

Article

Nucleation Work on Curved Substrates

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Abstract: Nucleation is the initial phase transition process when nuclei of a new phase form within an undercooled or supersaturated parent phase under appropriate conditions. Nucleation most often occurs through a heterogeneous process on active centers on which the probability of nucleus formation is high. In general, the origin of active centers may be difficult to distinguish. In this work, we consider the formation of crystalline nuclei in a melt on various curved substrates. Knowledge of excess free energy plays a key role in understanding the process of formation of clusters and it is not easy to express this quantity in a considered system. Excess free energy is often approximated within the framework of capillarity approximation based on interfacial energy, which depends on interatomic interactions near the interface, as well as the misfit between melts, surface roughness, temperature, composition, etc., near the phase interface. The formation of nuclei requires overcoming a certain energy (nucleation) barrier that is a consequence of balancing the volume and the interfacial free energy. Knowing the nucleation barrier (W) is crucial for understanding this process, as nuclei predetermine the physical properties of a newly formed phase. W is typically expressed as a function of the nucleus radius; however, in nucleation kinetics, one needs to determine (W) as a function of the number of molecules forming the nucleus. We analyze nucleation work on various substrates (flat, convex, and concave) for crystallization from an aluminum melt to show that the formation of nuclei is the most probable on concave substrates. An analytical expression for W can be easily applied to other systems under consideration. We show that under the same conditions, the critical radius of nuclei is identical for various substrate, in contrast with the critical number of molecules forming a nucleus.

Keywords: nucleation; growth from melt; metals

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1. Introduction

Clusters of a new phase are formed due to fluctuations within an undercooled or supersaturated parent phase. Under the appropriate conditions, these clusters overcome an energy barrier (nucleation work, W) to reach the critical size (i^*) and become nuclei of a new phase. Interfacial energy (W_i^S) increases, and the volumetric energy (W_i^V) decreases with the number of monomers (atoms or molecules, i) forming the cluster. At the critical size (i^*), the nucleation barrier ($W^* = W_{i^*}$) is reached. Subcritical clusters ($i < i^*$) have a tendency to diminish, and overcritical clusters ($i > i^*$) tend to grow.

The classical nucleation theory (CNT) [1–3] succeeded in determining the number of nuclei formed in unit volume per unit time, i.e., the nucleation rate in the stationary state under the assumption of constant supersaturation for vapor–liquid transitions. Gonçalves et al. [4] calculated crystal nucleation rates in supercooled liquid nickel using molecular dynamics (MD) simulations and showed excellent agreement between CNT and MD, which justified the use of the CNT. Turnbull and Fisher [5] suggested the transient probabilities (attachment and detachment frequencies) of monomers on a cluster surface for the liquid–solid transition. The nucleation rate and the number of nuclei (critical size clusters) are exponentially proportional to the nucleation barrier. Determination of the work of formation of clusters thus plays a very important role. In many cases, W is determined as a function of cluster radius (r). However, in the kinetic model [6], the attachment

frequency is proportional to $\Delta g_i = W_{i+1} - W_i$, and we need to determine W_i instead of $W(r)$ dependence, which is quite easy for homogeneous nucleation or heterogeneous nucleation on a flat surface. On other surfaces (convex and concave substrates), the situation is more complicated.

At a constant temperature (T) and pressure (P), the work of formation of an i -sized cluster (W_i) is determined based on the difference of the Gibbs free energy between final,

$$G_{fin} = (M - i) \mu_{liquid} + i \mu_{crystal} + \Phi(i, \Delta\mu), \quad (1)$$

and initial,

$$G_{ini} = M \mu_{liquid} \quad (2)$$

states, which yields

$$W_i = -i \Delta\mu + \Phi(i, \Delta\mu), \quad (3)$$

where $\Delta\mu = \mu_{liquid} - \mu_{solid}$ denotes the difference between chemical potentials of *liquid* and *solid* phases, M stands for the number of molecules in the system, and the excess free energy (Φ [7]) depends on the system under consideration (homogeneous or heterogeneous nucleation on a foreign surface).

In a supersaturated solution, $\Delta\mu$ decreases as a consequence of the formation of crystals; thus, nucleation work and nucleation kinetics change over time [8].

Nuclei are formed in the volume of a parent phase (homogeneous nucleation) or on foreign particles, impurities, point defects, etc. (heterogeneous nucleation) [1]. Nucleation on active centers is a special case [9,10] that occurs when a so-called nucleation agent [11] is added to the melt to increase nucleation rate.

Homogeneous nucleation starts on any monomer surface within the volume of the parent phase. Chen et al. [12] studied the influence of the cooling rate on the solidification process of pure metal Al via molecular dynamics (MD). It was shown that a supercooled Al melt tends to grow to a spherical shape. The number of nuclei formed in unit time (i.e., nucleation rate) and the critical size decrease with an increase in the cooling rate. Chen et al. [13] also applied MD simulations using the embedded-atom method (EAM) to show the influence of pressure on the isothermal solidification process of pure Al. The solidification process was characterized by the mean first-passage time (MFPT) method, X-ray diffraction analysis, and the Johnson–Mehl–Avrami law. The increase in the nucleation rate starts earlier with increasing pressure during isothermal solidification.

Heterogeneous nucleation starts on nucleation sites (foreign substrates or particles, defects, etc.), where the probability of nucleus formation is high. Wypych [14] summarized the nucleation agents in polymer materials, which are used to increase the crystallization rate and modify the structure and morphology. The addition of a nucleation agent contributes to faster crystallization and better organization of the internal structure. Polylactic acid (PLA), one of the most productive biodegradable materials, is difficult to crystallize. Shi et al. [15] summarized the biomass nucleation agents to regulate PLA crystallization behavior. Concerning inorganic systems, Li et al. [16] investigated the influence of aluminum on the morphologies and crystallization kinetics of hemihydrate calcium sulfate, using focused-beam reflectance measurement to show that Al^{3+} ions retard nucleation by increasing surface energy. He et al. [17] showed the effect of different kinds of nucleation agents on the crystallization and microstructure of magnesium aluminosilicate glass ceramics. Nasir et al. [18] observed the aluminum-induced crystallization of amorphous germanium thin films under heat treatment. Structural modifications triggered nucleation for controlled grain growth, which transformed Ge thin film from amorphous to polycrystalline. Understanding the role of foreign nucleation sites is crucial for the entire crystallization process and defines the final properties of crystallites.

O'Masta et al. [19] studied the liquid-phase epitaxy of aluminum on substrates of varying lattice spacing using molecular dynamics simulations to show the formation and growth of small islands. A thermodynamic analysis revealed island creation as a stochastic process. Large-scale molecular dynamics simulation of the solidification of pure aluminum

has had a positive impact on the development of solidification and nucleation theory [20]. Crystal nucleation and growth in aluminum and structural development in the aluminum melt after the addition of a nanoparticle modifier was studied using the electron-beam surface treatment method [21].

It is important to know the structure of heterogeneous substrates and the interfacial energies on a phase interface. Our understanding the process of heterogeneous nucleation and the role of the phase interface was improved through a combination of MD simulations and advanced high-resolution electron microscopy. Fan and Men [22] showed that atomistic mechanisms depend on the misfit between the substrate and the newly formed crystal phase. Structural templating plays a key role in heterogeneous nucleation and crystal growth. Fan et al. [23] used MD simulations to investigate the heterogeneous nucleation kinetics of metallic liquid Al on various substrates with a negative misfit. Heterogeneous nucleation occurs layer by layer when a 2D crystal nucleus is initially formed, after which solids can successively grow.

Using ab initio molecular dynamics simulations, Wang et al. [24] showed that heterogeneous nucleation plays an important role in the atomic arrangement of the substrate surface, which is influenced by the lattice misfit between the melt and solid, surface roughness, and the chemical interaction at the phase interface.

Men et al. [25] used classical and ab initio MD simulations to study prenucleation, i.e., atomic ordering in the liquid near the liquid/substrate interface at temperatures above nucleation temperature, which is influenced by surface roughness, lattice misfit, and chemical interactions between the liquid and the substrate. Prenucleation serves as a precursor for nucleation at the nucleation temperature.

Current experimental methods contribute significantly to the understanding of phase transition kinetics and contribute to the solution of the problem of how to control particle distributions in a considered system. Advances in X-ray sources (synchrotron) have enabled spatiotemporal resolutions sufficient to determine quantitative information related to crystal growth. Feng et al. [26] used in situ X-ray radiography to investigate the solidification of Al alloys. Improvements in spatiotemporal resolution provide a better understanding of the crystallization processes.

