

# A THERMOKINETIC MODEL FOR DROPWISE CONDENSATION ON A PLANAR SUBSTRATE WITH CONICAL PORES

Singha S.K.,\* Das P.K., and Maiti B.

\*Author for correspondence

Department of Mechanical Engineering,  
Indian Institute of Technology Kharagpur,  
Kharagpur, 721302,  
India,

E-mail: sanat.kgec@gmail.com

## ABSTRACT

Within the framework of the classical theory of heterogeneous condensation, a thermokinetic model has been developed for dropwise condensation on a planar substrate with conical pits. The development or the dissolution of the nucleated droplet is accounted due to both interfacial and peripheral mass transfer and by considering various geometric configurations, i.e. formed droplet within the conical pore, at the pore edge, and outside the pore respectively. Along with the principle of exergy maximization, detailed-balance-based kinetic approach has been employed to investigate the influence of the pore size and the substrate wettability on the thermokinetics of droplet nucleation of water vapor. The available energy for droplet formation and the time rate of nucleation are obtained. The twice-nucleation phenomenon is supposed to take place for some particular pore sizes and its thermokinetic trait is different from that obtained from the classical condensation theory. For a given conicity, there is an appreciable amount of reduction in the free energy barrier with increase in the contact angle. The slant height of the conical pit is found to have a great influence in the condensation enhancement or suppression. The barrier reduces considerably when the slant height reduces. These outcomes indicate a physical insight into the context of surface engineering for the promotion or the hindrance of dropwise condensation on real or engineered surfaces.

## INTRODUCTION

First order phase transition or nucleation can be defined as the process of the creation of new daughter phase in a form of cluster from a metastable parent phase [1]. Condensation or droplet nucleation is one type of nucleation in which supersaturated vapor phase transits to liquid phase. Nucleation can be homogeneous or heterogeneous in kind. Heterogeneous nucleation is not only widespread, but has many potent applications in biology and materials [2]. In spite of many arguments on the related postulations, the classical theory of heterogeneous nucleation is one of the most implemented methods for clarifying dropwise condensation and has been extensively employed for several substrate geometries. Heterogeneous nucleation on a planar or spherical substrate is most commonly encountered in literature [3-5]. However,

circular conical pits are abundant as defects in the actual substrates which are seemed to be planar and also mimics the microstructures of some typical plant leaves. Moreover, the mold wall consists of micro-sized cavities on a planar geometry related to the casting process. Therefore, for dropwise condensation, the planar substrate with conical pores can be considered as a basic geometry, although the topic is comparatively less studied in the literature [6,7].

## NOMENCLATURE

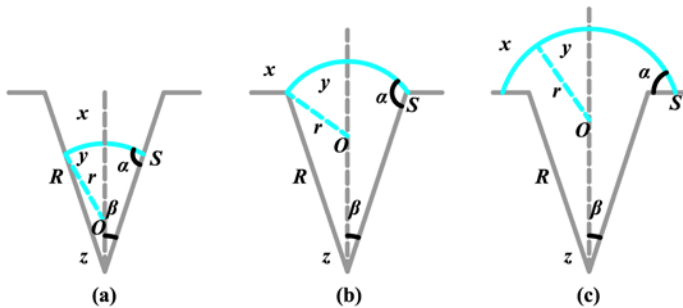
$A$	[m <sup>2</sup> ]	Interfacial area
$C$	[s <sup>-1</sup> ]	Condensation or forward rate
$E$	[s <sup>-1</sup> ]	Evaporation or backward rate
$F_H$	[J]	Helmholtz free energy
$F_V$	[J]	Volumetric free energy
$G$	[J]	Gibbs free energy
$G_{ads}$	[J]	Adsorption energy
$G_{diff}$	[J]	Diffusion energy
$f$	[-]	Dimensionless free energy barrier
$g$	[-]	Number of molecules within droplet
$h$	[-]	Dimensionless free energy change
$Ke$	[-]	Kelvin number
$Kn$	[-]	Knudsen number
$k_B$	[m <sup>2</sup> kg s <sup>-2</sup> K <sup>-1</sup> ]	Boltzmann constant
$L$	[m]	Length of the triple boundary line
$m_m$	[kg]	Molecular mass of water
$p$	[N m <sup>-2</sup> ]	Pressure
$r$	[m]	Radius of nanodroplet
$S$	[-]	Degree of supersaturation
$T$	[K]	Temperature
$t$	[s]	Time
$V$	[m <sup>3</sup> ]	Volume of nanodroplet
$v_m$	[m <sup>3</sup> ]	Molecular volume
Special characters		
$\alpha$	[°]	Microscopic contact angle
$\Delta$	[-]	Difference
$\delta$	[m]	Average jumping distance of a molecule
$\nu$	[s <sup>-1</sup> ]	Monomer impingement rate
$\sigma$	[N m <sup>-1</sup> ]	Interfacial tension
$\chi$	[-]	Kinetic factor
Subscripts		
$c$		Critical parameters
$l$		Peripheral parameters
$s$		Interfacial parameters
$sat$		Saturation properties
$v$		Properties of vapour
.		Temporal rate

