ABSTRACT

Heterogeneous nucleation is ubiquitous in nature and the promotion or the suppression of nucleation and the subsequent growth of the nucleated phase has many practical consequences in engineering and technology. In heterogeneous nucleation, a stable phase is formed on an extrinsic substrate from its metastable phase. Therefore, the geometry of the extrinsic substrate has a great impact on the mechanism of heterogeneous nucleation. For example, a spherical seed has to be considered in the analysis of cloud formation. On the other hand, a conically textured substrate must be pondered in the study of metal casting. Therefore, substrate-geometry-associated physical models of heterogeneous nucleation are important in the study of phase transition.

Despite the disputes about various associated assumptions, Classical Nucleation Theory (CNT) is one of the most versatile and widely adopted framework for explaining the physical models of heterogeneous nucleation. Based on this framework, thermodynamics, stability, and kinetic analyses have been postulated for heterogeneous nucleation on rigid as well as perfectly deformable substrates. In the present study, the influence of three-phase contact line on extrinsic-substrate-induced nucleation has been discussed elaborately. Various steady-state thermokinetic parameters – nucleation barrier, growth rate, nucleation rate etc. – have been evaluated within the purview of CNT. The free-energy extremization principle and a “detailed balance analysis” of molecular exchange have been used to determine the mentioned parameters related to the present formulation.

As three phases are involved in a very small length scale (of the order of nanometre), the effect of contact line tension cannot be neglected during the incipient stage of nucleation. From the first principles, the closed-form expressions in dimensionless form for the thermodynamic barrier of line tension associated nucleation have been formulated with respect to the system geometry and the substrate wettability. Line tension is found to have a considerable effect on thermodynamics and kinetics of heterogeneous nucleation. Moreover, the crossover situations associated with barrierless and homogeneous nucleation are found using the thermodynamic stability analysis of the three-phase metastable system. Various geometric configurations and related regime maps corresponding to these limiting scenarios have also been identified in the present study.

In the present study of growing length scale phenomena, the evaluated kinetic parameters are the rates of attachment and detachment of molecules with cluster, the growth rate of an individual cluster and the rate of nucleation on the foreign substrate. The implicit peripheral molecular transfer through the vicinity of the three-phase contact line from the adsorbed layer is found to be about two orders of magnitude higher than the implicit interfacial transfer at the interface of the formed cluster and the metastable phase.

During heterogeneous nucleation, the contact line may also be pinned under certain circumstances. This mode of heterogeneous nucleation is definitely different from heterogeneous nucleation with constant contact angle mode. From the present theoretical analysis, the nucleation barrier can be divided into two components related to the geometry of the metastable system and the pinning of the contact line in case of pinned nucleation. The resulting favourable or adverse pinning effect can induce pinning-depinning transition which may also lead to the corresponding crossover situations.

After the initiation of heterogeneous nucleation, subsequent growth takes place in terms of a propagating front throughout the metastable phase. One specific case of this growth can be the propagation of freezing front within a water droplet placed on a chilled substrate which is maintained at a sub-zero temperature. In the present work, experiments have been performed to investigate the effect of salinity on freezing droplets initiated by heterogeneous ice nucleation. By observing the temporal history of crystallization carefully, three parameters have been taken into consideration to quantify the kinetic mechanism of surface icing. Due to the depression of freezing point and the formation of molecularly solvation shells, an appreciable increase in the delay of heterogeneous ice nucleation has been observed with the salinity of the salt solution. Moreover, the associated kinetic sluggishness in surface icing is seen with the increasing salinity because of the low solubility of salt in ice and of the brine rejection during freezing. The icing singularity, which is essentially found after the completion of solidification of a freshwater droplet, gradually disappears with the increasing salt concentration. This is basically due to the incomplete solidification of the droplet as found from the corresponding phase diagram.

Keywords: Heterogeneous Nucleation and Growth, Thermodynamics, Kinetics, Stability, Line Tension, Molecular Flux, Contact Line Pinning, Surface Icing, Salinity