In this work, we focus on computation of the work of formation of crystalline clusters of single-component nucleation in a melt for homogeneous and heterogeneous nucleation on flat, concave, and convex substrates depending of the nucleus radius (r) and the number of monomers (i) forming the nucleus. In all computations (for homogeneous and heterogeneous nucleation), we selected material parameters of aluminum [6] at temperatures of $T = 800$ K and $\sigma = 0.075 \text{ Jm}^{-2}$. We performed computations under different conditions. However, under these conditions, we can easily compare our calculations with Turnbull [27]'s original results (the first experimental and theoretical study of aluminum crystallization in liquid droplets) and with our previous work [6].

2. Homogeneous Nucleation

For the sake of simplicity, we used capillarity approximation when Φ is identified using the cluster surface energy ($W_i^S = 4\pi r^2 \sigma$); thus,

$$W^{hom} = -i\Delta\mu + 4\pi r^2 \sigma = -\frac{4\pi r^3}{3v_1} \Delta\mu + 4\pi r^2 \sigma, \quad (4)$$

where $v_1 = m_1 / \rho_c$ is the mean volume per monomer in the crystal phase, m_1 is the atomic mass of the Al atom, and ρ_c denotes the density of the solid crystalline phase. The following simple relation

$$V_c \rho_c = i m_1 \quad (5)$$

implies

$$r = \sqrt[3]{\frac{3m_1}{4\pi\rho_c}} i^{1/3} \quad \text{and} \quad i = \frac{4\pi r^3 \rho_c}{3m_1}, \quad (6)$$

where V_c is the nucleus volume; thus, from Equations (4) and (6), we obtain

$$W^{hom}(i) = -i\Delta\mu + (36\pi)^{1/3} \left(\frac{m_1}{\rho_c}\right)^{2/3} \sigma i^{2/3}. \quad (7)$$

Critical size (r^* and i^* , respectively) follows from the extreme condition:

$$\left(\frac{dW^{hom}(r)}{dr} = 0\right)_{r=r^*} \quad \text{or} \quad \left(\frac{dW^{hom}(i)}{di} = 0\right)_{i=i^*} \quad (8)$$

Thus,

$$r^* = \frac{2\sigma v_1}{\Delta\mu} = \frac{2\sigma m_1}{\rho_c \Delta\mu}, \quad (9)$$

and

$$i^* = \frac{32\pi}{3} \left(\frac{m_1}{\rho_c}\right)^2 \left(\frac{\sigma}{\Delta\mu}\right)^3, \quad (10)$$

and the nucleation barrier is

$$W^* = \frac{16\pi}{3} \left(\frac{m_1}{\rho_c}\right)^2 \frac{\sigma^3}{\Delta\mu^2}. \quad (11)$$

The difference in chemical potentials between crystal and melt is usually approximated by:

$$\Delta\mu = \Delta h_f (T_E - T) / T_E, \quad (12)$$

yielding

$$r^* = \frac{2\sigma v_1 T_E}{\Delta h_f (T_E - T)}, \quad (13)$$

where Δh_f is the heat of fusion, T_E is the equilibrium melting temperature, and $\Delta T = T_E - T$ represents undercooling.

It is well known that smaller crystals are in equilibrium with melt at a lower temperatures than large crystals, and the melting point depression ($\Delta T_m = T_E - T_m$) is approximated by the Gibbs–Thomson equation [28]:

$$\Delta T_m = T_E - T_m = \frac{2\sigma v_1 T_E}{r \Delta h_f}. \quad (14)$$

From Equation (13) yields,

$$\Delta T = T_E - T = \frac{2\sigma v_1 T_E}{r^* \Delta h_f}, \quad (15)$$

which is identical to the Gibbs–Thomson Equation (14). It is not surprising if we consider that at the critical size, the nucleus is in metastable equilibrium with a melt.

However, generally, σ depends on the cluster size (i) and temperature (T). Surfaces of the crystal nucleus have various crystallographic orientations. The interfacial energy of the nucleus is determined by:

$$\Phi = \sum_i A_i \sigma_i \approx 4\pi r^2 \sigma_e, \quad (16)$$

where σ_i represents the interfacial energies on the A_i surfaces of the crystal nucleus, and σ_e is the effective surface energy. In this context, the surface energy (σ) needs to be understood.

The shape of nuclei can be polyhedral, and if we suppose the same shape for various nucleus sizes, only one characteristic dimension (r) can be selected to determine the nucleus surface area [29].

Moreover, σ depends on the cluster size i , and this dependency is most often unknown. Tolman [30] suggested an approximation for the size dependence of the surface energy:

$$\sigma(r) = \sigma_{\infty} \left(1 - \frac{2\delta}{r} \right), \quad (17)$$

where σ_{∞} is the surface energy in the limit of the flat interface, and δ is the Tolman length.

In this case,

$$W(r) = -\frac{4}{3}\pi \frac{r^3}{v_1} \Delta\mu + 4\pi r^2 \sigma_{\infty} \left(1 - \frac{2\delta}{r} \right), \quad (18)$$

and extreme conditions $((d\Delta W(r)/dr)_{r=r^*} = 0)$ yield

$$r_{1,2}^* = \frac{\sigma_{\infty} v_1 \pm \sqrt{\sigma_{\infty}^2 v_1^2 - 2\sigma_{\infty} \delta v_1 \Delta\mu}}{\Delta\mu}, \quad (19)$$

i.e., two solutions for the critical size exist. The work of cluster formation (W) changes in with Tolman length (δ) and reaches a minimum before reaching its maximum at the critical size, as shown in Figure 1. W reaches its maximum at the nucleation barrier (W^*) for homogeneous nucleation (solid line in Figure 1, $\delta = 0$) and decreases with δ (the dashed line in Figure 1 corresponds to $\delta = 0.5 \text{ \AA}$, and the dotted–dashed line corresponds to $\delta = 1.0 \text{ \AA}$).

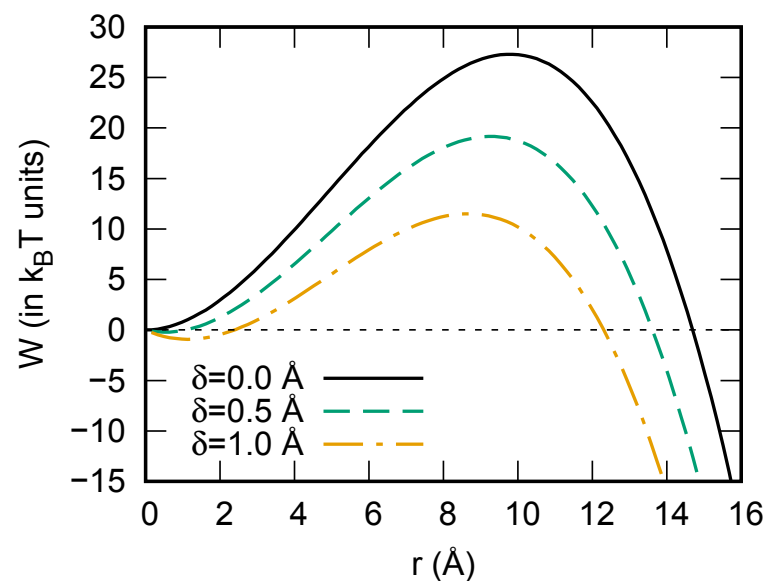


Figure 1. The work of cluster formation (W), as a function of cluster radius (r) for Tolman length, is $\delta = 0$. (solid line), 0.5 (dashed line), and $1.0 \text{ \AA}$ (dotted–dashed line) for aluminum nucleation at temperatures of $T = 800 \text{ K}$ and $\sigma = 0.075 \text{ Jm}^{-2}$.

3. Heterogeneous Nucleation

Nucleation often occurs on foreign substrates, point defects, impurities, etc., where the nucleation barrier is usually lower in comparison with homogeneous nucleation. Crystal nuclei are thus formed on some foreign surfaces, where the probability of nucleus formation is usually higher. In this work, we consider a geometric model of the nucleation barrier on flat, convex, and concave substrates (Figure 2).