In the thermodynamic study of dropwise condensation, the free energy barrier is usually determined to characterize the related nucleation phenomena. The kinetic analysis, based on the classical theory of dropwise condensation, is also an expedient method to investigate nucleation phenomena. Some kinetic models have been developed to reveal the characteristics of the dropwise condensation on the substrates of various geometries, e.g. lenticular, spherical-cap etc. [8,9] However, the kinetics of the surface condensation is still not clearly known due to the complicated effect of the roughness and wettability of the substrate. In the kinetic model for heterogeneous condensation, the addition of molecules to the formed nanodroplet can take place through two mechanisms: [10] (i) direct interfacial addition from the supersaturated vapor phase at the interface of the droplet and the vapor phase and (ii) indirect peripheral attachment through the vicinity of the contact line from the adsorbed molecules on the substrate. However, a similar thermokinetic formulation for dropwise condensation on a planar substrate with conical pores has not yet been developed.

In the present paper, within the framework of the classical theory of dropwise condensation, we discuss the thermokinetic characteristics of surface condensation on a planar substrate with conical pores by considering the collective influence of the two mechanisms of molecular addition. Taking water as the test fluid, a kinetic model for heterogeneous condensation on a planar substrate with conical pits is analyzed and the related rate coefficients are determined.

## GEOMETRIC MODEL

Consider the formation of a droplet of radius  $r$  from its supersaturated vapor within the conical pit, at the edge of the pit, and outside the pit of half-cone angle  $\beta$  as shown in Figure 1 (a), (b), and (c) respectively. The droplet ( $y$ ) is formed at the interface between the supersaturated vapor phase ( $x$ ) and the substrate ( $z$ ).  $O$  is the geometric center of  $y$ .  $S$  is the line where the three phases  $x$ ,  $y$ , and  $z$  meet each other.  $\alpha$  is the contact angle between  $y$  and  $z$ . Interestingly, the substrate becomes flat when  $\beta = 90^\circ$  with no conical pit. Moreover, the slant height of the conical pit is  $R$ .



**Figure 1** Three scenarios of heterogeneous droplet nucleation on a planar substrate with conical pores: (a) inside the conical pit, (b) at the edge of the conical cavity, and (c) outside the conical pore.

The volume of the formed nanodroplet can be expressed as

$$V = gv_m \quad (1)$$

where  $g$  is the number of molecules within the droplet and  $v_m$  is the molecular volume.

## THERMODYNAMIC MODEL

Capillarity approximation has been considered for developing the present model. To obtain the critical parameters of heterogeneous condensation, maximization of the change in Gibbs free energy with respect to the size ( $r$  or  $g$ ) of the cluster is needed. The Gibbs free energy change related to the formation of a cluster is

$$\Delta G = \Delta F_H - \Delta F_V \quad (2)$$

where  $\Delta F_H$  and  $\Delta F_V$  is the variation in the Helmholtz and volumetric free energy due to the formation of a droplet respectively.

The Helmholtz free energy change ( $\Delta F_H$ ) is related to the various interfacial tensions.  $\Delta F_H$  can be expressed as [1]

$$\Delta F_H = \sigma \{ A_{xy} - \cos \alpha \cdot A_{yz} \} \quad (3)$$

where  $\sigma$  is the interfacial tension between the droplet and the vapor phase and  $\alpha$  is the contact angle among the three phases.

The volumetric free energy change ( $\Delta F_V$ ) is associated with the variation in the free energy related to the difference in pressure ( $\Delta p$ ) between the formed droplet and the supersaturated vapor.  $\Delta F_V$  can be expressed as [2]

$$\Delta F_V = V \Delta p \quad (4)$$

where

$$\Delta p = \frac{k_B T}{v_m} \cdot \ln S, \quad (5)$$

$k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $S$  is the degree of supersaturation. The several associated geometric parameters can be obtained easily from Figure 1.

