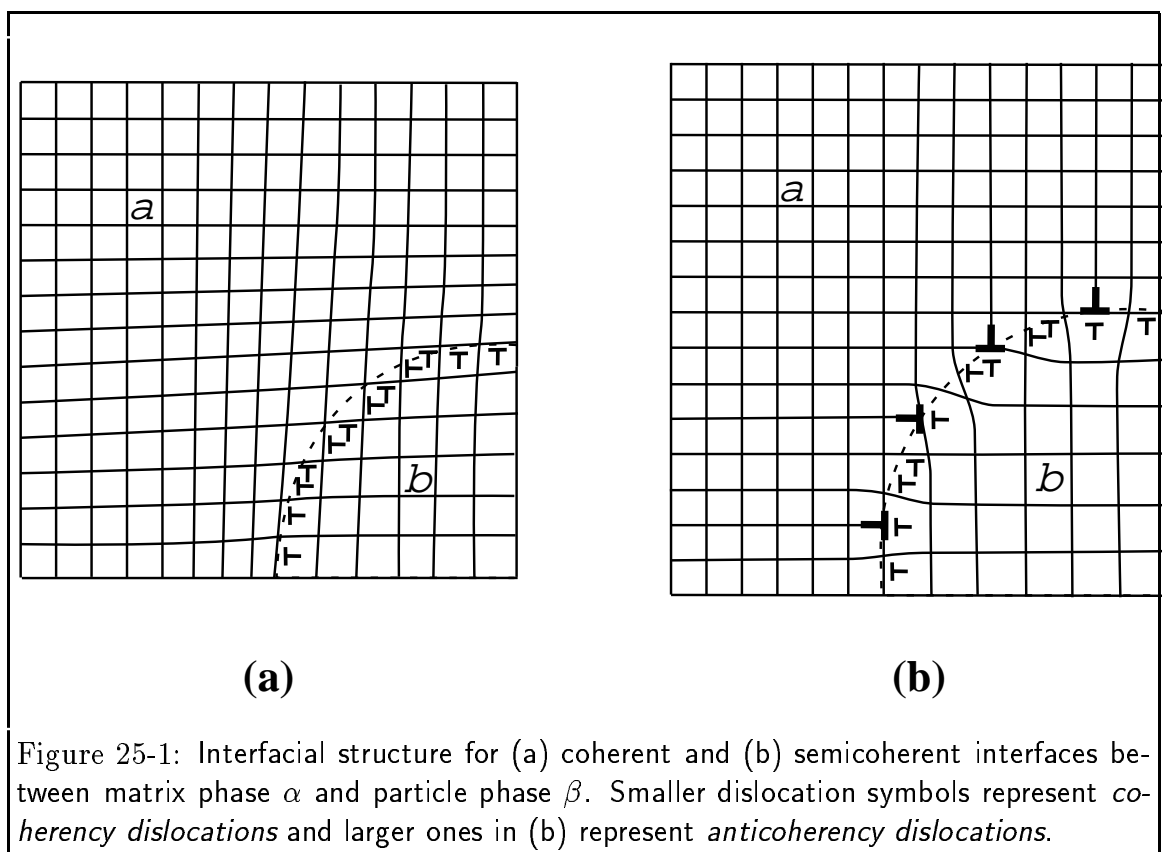
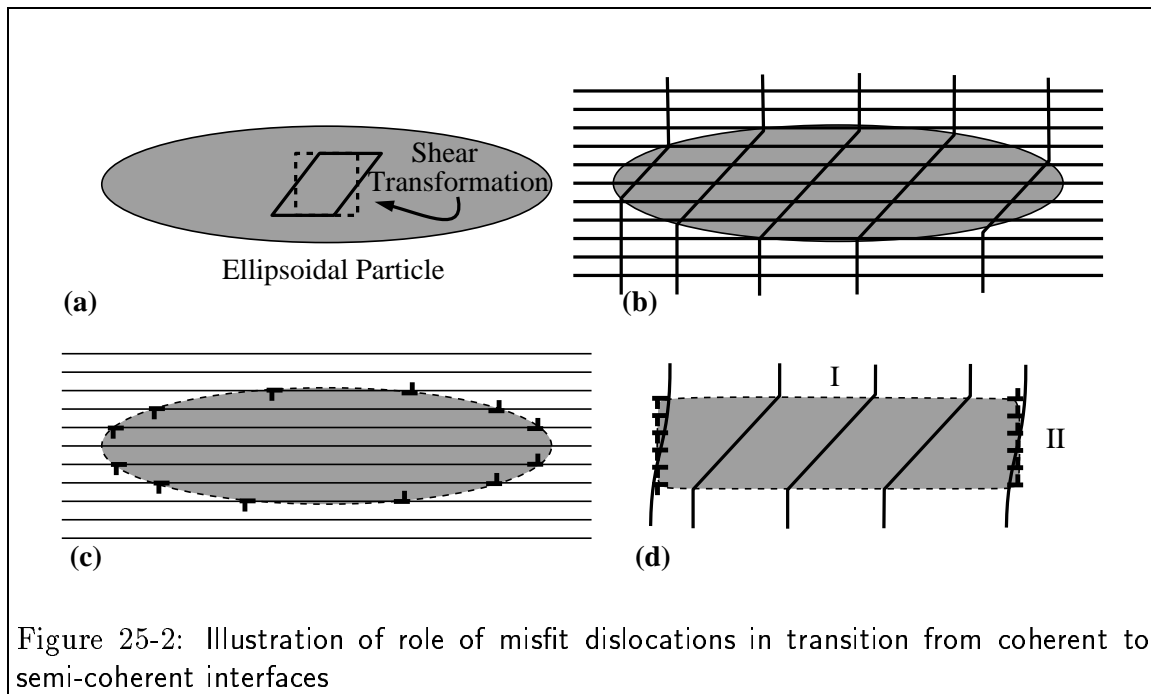