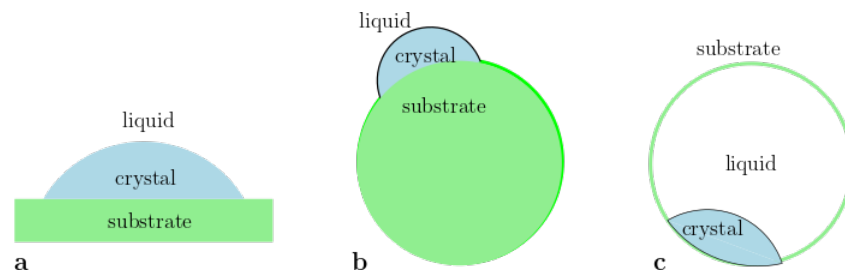


Figure 2. Scheme of the formation of a crystalline nucleus on a flat (a), convex (b), and concave (c) substrate.

3.1. Flat Substrate

The surface contribution to the work of cluster formation on a flat substrate is expressed as (Figure 3)

$$W^{f,S} = S_c \sigma + S_i (\sigma_{cs} - \sigma_{ls}), \quad (20)$$

and using Young's equation ($\sigma \cos \vartheta + \sigma_{cs} = \sigma_{ls}$), we obtain

$$W^f(r) = W^{hom}(r) \psi(\vartheta), \quad (21)$$

where S_c and S_i are the surface energies on the crystal–liquid and crystal–substrate interface, respectively, and

$$\psi(\vartheta) = \frac{1}{4}(1 - \cos \vartheta)^2(2 + \cos \vartheta) = \frac{1}{4}(2 - 3 \cos \vartheta + \cos^3 \vartheta). \quad (22)$$

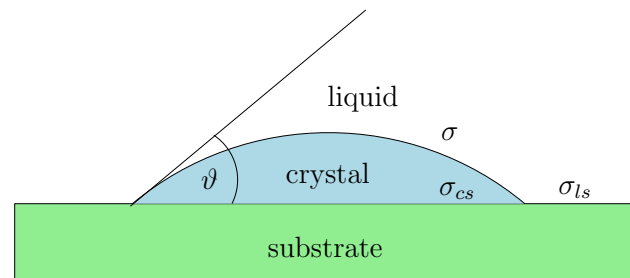


Figure 3. Schematic representation of the formation of a crystalline nucleus on a flat surface. σ_{ls} and σ_{cs} denote the interfacial energies on the liquid–solid and crystal–substrate interface, respectively, σ is the surface energy on the liquid–crystal interface, and ϑ is the wetting angle.

The relation between r and i follows from Equation (5),

$$r = \sqrt[3]{\frac{3m_1}{4\pi\varrho_c\psi(\vartheta)}} i^{1/3}. \quad (23)$$

The critical radius is determined by Equation (9); however, the critical number of monomers,

$$i^{*,f} = i^{*,hom} \psi(\vartheta), \quad (24)$$

differs from the homogeneous case, where $i^{*,hom}$ is determined by Equation (10).

The work of cluster formation on a flat substrate (W^f) can be expressed as a function of the number of monomers (i). Equations (21) and (23) yield

$$W^f(i) = -i\Delta\mu + \sqrt[3]{36\pi\psi(\vartheta)} \left(\frac{m_1}{\varrho_c}\right)^{2/3} \sigma i^{2/3}. \quad (25)$$

The critical radius (r^*) for homogeneous nucleation (thin dotted line in Figure 4a) coincides with the critical radius of heterogeneous nucleation on a flat surface ($r^{*,f}$) and does not

change with the wetting angle (ϑ). The difference in the critical number of monomers is i^* , with a higher value for homogeneous nucleation (thin dotted line in Figure 4b) than heterogeneous nucleation on a flat substrate. The work of cluster formation on a flat surface increases with the wetting angle (ϑ).

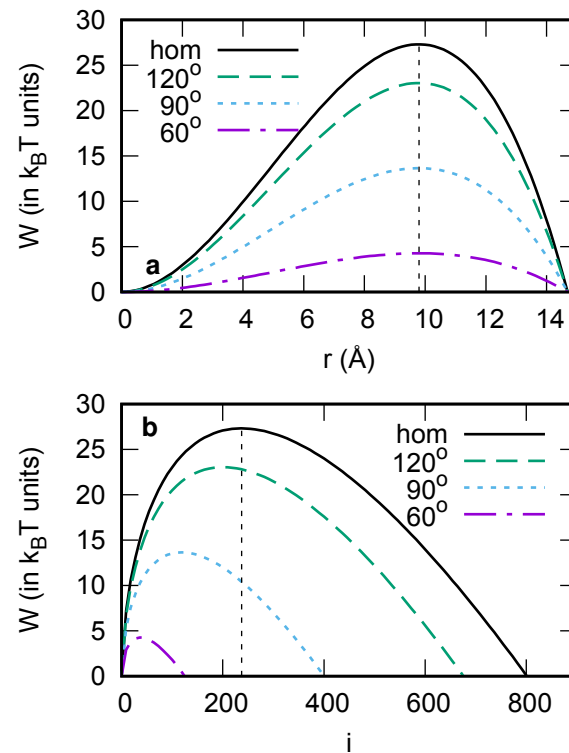


Figure 4. The work of cluster formation (W) as a function of cluster radius (r) (a) and the number of monomers (i) (b) for homogeneous (solid line) and heterogeneous nucleation on a flat substrate at $\vartheta = 120^\circ$ (dashed line), 90° (dotted line), and 60° (dotted–dashed line). Material parameters correspond to aluminum nucleation at a temperature of $T = 800$ K and $\sigma = 0.075$ Jm $^{-2}$.

3.2. Convex Substrate

Nucleation often occurs on curved surfaces of foreign particles serving as nucleation centers. Xu and Johnson [31] determined the work of cluster formation on a convex substrate as a function of cluster radius (Figures 2 and 5), with emphasis on the nucleation barrier.

The work of cluster formation on a convex substrate is expressed as

$$W^x = -\frac{\rho_c V_c}{m_1} \Delta\mu + S_c \sigma + S_i (\sigma_{cs} - \sigma_{ls}) = -\frac{\rho_c V_c}{m_1} \Delta\mu + S_c \sigma - S_i \sigma \cos \vartheta, \quad (26)$$

where the substrate radius (R) and wetting angle (ϑ) are fixed; however, φ depends on r (Appendix A),

$$\varphi = \arctan \frac{\sin \vartheta}{R/r - \cos \vartheta}, \quad (27)$$

and the nucleus volume

$$V_c = \frac{4\pi r^3}{3} \psi(\vartheta + \varphi) - \frac{4\pi R^3}{3} \psi(\varphi), \quad (28)$$

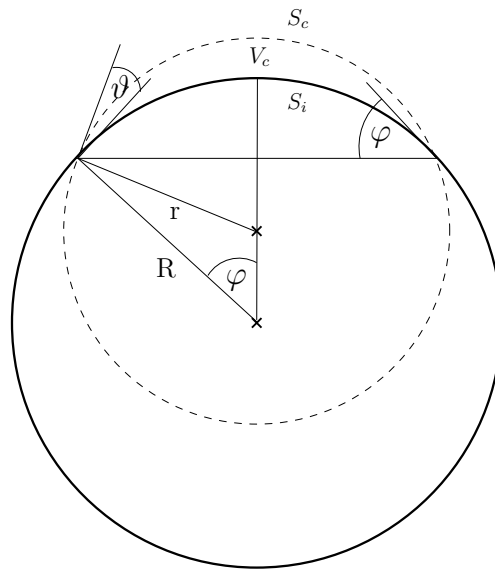


Figure 5. Schematic representation of crystal nucleation on a convex substrate.

Thus, Equations (27) and (28) yield

$$V_c = \frac{4}{3}\pi r^3 \left[\psi(\vartheta + \varphi) - \frac{\sin^3(\vartheta + \varphi)}{\sin^3 \varphi} \psi(\varphi) \right]. \quad (29)$$

where S_c is the surface area between the nucleus and a parent phase, and S_i denotes the surface area between the substrate and the nucleus. The work of cluster formation on a convex substrate can be expressed by (for details, see Appendix A):

$$W^x(r) = \frac{4\pi\varrho_c\Delta\mu r^3}{3m_1} \left[-\psi(\varphi + \vartheta) + \psi(\varphi) \frac{\sin^3(\varphi + \vartheta)}{\sin^3 \varphi} \right] + 2\pi\sigma r^2 \left[1 - \cos(\varphi + \vartheta) - \frac{\sin^2(\varphi + \vartheta)}{1 + \cos \varphi} \cos \vartheta \right]. \quad (30)$$

The relation between r and i follows from Equations (5), (27), and (28),

$$r = \left(\frac{3m_1 i}{4\pi\varrho_c [\psi(\vartheta + \varphi) - \sin^3(\vartheta + \varphi) \psi(\varphi) / \sin^3 \varphi]} \right)^{1/3}, \quad (31)$$

and we obtain

$$W^x(i) = -i\Delta\mu + \sqrt[3]{\frac{9\pi}{2} v_1^{2/3} \sigma i^{2/3} \left[1 - \cos(\varphi + \vartheta) - \frac{\sin^2(\varphi + \vartheta)}{1 + \cos \varphi} \cos \vartheta \right] \left[\psi(\vartheta + \varphi) - \frac{\sin^3(\varphi + \vartheta)}{\sin^3 \varphi} \psi(\varphi) \right]^{-2/3}}. \quad (32)$$

However, in Equations (31) and (32), φ depends on r according to Equation (27), and it is not easy to express $r(i)$ analytically. φ increases with cluster size and decreases with wetting angle (ϑ) for $r/R \gtrsim 0.2$ (Figure 6).