To determine the critical free energy barrier, one needs  $\partial \Delta G / \partial g|_{g=g_c} = 0$ .

After differentiating Equation (2) with respect to  $r$ , we have,

$$\frac{\partial \Delta G}{\partial r} = \frac{\partial \Delta F_H}{\partial r} - \frac{\partial \Delta F_V}{\partial r}. \quad (6)$$

So, from extremization principle one gets the critical radius after a rigorous algebraic manipulation as

$$r_c = \frac{2\sigma}{\Delta p}. \quad (7)$$

Moreover, the critical number of molecules within the formed stable droplet can also be given by

$$g_c = \frac{V(r_c)}{v_m}. \quad (8)$$

Substituting Equation (7) in Equation (2), the free energy barrier can be evaluated as

$$\Delta G_c = \Delta G(r_c) = \frac{4\pi r_c^2}{3} \cdot f, \quad (9)$$

where the geometric factor ( $f$ ) can be written as

$$f \equiv f(\alpha, \beta, R/r_c) \quad (10)$$

Moreover, Equation (2) can be written in non-dimensional form as

$$\Delta G = \frac{4\pi r_c^2}{3} \cdot h, \quad (11)$$

where the potency factor ( $h$ ) is expressed as

$$h \equiv f(r/r_c; \alpha, \beta, R/r_c) \quad (12)$$

Therefore,  $h = f$  when  $r = r_c$  as expected. The associated potency factor for different nucleation scenarios can be evaluated as

$$h_{in} = \left\{ 3 \left( \frac{r}{r_c} \right)^2 - 2 \left( \frac{r}{r_c} \right)^3 \right\} \times \left\{ \frac{1}{2} \left( \frac{2 - \sin(\alpha + \beta)}{-\frac{\cos \alpha \cos^2(\alpha + \beta)}{2 \sin \beta}} \right) \right\}, \quad (13)$$

$$h_{pin} = \frac{1}{2} \times \left\{ \begin{array}{l} 3 \left( \frac{r}{r_c} \right)^2 [1 - \sin(\alpha + \beta)] \\ - \left( \frac{r}{r_c} \right)^3 [2 - 3 \sin(\alpha + \beta) + \sin^3(\alpha + \beta)] \\ - 3 \left( \frac{R}{r_c} \right)^2 \cos \alpha \sin \beta - \left( \frac{R}{r_c} \right)^3 \sin^2 \beta \cos \beta \end{array} \right\}, \quad (14)$$

and

$$h_{out} = \left\{ 3 \left( \frac{r}{r_c} \right)^2 - 2 \left( \frac{r}{r_c} \right)^3 \right\} \times \left\{ \frac{1}{4} (2 - 3 \cos \alpha - \cos^3 \alpha) \right\} \\ - \frac{3}{4} \left( \frac{R}{r_c} \right)^2 \cos \alpha \sin \beta (1 - \sin \beta) \\ - \frac{1}{2} \left( \frac{R}{r_c} \right)^3 \sin^2 \beta \cos \beta. \quad (15)$$

The corresponding potency factor for nucleation to occur inside the conical pit is expressed by  $h_{in}$ . The factor is found to be independent of the dimension of the cavity, as expected. The factor ( $h_{pin}$ ) associated with pinning condition, *i.e.* nucleation at the edge of the cavity. Moreover,  $h_{out}$  is the factor related to the condition of nucleation outside the conical pore. Both  $h_{pin}$  and  $h_{out}$  are depends on the slant height of the pore ( $R$ ).

## KINETIC MODEL

In the preceding thermodynamic analysis of the heterogeneous condensation we are concerned neither in the details of the nanodroplet formation nor in its subsequent development, *i.e.* we treat the droplet as a constrained thermodynamic quasi-equilibrium both internally or externally. However, the emergence of the nanodroplet is actually a transient stochastic mechanism with a very short lifespan (typically a nano- or even a picosecond) which depends essentially on the droplet radius. Apart from the fundamental query about the relevance of using the conventional energetics to such formation, clearly, a more thorough understanding of the process of condensation necessitates a kinetic model using which the growth rate of the nanodroplet can be estimated due to the variation in their size. Moreover, the kinetic mechanism of condensation can be treated as a ‘‘Markov process’’ which

can further be formulated using the Becker-Döring equations. In this connection, it can be mentioned that the thermodynamic and the kinetic aspects of condensation are linked through the exponential dependence of the equilibrium nanocluster size distribution with the free energy barrier which is a self-consistent assumption within the framework of the thermodynamic fluctuation theory [1,2].