Figure 25-1: Interfacial structure for (a) coherent and (b) semicoherent interfaces between matrix phase α and particle phase β . Smaller dislocation symbols represent *coherency dislocations* and larger ones in (b) represent *anticoherency dislocations*.



When there is no long-range lattice matching across an interface, the interface is *incoherent*.

Role of Elastic Energy in Nucleation

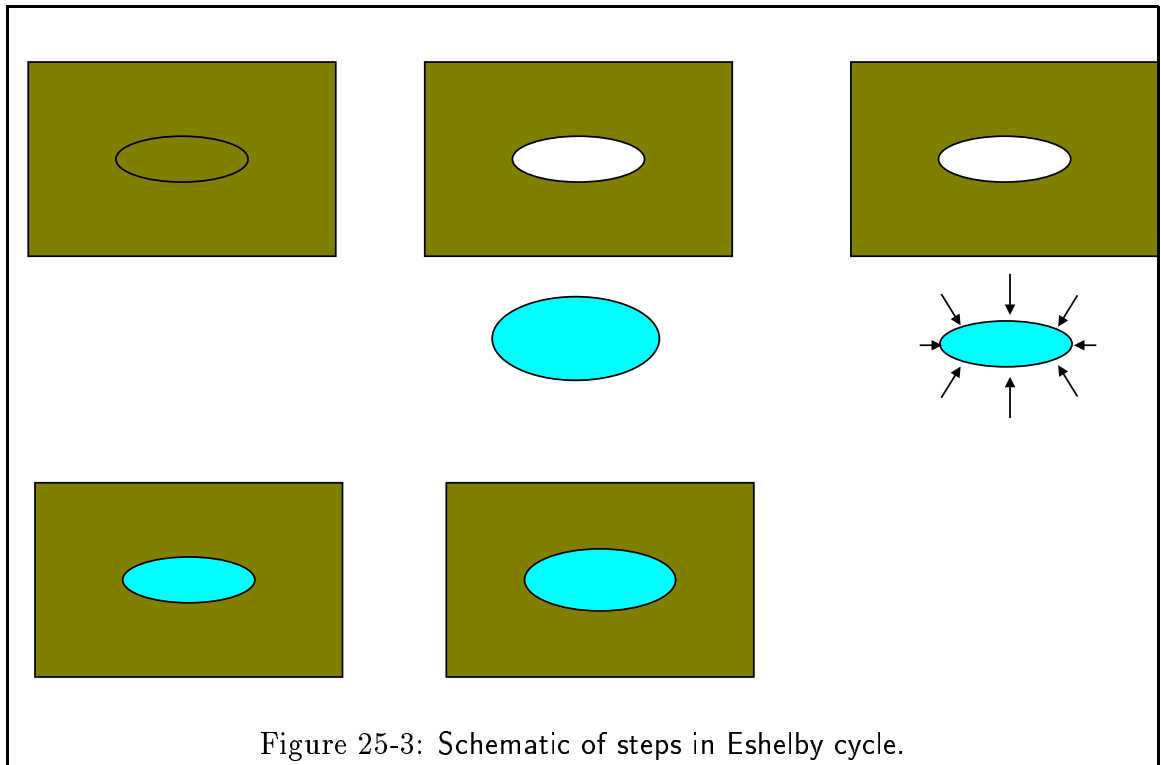
In supersaturated crystalline solid solutions the first particles of the new phase that form are generally coherent with the matrix, because of the lower interphase boundary energy relative to semicoherent or incoherent interfaces. However, coherent inclusions have an associated elastic strain energy that resists nucleation. This elastic strain energy is not easy to express with simple algebraic expressions, except for particularly ideal cases.