At the critical size, the nucleus barrier reaches its maximum, so for the critical radius on a convex substrate ($r^{*,x}$), we obtain Equation (9). The critical radius of the nucleus does not depend on either the wetting angle (ϑ) or the radius (R) of the particle where nucleation occurs, and the critical radius of homogeneous nucleation is $r^{*,hom} = r^{*,x}$.

The nucleation barrier can be expressed by [31]

$$W^{*,x} = \frac{16\pi v_1^2 \sigma^3}{3\Delta\mu^2} \psi^x(R/r^*, \vartheta) = W^{*,hom} \psi^x(R/r^*, \vartheta), \quad (33)$$

where

$$\begin{aligned} \psi^x(R/r^*, \vartheta) &= 2[-\psi(\varphi + \vartheta) + \frac{\sin^3(\varphi + \vartheta)}{\sin^3 \varphi} \psi(\varphi)] + \frac{3}{2}[1 - \cos(\varphi + \vartheta) - \frac{\sin^2(\varphi + \vartheta)}{1 + \cos \varphi} \cos \vartheta]. \\ &= \frac{1}{2}[1 - \cos^3(\varphi + \vartheta) + \frac{\sin^3(\varphi + \vartheta)}{\sin^3 \varphi} (2 - 3 \cos \varphi + \cos^3 \varphi) \\ &\quad - 3 \frac{\sin^2(\varphi + \vartheta)}{1 + \cos \varphi} \cos \vartheta]. \end{aligned} \quad (34)$$

where φ depends on R/r^* and, in the limit of a flat interface, we obtain

$$\psi^x(R \rightarrow \infty, \vartheta) = \psi(\vartheta) = \frac{1}{4}(2 - 3 \cos \vartheta + \cos^3 \vartheta) \quad (35)$$

in coincidence with Equation (22).

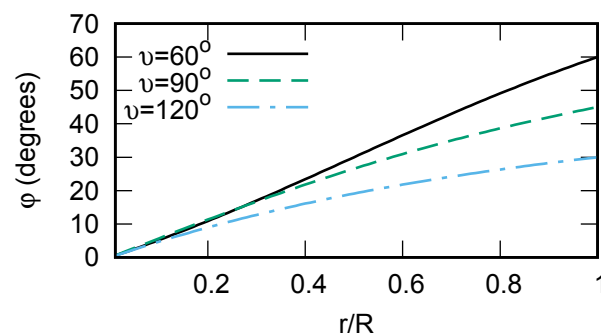


Figure 6. Angle φ as a function of the cluster radius (r) scaled by substrate radius (R) for wetting angles of $\vartheta = 60^\circ$ (solid line), 90° (dashed line), and 120° (dotted–dashed line).

It is clear that under the same conditions, nucleus formation is more probable on a flat substrate in comparison with a convex substrate (Figure 7). The nucleation barrier on a convex substrate ($W^{*,x}$) is equal to that of homogeneous nucleation ($W^{*,hom}$) reduced by a function of ψ^x . For the same considered system, (the same wetting angle (ϑ)), ψ^x decreases with substrate radius (R); thus, the probability of nucleus formation is higher on a flat surface in comparison with a convex substrate.

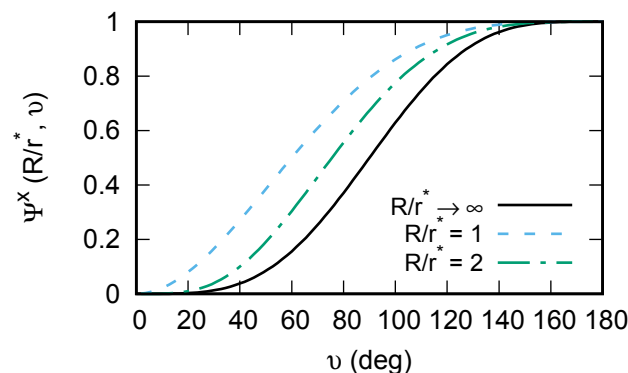


Figure 7. ψ^x as a function of the wetting angle (ϑ) for $R/r^* = 1$ (dashed line), $R/r^* = 2$ (dotted–dashed line), and $R/r^* \rightarrow \infty$ (solid line).

3.3. Concave Substrate

Cooper et al. [28] studied crystallization in small confinement volumes and computed the work of cluster formation on a concave substrate (for details, see Appendix B).

$$W^e(r) = -\frac{4}{3}\pi r^3 \frac{\varrho_c \Delta\mu}{m_1} \left[\psi(\vartheta - \varphi) + \frac{\sin^3(\vartheta - \varphi)}{\sin^3 \varphi} \psi(\varphi) \right] + 2\pi r^2 \sigma \left[1 - \cos(\vartheta - \varphi) - \frac{\sin^2(\vartheta - \varphi)}{1 + \cos \varphi} \cos \vartheta \right], \quad (36)$$

where

$$\varphi = \arctan \frac{\sin \vartheta}{R/r + \cos \vartheta}. \quad (37)$$

If we consider a negative angle ($\tilde{\varphi} = \varphi$), Equation (36) yields

$$W^e(r) = -\frac{4}{3}\pi r^3 \frac{\varrho_c \Delta\mu}{m_1} \left[\psi(\vartheta + \tilde{\varphi}) + \frac{\sin^3(\vartheta + \tilde{\varphi})}{-\sin^3 \tilde{\varphi}} \psi(\tilde{\varphi}) \right] + 2\pi r^2 \sigma \left[1 - \cos(\vartheta + \tilde{\varphi}) - \frac{\sin^2(\vartheta + \tilde{\varphi})}{1 + \cos \tilde{\varphi}} \cos \vartheta \right]. \quad (38)$$

Thus, W can be expressed by the same analytical expression for both convex and concave substrates (compare Equations (30) and (38)) considering R and φ as negative in a concave system.

The nucleus volume on a concave substrate with a radius of R is

$$V_c(R) = \frac{4}{3}\pi R^3 \left[\frac{\sin^3 \varphi}{\sin^3(\vartheta - \varphi)} \psi(\vartheta - \varphi) + \psi(\varphi) \right], \quad (39)$$

or, as a function of the nucleus radius (r),

$$V_c(r) = \frac{4}{3}\pi r^3 \left[\psi(\vartheta - \varphi) + \frac{\sin^3(\vartheta - \varphi)}{\sin^3 \varphi} \psi(\varphi) \right], \quad (40)$$

where φ and r are related by Equation (37). Equations (5) and (40) yield

$$r(i) = \left(\frac{3m_1 i}{4\pi \varrho_c} \right)^{1/3} \left[\psi(\vartheta - \varphi) + \frac{\sin^3(\vartheta - \varphi)}{\sin^3 \varphi} \psi(\varphi) \right]^{-1/3}, \quad (41)$$

and Equations (36) and (41) yield a rather complex analytical expression for the work of cluster formation on a concave substrate as a function of cluster size (i):

$$W^e(i) = -i\Delta\mu + \sqrt[3]{\frac{9\pi}{2} \left(\frac{m_1}{\varrho_c} \right)^{2/3}} \sigma i^{2/3} \left[1 - \cos(\vartheta - \varphi) - \frac{\sin^2(\vartheta - \varphi)}{1 + \cos \varphi} \cos \vartheta \right] \left[\psi(\vartheta - \varphi) + \frac{\sin^3(\vartheta - \varphi)}{\sin^3 \varphi} \psi(\varphi) \right]^{-2/3}. \quad (42)$$

The nucleation barrier and critical radius are determined by the extreme condition of the work of cluster formation; thus, we obtain (for details, see Appendix B)

$$W^{*,e} = \frac{16\pi v_1^2 \sigma^3}{3\Delta\mu^2} \psi^e(R, \vartheta) = W^{*,hom} \psi^e(R, \vartheta), \quad (43)$$

where

$$\psi^e(R, \vartheta) = \frac{1}{2} \left[1 - \cos^3(\vartheta - \varphi) - \frac{\sin^3(\vartheta - \varphi)}{\sin^3 \varphi} (2 - 3\cos \varphi + \cos^3 \varphi) - 3 \frac{\sin^2(\vartheta - \varphi)}{1 + \cos \varphi} \cos \vartheta \right]. \quad (44)$$

The critical nucleus radius ($r^{*\ell}$) on a concave substrate is determined by Equation (9), i.e., the analytical solution for the critical radius is the same for flat, convex, and concave substrates.