In the kinetics of heterogeneous condensation, as mentioned earlier, the attachment of monomers to the nanodroplet can occur by two means: [10] (i) the explicit interfacial accumulation on the neighborhood of the nanodroplet-vapor interface from the supersaturated vapor and (ii) the implicit peripheral addition via the vicinity of the triple line from the adsorbed layer of monomers on the substrate. Therefore, the attachment rate of monomers, also widely known as the forward rate or the condensation coefficient, can be given as

$$C = S \cdot C^{sat} = S \cdot (C_s^{sat} + C_l^{sat}), \quad (16)$$

where the contribution of the attachment rate under saturation conditions based on the interfacial accumulation of monomers on the neighborhood of the nanodroplet-vapor interface can be expressed as

$$C_s^{sat} = v^{sat} A_{xy}, \quad (17)$$

the contribution of the attachment rate under saturation conditions due to the peripheral addition via the vicinity of the triple line can be expressed as

$$C_l^{sat} = \delta v^{sat} \exp\left\{ (G_{ads} - G_{diff}) / k_B T \right\} L \quad (18)$$

and under saturation conditions, the monomer impingement rate or the flux of monomers per unit interfacial area and per unit time can be given as  $v^{sat} = p_v^{sat} / \sqrt{2\pi m_m k_B T}$ .

The cluster can grow or shrink due to the thermal fluctuations. So, both forward or condensation rate and backward or evaporation rate is required for determining the growth rate of the cluster and the rate of nucleation. To obtain the monomer detachment rate, usually classical theory of condensation employs the notion of constrained equilibrium, despite the fact that the metastable supersaturated vapor at a given temperature is not basically an equilibrium state. In a different method derived by Katz without considering ‘‘Maxwell’s demon’’, the detachment rate is found from the ‘‘detailed balance’’ situation at the stable equilibrium state of the saturated vapor at the same temperature [1,2]. We have used the Katz kinetic approach to determine the detachment rate of monomers from the nanodroplet in the present paper. So, monomer detachment rate for explicit interfacial accumulation can be expressed as

$$E = \chi \cdot C^{sat} = E_s^{sat} + E_l^{sat}, \quad (19)$$

where  $E_s^{sat} = \chi \cdot C_s^{sat}$ ,  $E_l^{sat} = \chi \cdot C_l^{sat}$ , and  $\chi$  is a kinetic factor.

With the help of Equation (15), the kinetic factor  $\chi$  can be formulated as [10]

$$\chi = \exp\left( \frac{1}{k_B T} \cdot \frac{\partial \Delta G}{\partial g} \Big|_{\Delta p=0}^{sat} \right) = \exp(Ke), \quad (20)$$

where Kelvin number ( $Ke$ ) can be given by

$$Ke = \frac{2\sigma v_m}{rk_B T} \quad (21)$$

**Table 1** Parameters used for evaluation of various rates

Parameter	Symbol [Unit]	Value
Boltzmann constant	$k_B$ [J K <sup>-1</sup> ]	$1.381 \times 10^{-23}$
Supersaturation	$S$	2.0
Temperature	$T$ [K]	300.0
Molecular volume	$v_m$ [m <sup>3</sup> molecule <sup>-1</sup> ]	$2.992 \times 10^{-29}$
Molecular mass	$m_m$ [kg molecule <sup>-1</sup> ]	$2.982 \times 10^{-26}$
Saturation vapor pressure	$p_v^{sat}$ [N m <sup>-2</sup> ]	3570.0
Surface tension of water	$\sigma$ [N m <sup>-1</sup> ]	$7.174 \times 10^{-2}$
Average jumping distance	$\mathcal{D}$ [m]	$3.2 \times 10^{-10}$
Adsorption energy	$G_{ads}$ [J molecule <sup>-1</sup> ]	$2.9 \times 10^{-20}$
Diffusion energy	$G_{diff}$ [J molecule <sup>-1</sup> ]	$2.9 \times 10^{-21}$