If nucleation of an incoherent particle were to occur, it would do so without attendant elastic strain energy, because the incoherent interface would act as a perfect source or sink of point defects and the successful critical nucleus, with the lowest ΔG_c , would be a configuration without the energy penalty of elastic strain energy.

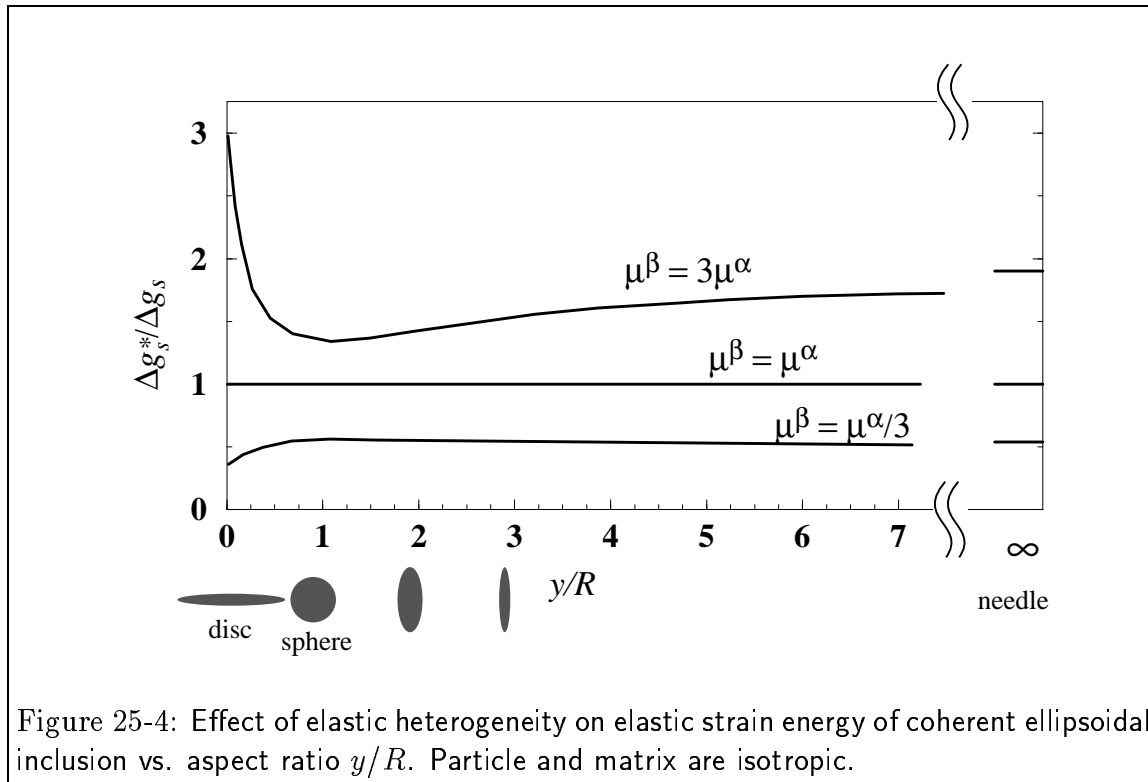
The method for calculating the elastic strain energy of coherent inclusions was developed most elegantly by J.D. Eshelby, and it uses an idealized procedure to create the inclusion and calculate the accompanying strain energy. Eshelby's procedure consists of four steps:

1. Excise region to be transformed from matrix (Increases energy by $\int 2\gamma_{\beta\text{-vapor}} dA$.)
2. Alloy excised region to undergo stress-free transformation strain ϵ_{ij}^T . (Decreases energy by transformation driving force).
3. Apply surface tractions to particle to restore it to its *untransformed* shape (Increases elastic energy of particle).

4. Place particle back into matrix and allow interface to reform (decreases energy by $\int(\gamma_{\alpha-\beta} - 2\gamma_{\beta-\text{vapor}})dA$).
5. Allow particle/matrix system to relax elastically (Increases matrix elastic energy; decreases nucleus elastic energy).



The easiest class of problems of this type to solve make these assumptions: elastic isotropy, elastic homogeneity (same elastic constants in particle and matrix), and that the particle shape is an ellipsoid of revolution (semiaxes a , b , and c). Thus, the theory allows for a *particle-shape dependence of elastic strain energy*.



Heterogeneous Nucleation

Heterogeneous nucleation can occur on imperfections when the nucleating particle effectively “replaces” some energetic feature of the original configuration. For instance, nucleation

on a grain boundary removes grain boundary area and replaces it with interphase boundary area that would have been created anyway by formation of the new phase. Thus, preexisting imperfections effectively “catalyze” the nucleation process.

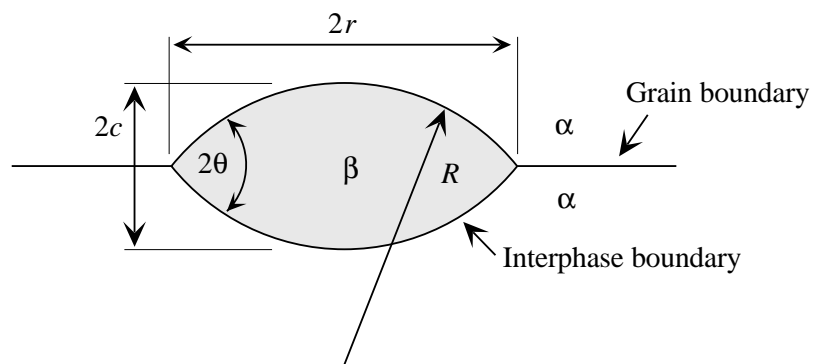


Figure 25-5: Geometrical parameters defining size and shape of a lenticular β particle situated on a grain boundary in phase α for the case of isotropic surface energy. Students should be able to derive an expression for the critical volume for this case. In this case, the mathematics will show that the radius of the heterogeneous particle is the same as that of the homogeneous (spherical) particle.

Heterogeneous nucleation is a commonly observed phenomenon.

Question: How do you explain the following phenomena?