4. Discussion

The number of crystal nuclei formed within a melt as a function of time can be determined by the solution of kinetic equations [6]. Transient probabilities of attachment/detachment of atoms on/from a crystal surface are proportional to $\Delta g_i = W_{i+1} - W_i$; thus, it is important to determine the work of cluster formation (W) as a function of the number of atoms (i) forming the crystal cluster. We focus on heterogeneous curved substrates, where W was determined as a function of the nucleus radius (r) [28,31]; however, the W_i dependence is missing.

Generally, the excess free energy of clusters depends on the phase interface, which is governed by temperature, undercooling, supersaturation, cluster size, etc. It is possible to take into account a simple approach to the dependence of the surface energy on cluster size ($\sigma(i)$) for homogeneous nucleation [30] to express $W(r)$ or $W(i)$ dependency (Figure 1). Heterogeneous nucleation on curved substrates is more complicated, which is why we approach σ as size-independent.

The nucleation barrier ($W^{*,het}$) of heterogeneous nucleation on various substrates decreases with the wetting angle (θ) (Figure 3). We compared $W(r)$ and $W(i)$ dependencies for homogeneous and heterogeneous nucleation on flat, convex, and concave substrates (Figure 8). Analytical solutions of $W(r)$ for homogeneous and heterogeneous nucleation are known. However, $W(i)$ dependence was determined by the numerical solution of Equations (32), (27), and (31) for a convex substrate and Equations (42), (37), and (41) for a concave substrate.

The heterogeneous nucleation barrier (maximum of $W^{het}(r)$ = maximum of $W^{het}(i)$) is equal to the homogeneous nucleation barrier ($W^{*,hom}$) (dotted line in Figure 8) reduced by a function of ψ that depends on the substrate shape (compare Equation (22) for a flat substrate with Equation (34) for a convex substrate and Equation (44) for a concave substrate). Interfacial energies strongly influence the heterogeneous nucleation barrier ($W^{*,het}$), and for wetting angles (θ) close to 180° , $W^{*,het}$ is close to $W^{*,hom}$. For $\theta = 180^\circ$, the work of cluster formation on flat, convex, and concave substrates coincides with the homogeneous nucleation case (dotted line in Figure 8).

Under the same conditions (see Figure 8 for a wetting angle of $\theta = 90^\circ$ and a substrate radius of $R = 20$), the lowest heterogeneous nucleation barrier ($W^{*,het}$) belongs to the concave substrate (dotted–dashed line), and the highest barrier belongs to the convex substrate (dashed line in Figure 8) under the same conditions. The nucleation barrier on a flat surface (solid line in Figure 8) lies between $W^{*,het}$ on concave and convex substrates; thus, nucleation on a concave substrate is more probable than on a planar interface, unlike a convex substrate.

The critical nucleation radius (r^*) is determined by Equation (9) for homogeneous and heterogeneous nucleation on various surfaces. Hu and Chen [32] showed that the same equation is valid for r^* on a conic substrate. In all cases (homogeneous or heterogeneous nucleation), the critical radius of nuclei is the same for all systems, unlike the critical number of monomers (i^*) (compare Figure 8a,b).

In a very small encapsulated volume (nanosystems), the scarcity of crystallizing material reduces the formation of nuclei [28,33]. During nucleus formation, liquid droplets are depleted; thus, the nucleus can be in equilibrium with the remaining liquid. We can imagine that in the case of crystallization of a supersaturated solution, supersaturation decreases with nucleus evolution and, at a certain nucleus size (i_{min}), reaches the equilibrium value [34]. Kožíšek et al. [6] showed that the main contribution to the decrease in monomers in the liquid phase, which depends on the time evolution of the cluster size distribution, is caused by the formation of subcritical clusters.

The size distribution of nuclei can be determined by the solution of kinetic equations. In that case, we need to determine the formation energy change for two successive cluster

sizes, i.e., $\Delta g_i = W(i+1) - W(i)$. It is easy to determine $W(i)$ for homogeneous nucleation and heterogeneous nucleation on a flat substrate. However, an analytical solution for $W(i)$ on a general surface shape (convex, concave, conic, etc.) is too complicated, and a numerical solution is needed.

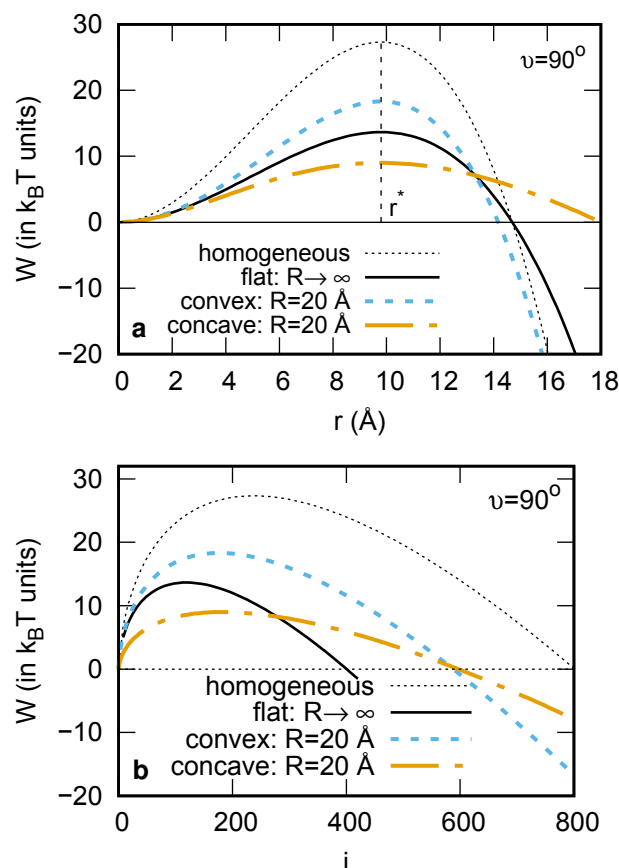


Figure 8. The work of cluster formation (W) as a function of radius (r) (a) and cluster size (i) (b) for homogeneous (dotted line) and heterogeneous nucleation on flat (solid line), convex (dashed line), and concave (dotted–dashed line) substrates with a radius of $R = 20$ and a wetting angle of $\theta = 90^\circ$.

5. Conclusions

It is a known fact that crystallization occurs via nucleation and subsequent growth of nuclei. During crystal nucleation, it is necessary to overcome a certain energy barrier. We summarized the energy of the formation of clusters (W) on various substrates (flat, concave, and convex). The critical radius of nuclei (r^*) reaches the same value for homogeneous and heterogeneous nucleation on different substrates, and the analytical solution is quite easy. However, the critical number of monomers (i^*) differs in various systems under consideration (homogeneous or heterogeneous nucleation on various substrate shapes). A simple analytical solution of i^* exists for homogeneous (see Equation (10)) and heterogeneous nucleation on a flat surface (see Equation (24)). On the other hand, it is too complicated to find an analytical solution of i^* for heterogeneous nucleation on convex and concave substrates. We have summarized the analytical solution for the work of cluster formation (W) as a function of radius (r). The analytical solution of W as a function of the number of atoms (i) forming the cluster is too complicated, and a numerical solution is necessary. The heterogeneous nucleation barrier is lower in comparison with the homogeneous barrier and increases with wetting angle (θ). At the same wetting angle (θ) and substrate radius (R), the most probable is the formation of nuclei on a concave substrate (lowest nucleation barrier), and the least probable is nucleation on a convex substrate (highest nucleation barrier). The extreme of nucleation for homogeneous nucleation is reached at the same

critical radius (r^*), in contrast to the critical size (i^*), which differs for various substrate shapes (Figure 8).