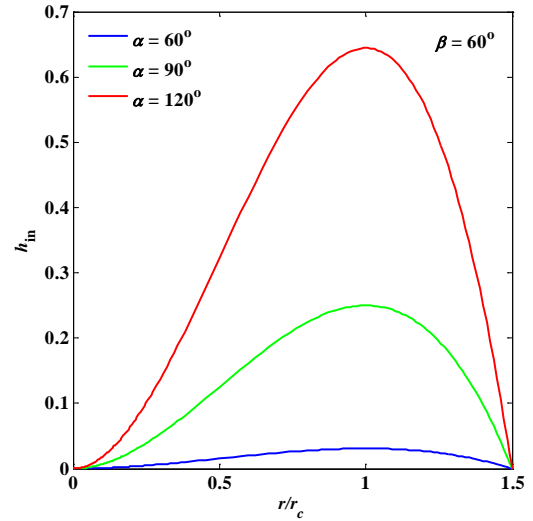
The characteristics of the growth of a nanodroplet depend essentially on the Knudsen number,  $Kn$ , which can be defined as the ratio of the molecular mean free path ( $\lambda$ ) of water vapor molecules to the critical diameter ( $2r_c$ ) of the formed nanodroplet [10]. Although the explicit expression for  $\lambda$  of water molecules are unavailable in the literature,  $\lambda$  is considered as about 42 nm from the kinetic theory of gases for the given supersaturated vapor pressure ( $p_v^{sat}$ ). From Table 1, the diameter of the nanodroplet is found to be 3 nm. Therefore, the mean free path is much larger than the molecular size of the nanodroplet as  $Kn \leq 14$  during the period of the nanodroplet growth. So, the growth is controlled by kinetics of the monomers in the surrounding supersaturated vapor. Therefore, considering the present thermokinetic model as kinetically controlled or ballistic limited growth, the volumetric growth rate of nanodroplet can be approximated to be proportional to the difference of the monomer attachment and detachment rates and can be expressed as

$$\dot{V} = \frac{dV}{dt} = v_m \cdot \frac{dg}{dt} \approx v_m (C - E) = v_m (S - \chi) \cdot C^{sat} \quad (22)$$

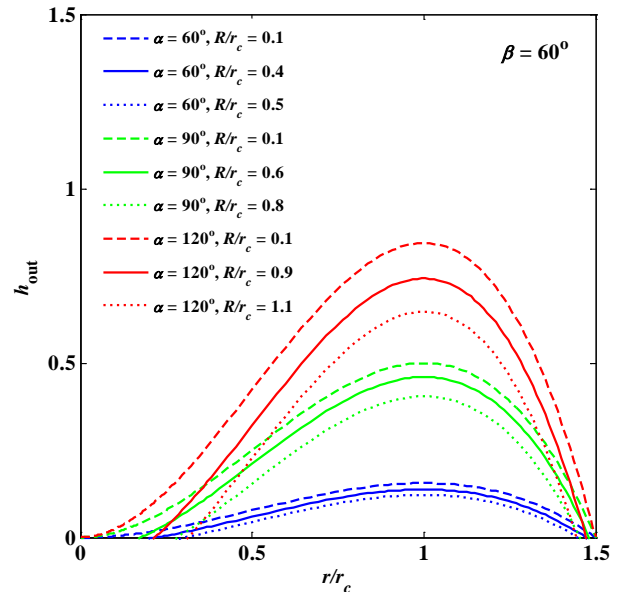
## DISCUSSIONS ON RESULTS

From the thermodynamic study, it is found that the potency factor is independent of size of the substrate when nucleation occurs inside the conical pore. However, it is dependent on the wettability and the conicity of the substrate as can be seen from Figure 2. The critical value, which is the geometric factor in the present case, is the maxima of all the curves shown in Figure 2,

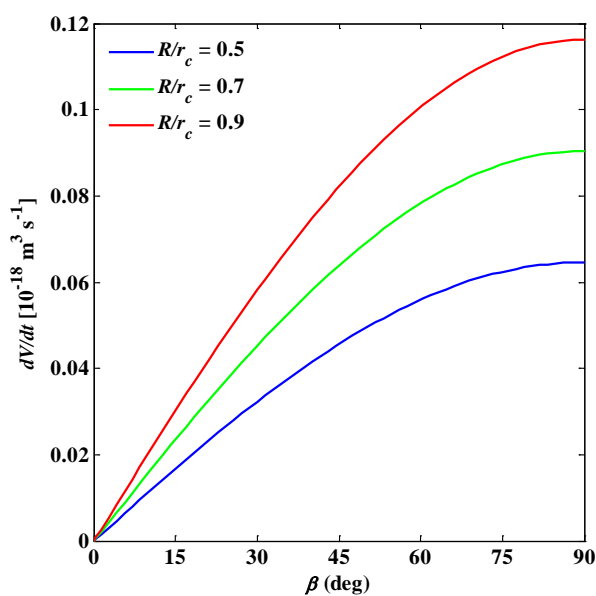
as expected. For a given conicity, there is a considerable amount of reduction in the free energy barrier with increase in the substrate wettability.