1. If you gently open a carbonated beverage without shaking it, how does it approach equilibrium?

2. If you open a carbonated beverage soon after vigorously shaking it, how does it approach equilibrium?

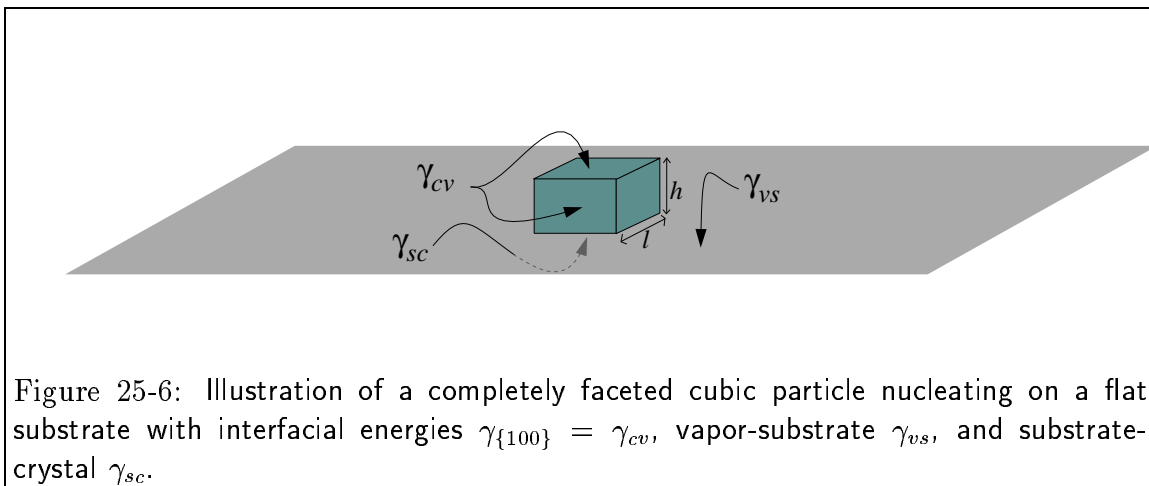
3. If you leave a (previously shaken) carbonated beverage undisturbed for a long time and then gently open it, how does it approach equilibrium? What sets the time scale for the time it must be left undisturbed?
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Heterogeneous nucleation can be understood by considerations of the geometry of the nucleus. A simple model for the case of nucleation of a new phase on an isotropic grain boundary can be obtained by assuming that the nuclei have the shape of two hemispherical caps that abut with an equilibrium dihedral angle given by the Young force balance equation. The model equations can be derived in a parallel to the critical spherical nucleus size that balanced the rate of volumetric energy decrease with the rate of interfacial energy increase.

The following results apply.

1. R_{crit} is the same as for homogeneous nucleation—this makes sense as the critical chemical potential is a function of local curvature in the isotropic case.
 2. ΔG_{crit} is reduced proportionally to the volume reduction of the critical nucleus.
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The steps can be illustrated for a highly anisotropic interface by a simple example of a cubic crystal with $\{100\}$ -facets nucleating in a (100) -direction.



For this case, the ΔG for homogeneous nucleation is given by the maximum of

$$\Delta G_{homog\ nuc} = \Delta g w^3 + 6\gamma_{cv} w^2 \quad (25-1)$$

Therefore,

$$w^* = -\frac{4\gamma_{cv}}{\Delta g}$$

$$\Delta G_{homog}^* = \frac{32\gamma_{cv}^3}{\Delta g^2} \quad (25-2)$$

For heterogeneous nucleation,

$$\Delta G_{heter} = \Delta g l^2 h \gamma_{cv} (l^2 + 4lh) + (\gamma_{sc} - \gamma_{vs}) l^2 \quad (25-3)$$

Therefore,

$$l^* = \frac{-4\gamma_{cv}}{\Delta g}$$

$$h^* = \frac{-2(\gamma_{cv} + \gamma_{sc} - \gamma_{vs})}{\Delta g} \quad (25-4)$$

$$\Delta G_{heter}^* = \frac{16\gamma_{cv}^2 (\gamma_{cv} + \gamma_{sc} - \gamma_{vs})}{\Delta g^2}$$

The shape of the particle is determined by the differences in surface tensions and the geometrical factors associated with the shape of the particle determine the nucleation barrier for heterogeneous diffusion.