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Appendix A. Convex Substrate

In this section, we present a derivation of analytical formulas for the energy associated with the formation of the nucleus on a convex substrate. Some relations are evident from Figure 5, where ϑ is the wetting angle; r is the nucleus radius; R denotes the substrate radius; S_c and S_i stand for the surface area between nucleus–melt and substrate–nucleus interface; and V_c is the nucleus volume. The following relations hold: $\beta = \pi/2 - (\vartheta + \varphi)$, $\alpha = \pi/2 - \beta = \vartheta + \varphi$,

$$S_c = 2\pi r^2 [1 - \cos(\vartheta + \varphi)], \quad (\text{A1})$$

$$S_i = 2\pi R^2 (1 - \cos \varphi), \quad (\text{A2})$$

$$\varrho = R \sin \varphi = r \sin(\vartheta + \varphi), \quad (\text{A3})$$

and thus,

$$\sin \vartheta \cos \varphi + \cos \vartheta \sin \varphi = \frac{R}{r} \sin \varphi, \quad (\text{A4})$$

$$\sin \vartheta + \cos \vartheta \tan \varphi = \frac{R}{r} \tan \varphi, \quad (\text{A5})$$

$$\cot \varphi = \frac{R/r - \cos \vartheta}{\sin \vartheta}, \quad (\text{A6})$$

and thus, we obtain Equation (27).

The volumetric contribution ($W^{x,V}$) to the work of cluster formation on a convex substrate (W^x) follows from Equations (5) and (A3),

$$\begin{aligned} W^{x,V}(r) &= -i\Delta\mu = -\frac{V_c \varrho_c}{m_1} \Delta\mu \\ &= -\frac{4}{3} \pi r^3 \frac{\varrho_c}{m_1} \Delta\mu \psi(\vartheta + \varphi) + \frac{4}{3} \pi R^3 \frac{\varrho_c}{m_1} \Delta\mu \psi(\varphi), \end{aligned} \quad (\text{A7})$$

and thus,

$$W^{x,V} = \frac{4\pi \varrho_c \Delta\mu r^3}{3m_1} \left[-\psi(\varphi + \vartheta) + \psi(\varphi) \frac{\sin^3(\varphi + \vartheta)}{\sin^3 \varphi} \right]. \quad (\text{A8})$$

The surface contribution to W^x is expressed by

$$W^{x,S} = \sigma S_c + S_i(\sigma_{cs} - \sigma_{ls}), \quad (\text{A9})$$

and Young's equation yields

$$W^{x,S} = \sigma S_c - \sigma \cos \vartheta S_i. \quad (\text{A10})$$

Equations (A1)–(A3), and (A10) yield

$$W^{x,S} = 2\pi r^2 \sigma [1 - \cos(\vartheta + \varphi)] - 2\pi R^2 \sigma \cos \vartheta (1 - \cos \varphi), \quad (\text{A11})$$

and

$$W^{x,S} = 2\pi\sigma r^2 \left[1 - \cos(\varphi + \vartheta) - \frac{\sin^2(\varphi + \vartheta)}{1 + \cos \varphi} \cos \vartheta \right]. \quad (\text{A12})$$

The work of cluster formation on a convex substrate is $W^x = W^{x,vol} + W^{x,sur}$; thus, we obtain Equation (30). The critical size follows from the extreme condition:

$$(dW^x/dr)_{r=r^*} = 0, \quad (\text{A13})$$

and

$$\frac{dW^x}{dr} = \frac{\partial W^{x,V}}{\partial r} + \frac{\partial W^{x,V}}{\partial \varphi} \frac{d\varphi}{dr} + \frac{dW^{x,S}}{dr}, \quad (\text{A14})$$

where

$$\frac{dr}{d\varphi} = R \frac{\cos \varphi \sin(\varphi + \vartheta) - \sin \varphi \cos(\varphi + \vartheta)}{\sin^2(\varphi + \vartheta)} = R \frac{\sin \vartheta}{\sin^2(\varphi + \vartheta)}. \quad (\text{A15})$$

The volumetric contribution to dW^x/dr is

$$\begin{aligned} \frac{dW^{x,V}}{dr} &= -\frac{\pi r^2 \varrho_c \Delta \mu}{m_1} [2 - 3 \cos(\varphi + \vartheta) + \cos^3(\varphi + \vartheta)] \\ &\quad + \frac{d\varphi}{dr} \left\{ -\frac{\pi r^3 \varrho_c \Delta \mu}{3m_1} [3 \sin(\varphi + \vartheta) - 3 \cos^2(\varphi + \vartheta) \sin(\varphi + \vartheta)] \right. \\ &\quad \left. + \frac{\pi R^3 \varrho_c \Delta \mu}{3m_1} (3 \sin \varphi - 3 \cos^2 \varphi \sin \varphi) \right\} \\ &= -\frac{\pi r^2 \varrho_c \Delta \mu}{m_1} [2 - 3 \cos(\varphi + \vartheta) + \cos^3(\varphi + \vartheta)] \\ &\quad + \frac{\pi \varrho_c \Delta \mu}{m_1} \frac{d\varphi}{dr} [-r^3 \sin^3(\varphi + \vartheta) + R^3 \sin^3 \varphi] \\ &= -\frac{4\pi r^2 \varrho_c \Delta \mu}{m_1} \psi(\varphi + \vartheta) + \frac{\pi \varrho_c \Delta \mu}{m_1} \frac{\sin^2(\varphi + \vartheta)}{R \sin \vartheta} [-r^3 \sin^3(\varphi + \vartheta) + R^3 \sin^3 \varphi], \end{aligned} \quad (\text{A16})$$

and using Equation (A3), we obtain

$$\begin{aligned} \frac{dW^{x,V}}{dr} &= -\frac{4\pi r^2 \varrho_c \Delta \mu}{m_1} \psi(\varphi + \vartheta) \\ &\quad + \frac{\pi \varrho_c \Delta \mu}{m_1} \frac{\sin^2(\varphi + \vartheta) \sin \varphi}{r \sin(\varphi + \vartheta)} [-r^3 \sin^3(\varphi + \vartheta) + \frac{r^3 \sin^3(\varphi + \vartheta) \sin^3 \varphi}{\sin^3 \varphi}] \\ &= -\frac{4\pi r^2 \varrho_c \Delta \mu}{m_1} \psi(\varphi + \vartheta) + \frac{\pi \Delta \mu r^2 \varrho_c}{m_1} [-\sin^4(\varphi + \vartheta) \sin \varphi + \sin^4(\varphi + \vartheta) \sin \varphi], \end{aligned}$$

and thus,

$$\frac{dW^{x,V}}{dr} = -\frac{4\pi r^2 \varrho_c \Delta \mu}{m_1} \psi(\vartheta + \varphi). \quad (\text{A17})$$

Remember that φ depends on r (Equation (A3)).

Equations (A3), (A12), and (A15) yield

$$\begin{aligned}
\frac{dW^{x,S}}{dr} &= 2\pi\sigma R^2 \frac{d\varphi}{dr} \frac{d}{d\varphi} \left\{ \frac{\sin^2 \varphi}{1 + \cos(\varphi + \vartheta)} - \cos \vartheta (1 - \cos \varphi) \right\} \\
&= 2\pi\sigma R \frac{\sin^2(\varphi + \vartheta)}{\sin \vartheta} \left\{ \frac{2 \sin \varphi \cos \varphi}{1 + \cos(\varphi + \vartheta)} + \frac{\sin^2 \varphi \sin(\varphi + \vartheta)}{[1 + \cos(\varphi + \vartheta)]^2} - \cos \vartheta \sin \varphi \right\} \\
&= 2\pi\sigma r \frac{\sin(\varphi + \vartheta)}{\sin \varphi} \frac{1 - \cos^2(\varphi + \vartheta)}{\sin \vartheta} \sin \varphi \left\{ \frac{2 \cos \varphi}{1 + \cos(\varphi + \vartheta)} + \frac{\sin \varphi \sin(\varphi + \vartheta)}{[1 + \cos(\varphi + \vartheta)]^2} - \cos \vartheta \right\} \\
&= 2\pi\sigma r \frac{1 - \cos(\varphi + \vartheta)}{\sin \vartheta} \left\{ 2 \cos \varphi \sin(\varphi + \vartheta) + \frac{\sin \varphi \sin^2(\varphi + \vartheta)}{1 + \cos(\varphi + \vartheta)} \right. \\
&\quad \left. - \cos \vartheta \sin(\varphi + \vartheta) [1 + \cos(\varphi + \vartheta)] \right\} \quad (A18)
\end{aligned}$$