**Figure 2** Variation of the potency factor with dimensionless radius of the formed nanodroplet inside the conical pit

The potency factor associated with heterogeneous nucleation outside the cavity depends on the size of the substrate, *i.e.* slant height of the conical pore. The optimum value, which is the geometric factor, is the maxima of all the curves shown in Figure 3, as expected. For a given cone angle, there is an appreciable amount of reduction in the free energy barrier with increase in the contact angle. The slant height of the conical pit is found to have a great influence in the condensation enhancement or suppression. The barrier reduces considerably when the slant height reduces. So, the promotion of dropwise condensation is possible for lower values of slant height of the conical pore.


**Figure 3** Variation of the potency factor with dimensionless radius of the formed nanodroplet outside the conical pore

As mentioned earlier, the present kinetic model as ballistic limited growth, the volumetric growth rate of nanodroplet can be approximated to be proportional to the difference of the monomer addition and deduction rates. Using Table 1, it is found that the indirect peripheral mass transfer through the neighbourhood of the three-phase contact line from the thin adsorbed layer is about two orders of magnitude higher than the direct interfacial mass transfer at the droplet-vapour interface. Moreover, the growth rate is found to be one order of magnitude higher when nucleation occurs outside the cavity than the edge of the cavity. Outside the cavity, the kinetics of dropwise nucleation does not depend on the size of the pore or the pore conicity. It only depends on the pore wettability. On the other hand, the volumetric growth rate depends on the conicity and the wettability of the substrate when nucleation occurs inside the cavity.



**Figure 4** Variation of the volumetric growth rate of the formed nanodroplet at the edge of the conical pore

Figure 4 shows a typical variation of the volumetric growth rate of the formed nanodroplet at the edge of the conical pore. In this regard, it can be mentioned that twice nucleation is possible thermodynamically in this case. The rate does not implicitly depend on the wettability of the substrate. However, the rate depends on the geometry of the conical pore. The volumetric droplet growth increases with increase in the conicity and the size of the conical pore.

## CONCLUSIONS

Within the framework of the classical theory of heterogeneous condensation, a thermokinetic model has been developed for dropwise condensation on a planar substrate with conical pits. The development or the dissolution of the nucleated droplet is accounted due to both interfacial and peripheral mass transfer and by considering various geometric configurations, i.e. formed droplet within the conical pore, at the pore edge, and outside the pore respectively.

Along with the principle of exergy maximization, detailed-balance-based kinetic approach has been employed to investigate the influence of the pore size and the substrate wettability on the thermokinetics of droplet nucleation of water vapor. The available energy for droplet formation and the time rate of nucleation are obtained. The twice-nucleation phenomenon is supposed to take place for some particular pore sizes and its thermokinetic trait is different from that obtained from the classical condensation theory. The indirect peripheral mass transfer through the neighborhood of the three-phase contact line from the thin adsorbed layer is about two orders of magnitude higher than the direct interfacial mass transfer at the droplet-vapor interface. Therefore, the presence of the three-phase contact line is found to have an appreciable influence on the thermokinetics of droplet nucleation. For a given cone angle, there is an appreciable amount of reduction in the free energy barrier with increase in the contact angle. The slant height of the conical pit is found to have a great influence in the condensation enhancement or suppression. The barrier reduces considerably when the slant height reduces. So, the promotion of dropwise condensation is possible for lower values of slant height of the conical pore. These outcomes indicate a physical insight into the context of surface engineering for the promotion or the hindrance of dropwise condensation on real or engineered surfaces. Moreover, an indirect approach [8] has recently been developed for predicting the microscopic characteristics of wetting using the experimental data of the nucleation rate. Therefore, experimental validation of the present thermokinetic formulation is possible on the accessibility of such experimental data.

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