Nucleation on Dislocations

Dislocations provide sites of increased energy in a crystal where nucleation can be assisted by reduction of the core and elastic energy of a dislocation.

Location of Heterogeneous Nucleation

The heterogeneous nucleation kinetics will be influenced by both the reduction in ΔG_{crit} (which favors heterogeneous nucleation) and by the number of sites available for heterogeneous nucleation (which favors homogeneous nucleation). These two competing factors can be sorted out by working through the equations and using a model for the dependence of the number of sites available for heterogeneous nucleation on the microstructure (e.g., grain size for heterogeneous nucleation on grain boundaries).

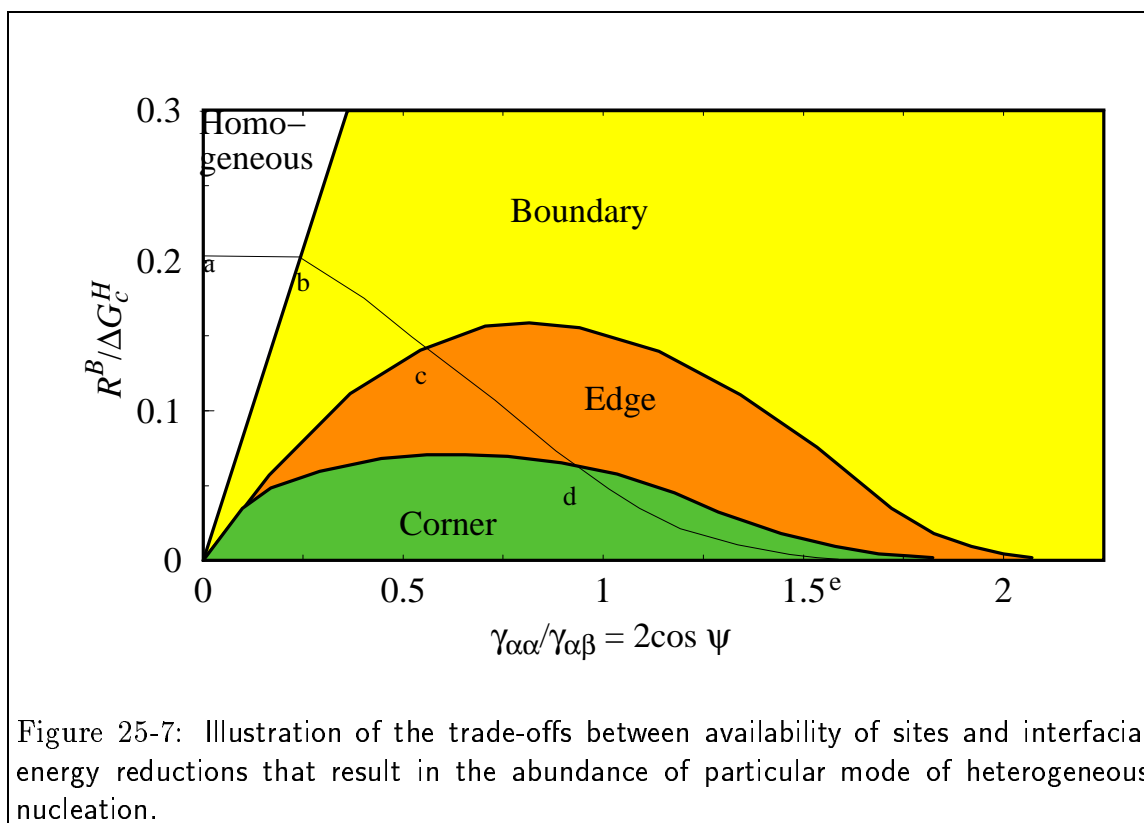


Figure 25-7: Illustration of the trade-offs between availability of sites and interfacial energy reductions that result in the abundance of particular mode of heterogeneous nucleation.