The first term in the braces of Equation (A18) can be expressed by:

$$\begin{aligned}
\cos \varphi \sin(\varphi + \vartheta) &= \cos \varphi (\sin \varphi \cos \vartheta + \sin \vartheta \cos \varphi) \\
&= \cos \varphi \sin \varphi \cos \vartheta + \sin \vartheta (1 - \sin^2 \varphi) \\
&= \sin \varphi \cos \varphi \cos \vartheta + \sin \vartheta - \sin^2 \varphi \sin \vartheta \\
&= \sin \vartheta + \sin \varphi \cos(\varphi + \vartheta), \quad (A19)
\end{aligned}$$

and Equations (A18) and (A19) yield

$$\begin{aligned}
\frac{dW^{x,S}}{dr} &= 2\pi\sigma r \frac{1 - \cos(\varphi + \vartheta)}{\sin \vartheta} \{ 2[\sin \vartheta + \sin \varphi \cos(\varphi + \vartheta)] + \sin \varphi [1 - \cos(\varphi + \vartheta)] \\
&\quad - \cos \vartheta \sin(\varphi + \vartheta) [1 + \cos(\varphi + \vartheta)] \} \\
&= 2\pi\sigma r \frac{1 - \cos(\varphi + \vartheta)}{\sin \vartheta} \{ 2 \sin \vartheta + \sin \varphi [1 + \cos(\varphi + \vartheta)] - \cos \vartheta \sin(\varphi + \vartheta) [1 + \cos(\varphi + \vartheta)] \} \\
&= 2\pi\sigma r \frac{1 - \cos(\varphi + \vartheta)}{\sin \vartheta} \{ 2 \sin \vartheta + [\sin \varphi - \cos \vartheta \sin(\varphi + \vartheta)] [1 + \cos(\varphi + \vartheta)] \}. \quad (A20)
\end{aligned}$$

The relation in the first brackets in Equation (A20) can be simplified as:

$$\begin{aligned}
[\sin \varphi - \cos \vartheta \sin(\varphi + \vartheta)] &= \sin \varphi - \cos \vartheta \sin \varphi \cos \vartheta - \cos \vartheta \sin \vartheta \cos \varphi \\
&= \sin \varphi (1 - \cos^2 \vartheta) - \cos \vartheta \sin \vartheta \cos \varphi \\
&= -\sin \vartheta (\cos \varphi \cos \vartheta - \sin \varphi \sin \vartheta) \\
&= -\sin \vartheta \cos(\varphi + \vartheta), \quad (A21)
\end{aligned}$$

and Equations (A20) and (A21) yield the nucleation barrier:

$$\begin{aligned}
\frac{dW^{x,S}}{dr} &= 2\pi\sigma r \frac{1 - \cos(\varphi + \vartheta)}{\sin \vartheta} \{ 2 \sin \vartheta - \sin \vartheta \cos(\varphi + \vartheta) [1 + \cos(\varphi + \vartheta)] \} \\
&= 2\pi\sigma r [1 - \cos(\varphi + \vartheta)] [2 - \cos(\varphi + \vartheta) - \cos^2(\varphi + \vartheta)] \\
&= 2\pi\sigma r [2 - \cos(\varphi + \vartheta) - \cos^2(\varphi + \vartheta) - 2 \cos(\varphi + \vartheta) + \cos^2(\varphi + \vartheta) + \cos^3(\varphi + \vartheta)] \\
&= 2\pi\sigma r [2 - 3 \cos(\varphi + \vartheta) + \cos^3(\varphi + \vartheta)] = 8\pi\sigma r \psi(\varphi + \vartheta), \quad (A22)
\end{aligned}$$

and from Equations (9) and (30) yield

$$\begin{aligned}
W^{*,x} &= \frac{32\pi v_1^2 \sigma^3}{3\Delta\mu^2} [-\psi(\varphi + \vartheta) + \frac{\sin^3(\varphi + \vartheta)}{\sin^3 \varphi} \psi(\varphi)] \\
&\quad + \frac{8\pi v_1^2 \sigma^3}{\Delta\mu^2} [1 - \cos(\varphi + \vartheta) - \frac{\sin^2(\varphi + \vartheta)}{1 + \cos \varphi} \cos \vartheta],
\end{aligned}$$

which can be simplified to Equation (33).

and using Equation (A23), we obtain

$$W^e(r) = -\frac{4}{3}\pi r^3 \frac{\Delta\mu_{Q_c}}{m_1} \psi(\vartheta - \varphi) - \frac{4}{3}\pi r^3 \frac{\Delta\mu_{Q_c}}{m_1} \frac{\sin^3(\vartheta - \varphi)}{\sin^3 \varphi} \psi(\varphi) + 2\pi r^2 \sigma [1 - \cos(\vartheta - \varphi)] - 2\pi r^2 \sigma \frac{\sin^2(\vartheta - \varphi)}{\sin^2 \varphi} (1 - \cos \varphi) \cos \vartheta, \quad (\text{A25})$$

and thus, Equation (36) holds.

The nucleation barrier and the critical radius follow from the extreme condition,

$$\frac{dW^e}{dr} = \frac{\partial W^e}{\partial r} + \frac{\partial W^e}{\partial \varphi} \frac{d\varphi}{dr}, \quad (\text{A26})$$

where

$$\frac{dr}{d\varphi} = R \frac{\cos \varphi \sin(\vartheta - \varphi) + \sin \varphi \cos(\vartheta - \varphi)}{\sin^2(\vartheta - \varphi)} = R \frac{\sin \vartheta}{\sin^2(\vartheta - \varphi)} \quad (\text{A27})$$

The derivative of the volume contribution to W^e is expressed by

$$\begin{aligned} \frac{dW^{e,V}}{dr} &= -\pi r^2 \frac{\Delta\mu}{v_1} [2 - 3 \cos(\vartheta - \varphi) + \cos^3(\vartheta - \varphi)] \\ &\quad + \frac{d\varphi}{dr} \left\{ -\pi r^3 \frac{\Delta\mu}{3v_1} [-3 \sin(\vartheta - \varphi) + 3 \cos^2(\vartheta - \varphi) \sin(\vartheta - \varphi)] \right. \\ &\quad \left. - \pi R^3 \frac{\Delta\mu}{3v_1} (3 \sin \varphi - 3 \cos^2 \varphi \sin \varphi) \right\} \\ &= -\pi r^2 \frac{\Delta\mu}{v_1} [2 - 3 \cos(\vartheta - \varphi) + \cos^3(\vartheta - \varphi)] \\ &\quad + \frac{d\varphi}{dr} \pi \frac{\Delta\mu}{v_1} \left\{ -r^3 [-\sin(\vartheta - \varphi) + \cos^2(\vartheta - \varphi) \sin(\vartheta - \varphi)] \right. \\ &\quad \left. - r^3 \frac{\sin^3(\vartheta - \varphi)}{\sin^3 \varphi} (\sin \varphi - \cos^2 \varphi \sin \varphi) \right\} \\ &= -\pi r^2 \frac{\Delta\mu}{v_1} [2 - 3 \cos(\vartheta - \varphi) + \cos^3(\vartheta - \varphi)] \\ &\quad + \frac{d\varphi}{dr} \pi r^3 \frac{\Delta\mu}{v_1} \left\{ \sin(\vartheta - \varphi) [1 - \cos^2(\vartheta - \varphi)] + \frac{\sin^3(\vartheta - \varphi)}{\sin^2 \varphi} (-1 + \cos^2 \varphi) \right\} \\ \frac{d\varphi}{dr} &= \frac{1}{R} \frac{\sin^2(\vartheta - \varphi)}{\sin \vartheta} = \frac{\sin \varphi}{r \sin(\vartheta - \varphi)} \frac{\sin^2(\vartheta - \varphi)}{\sin \vartheta} = \frac{1}{r} \frac{\sin \varphi \sin(\vartheta - \varphi)}{\sin \vartheta}. \end{aligned} \quad (\text{A28})$$

$$\begin{aligned} \frac{dW^{e,V}}{dr} &= -\pi r^2 \frac{\Delta\mu}{v_1} [2 - 3 \cos(\vartheta - \varphi) + \cos^3(\vartheta - \varphi)] \\ &\quad + \pi r^2 \frac{\Delta\mu}{v_1} \frac{\sin \varphi \sin(\vartheta - \varphi)}{\sin \vartheta} [\sin^3(\vartheta - \varphi) - \sin^3(\vartheta - \varphi)], \end{aligned}$$

and thus,

$$\frac{dW^{e,V}}{dr} = -\pi r^2 \frac{\Delta\mu}{v_1} [2 - 3 \cos(\vartheta - \varphi) + \cos^3(\vartheta - \varphi)]. \quad (\text{A29})$$

The surface contribution to W^e is

$$W^{e,S} = 2\pi r^2 \sigma [1 - \cos(\vartheta - \varphi)] - 2\pi \sigma R^2 \sigma \cos \vartheta (1 - \cos \varphi), \quad (\text{A30})$$

and using Equation (A23), we obtain

$$W^{e,S} = 2\pi R^2 \sigma \left\{ \frac{\sin^2 \varphi}{\sin^2(\vartheta - \varphi)} [1 - \cos(\vartheta - \varphi)] - \cos \vartheta (1 - \cos \varphi) \right\}, \quad (\text{A31})$$

and according to Equation (A26),

$$\begin{aligned}
 \frac{dW^{e,S}}{dr} &= 2\pi R^2 \sigma \frac{d\varphi}{dr} \frac{\partial}{\partial \varphi} \left\{ \frac{\sin^2 \varphi}{1 + \cos(\vartheta - \varphi)} - \cos \vartheta (1 - \cos \varphi) \right\} \\
 &= 2\pi R^2 \sigma \frac{d\varphi}{dr} \left\{ \frac{2 \sin \varphi \cos \varphi [1 + \cos(\vartheta - \varphi)] - \sin^2 \varphi \sin(\vartheta - \varphi)}{[1 + \cos(\vartheta - \varphi)]^2} - \cos \vartheta \sin \varphi \right\} \\
 &= 2\pi R \sigma \frac{\sin^2(\vartheta - \varphi)}{\sin \vartheta} \left\{ \frac{2 \sin \varphi \cos \varphi}{1 + \cos(\vartheta - \varphi)} - \frac{\sin^2 \varphi \sin(\vartheta - \varphi)}{[1 + \cos(\vartheta - \varphi)]^2} - \cos \vartheta \sin \varphi \right\} \\
 &= 2\pi r \sigma \frac{\sin(\vartheta - \varphi)}{\sin \varphi} \frac{1 - \cos^2(\vartheta - \varphi)}{\sin \vartheta} \left\{ \frac{2 \sin \varphi \cos \varphi}{1 + \cos(\vartheta - \varphi)} - \frac{\sin^2 \varphi \sin(\vartheta - \varphi)}{[1 + \cos(\vartheta - \varphi)]^2} - \cos \vartheta \sin \varphi \right\} \\
 &= 2\pi r \sigma \frac{1 - \cos(\vartheta - \varphi)}{\sin \vartheta} \left\{ 2 \cos \varphi \sin(\vartheta - \varphi) - \frac{\sin \varphi \sin^2(\vartheta - \varphi)}{1 + \cos(\vartheta - \varphi)} \right. \\
 &\quad \left. - \cos \vartheta \sin(\vartheta - \varphi) [1 + \cos(\vartheta - \varphi)] \right\}
 \end{aligned}$$

After simplification,

$$\begin{aligned}
 \cos \varphi \sin(\vartheta - \varphi) &= \cos \varphi (\sin \vartheta \cos \varphi - \cos \vartheta \sin \varphi) \\
 &= \sin \vartheta \cos^2 \varphi - \cos \varphi \cos \vartheta \cos \varphi \\
 &= \sin \vartheta - \sin \vartheta \sin^2 \varphi - \cos \varphi \cos \vartheta \sin \varphi \\
 &= \sin \vartheta - \sin \varphi (\sin \vartheta \sin \varphi + \cos \vartheta \cos \varphi) \\
 &= \sin \vartheta - \sin \varphi \cos(\vartheta - \varphi),
 \end{aligned}$$

and we obtain

$$\begin{aligned}
 \frac{dW^{e,S}}{dr} &= 2\pi r \sigma \frac{1 - \cos(\vartheta - \varphi)}{\sin \vartheta} \{ 2 \sin \vartheta - 2 \sin \varphi \cos(\vartheta - \varphi) - \sin \varphi [1 - \cos(\vartheta - \varphi)] \\
 &\quad - \cos \vartheta \sin(\vartheta - \varphi) [1 + \cos(\vartheta - \varphi)] \} \\
 &= 2\pi r \sigma \frac{1 - \cos(\vartheta - \varphi)}{\sin \vartheta} \{ 2 \sin \vartheta - \sin \varphi [1 + \cos(\vartheta - \varphi)] - \cos \vartheta \sin(\vartheta - \varphi) [1 + \cos(\vartheta - \varphi)] \} \\
 &= 2\pi r \sigma \frac{1 - \cos(\vartheta - \varphi)}{\sin \vartheta} \{ 2 \sin \vartheta - [\sin \varphi + \cos \vartheta \sin(\vartheta - \varphi)] [1 + \cos(\vartheta - \varphi)] \}
 \end{aligned}$$

Taking into account that

$$\begin{aligned}
 \sin \varphi + \cos \vartheta \sin(\vartheta - \varphi) &= \sin \varphi + \cos \vartheta \sin \vartheta \cos \varphi - \cos^2 \vartheta \sin \varphi \\
 &= \sin \varphi (1 - \cos^2 \vartheta) + \cos \vartheta \sin \vartheta \cos \varphi \\
 &= \sin \vartheta (\sin \varphi \sin \vartheta + \cos \vartheta \cos \varphi) \\
 &= \sin \cos(\vartheta - \varphi),
 \end{aligned}$$

we obtain

$$\begin{aligned}
 \frac{dW^{e,S}}{dr} &= 2\pi r \sigma \frac{1 - \cos(\vartheta - \varphi)}{\sin \vartheta} \{ 2 \sin \vartheta - \sin \vartheta \cos(\vartheta - \varphi) [1 + \cos(\vartheta - \varphi)] \} \\
 &= 2\pi r \sigma \{ 2 - 2 \cos(\vartheta - \varphi) - \cos(\vartheta - \varphi) [1 - \cos^2(\vartheta - \varphi)] \} \\
 &= 2\pi r \sigma [2 - 2 \cos(\vartheta - \varphi) - \cos(\vartheta - \varphi) + \cos^3(\vartheta - \varphi)],
 \end{aligned}$$

and thus,

$$\frac{dW^{e,S}}{dr} = 2\pi r \sigma [2 - 3 \cos(\vartheta - \varphi) + \cos^3(\vartheta - \varphi)] = 8\pi r \sigma \psi(\vartheta - \varphi). \quad (\text{A32})$$

The derivative of W^e can be expressed by

$$\begin{aligned} \frac{dW^e}{dr} = & -\pi r^2 \frac{\Delta\mu\varrho_c}{m_1} [2 - 3\cos(\vartheta - \varphi) + \cos^3(\vartheta - \varphi)] \\ & + 2\pi r\sigma [2 - 3\cos(\vartheta - \varphi) + \cos^3(\vartheta - \varphi)] \end{aligned} \quad (\text{A33})$$

For the critical radius, Equations (A13) and (A33), yield Equation (9), i.e., r^* is determined by the same equation for concave and convex substrates. The relation between the cluster radius (r) and the number of monomers forming the cluster (i) is determined by Equations (5), (37), and (40).

Equations (9) and (36) yield

$$\begin{aligned} W^{*,e} = & -\frac{4}{3}\pi \frac{8\sigma^3 m_1^2}{\Delta\mu^2 \varrho_c^2} [\psi(\vartheta - \varphi) + \frac{\sin^3(\vartheta - \varphi)}{\sin^3 \varphi} \psi(\varphi)] \\ & + 2\pi \frac{4\sigma^2 v_1^2}{\Delta\mu^2} \sigma [1 - \cos(\vartheta - \varphi) - \frac{\sin^2(\vartheta - \varphi)}{1 + \cos \varphi} \cos \vartheta] \\ = & -\frac{32\pi m_1^2 \sigma^3}{3\Delta\mu^2 \varrho_c^2} [\psi(\vartheta - \varphi) + \frac{\sin^3(\vartheta - \varphi)}{\sin^3 \varphi} \psi(\varphi)] \\ & + \frac{8\pi v_1^2 \sigma^3}{\Delta\mu^2} [1 - \cos(\vartheta - \varphi) - \frac{\sin^2(\vartheta - \varphi)}{1 + \cos \varphi} \cos \vartheta], \end{aligned}$$

and thus, Equation (43) is derived.

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