



A free energy model and availability analysis for onset of condensation on rigid and liquid surfaces in moist air



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ABSTRACT

A thermodynamic model based on changes in Gibbs free energy and availability is developed for onset of heterogeneous condensation on subcooled rigid and liquid surfaces in moist air. Effects of wettability of the wall, subcooled wall temperature, relative humidity and dew point temperature of the surrounding air on critical radii for heterogeneous condensation on a rigid surface are investigated based on the change of Gibbs free energy. From the analysis of changes in availability, it is found that onset of droplet condensation is easier to occur on a hydrophilic surface than on a hydrophobic surface, in moist air than in a dry air environment, on a colder surface than a warmer surface, on a liquid surface than a rigid surface. It is also found that condensation droplet occurs earlier on oil surfaces with small surface tensions than on oil surfaces with large surface tensions.

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1. Introduction

As an efficient heat transfer mode for cooling, condensation heat transfer has been widely studied in the past several decades [1]. Most of early experiments were conducted for condensation heat transfer coefficients in tubes [2,3] as well as for onset of condensation on subcooled surfaces [4–6]. Recent research work on condensation focuses on condensation of vapor on nano-structure surfaces [7–9] and soft surfaces [10–12], as well as on condensation of moist air [13]. The latter is owing to the increasing demands for non-wetting or anti-freezing surfaces for industrial applications. It has been reported that a surface structure filled with hydrophobic liquids can achieve a much better performance on de-wetting or anti-freezing than conventional super-hydrophobic surfaces [14–20]. Some researchers have studied soft surface heterogeneous condensation [21–24] and liquid surface condensation [25], and others have calculated the deformation [23] and redefined the contact angle [19] for the purposes of identifying droplet shape on a deformable surface. In particular, Sokuler et al. [24] observed that onset of heterogeneous condensation was easier to occur on soft substrates than on rigid substrates under the same condition. It is pertinent to note that most previous research work on dewetting and anti-icing had been focused on experimental observations, and relatively few theoretical studies on these topics have been performed.

In 1876, Gibbs [26] introduced the free energy concept for the equilibrium of heterogeneous substances under constant pressure conditions. Since that time, a number of analyses have been carried out for onset of phase-change processes based on changes in Gibbs free energy. For example, Eslami and Elliot [25] carried out an analysis on onset of heterogeneous condensation of pure vapor on both rigid and liquid surfaces in a uniform temperature environment using a free energy method, and they concluded that onset of condensation occurred easier on a liquid surface than on a rigid surface. Fletcher [35] used Gibbs free energy analysis to predict the onset of homogeneous condensation of ice. Based on Fletcher's work, Jung et al. [34] estimated freezing delay time, and proved that surfaces with roughness close to the critical nucleus radius will be more ice-phobic. On the other hand, availability analyses [27] have been used as stability criteria for many thermodynamic studies of phase change processes. Recently, Cheng and co-workers [28–31] have carried out analytical studies on heterogeneous nucleation and condensation under different conditions based on Gibbs free energy and availability analyses.

As far as the authors are aware, the analysis on onset of heterogeneous condensation on rigid and soft surfaces in moist air, with effects of air's humidity and temperature, contact angle and wall-temperature gradient fully taken into consideration, has not yet been developed. In this paper, we have developed such a non-equilibrium model to predict onset of heterogeneous condensation from moist air with these effects fully taken into consideration, and have obtained critical radii for onset of heterogeneous condensation under various conditions.

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Nomenclature

G	specific Gibbs free energy (J/kg)
G	Gibbs free energy (J)
h	specific enthalpy (J/kg)
h_{fg}	latent heat (J/kg)
k	temperature gradient (K/m)
m	mass (kg)
p	pressure (Pa)
q	heat flux (W/m ²)
r	droplet radius (m)
R	gas constant (J/(kg K))
s	specific entropy (J/(kg K))
S	entropy (J/K)
T	temperature (K)
U	internal energy (J)
V	volume (m ³)
x	height from the subcooled substrate surface (m)

Greek symbols

α	degree
β	degree
χ_v	vapor ratio

δ	height (m)
λ	thermal conductivity (W/(m K))
μ	specific chemical potential (J/kg)
θ	degree
ρ	density (kg/m ³)
σ	interfacial tension (N/m)
ψ	availability (J)

Subscripts

0	reference condition, initial state
c	critical
d	droplet
l	liquid
o	oil
p	horizontal plane
s	saturated state
v	vapor
w	wall
L	lower
U	upper

2. Onset of heterogeneous condensation on rigid surfaces in moist air

We now develop a thermodynamic model, based on stability criteria of Gibbs free energy and availability changes, to study onset of heterogeneous condensation on a rigid subcooled substrate in moist air. It is assumed that at the onset of heterogeneous condensation, a droplet of hemispherical shape is formed on the surface. The physical model of this analysis is shown in Fig. 1, where x is the vertical axis pointing upward. The horizontal surface having a subcooled wall temperature T_w and a contact angle θ is located at $x=0$. The semi-infinite extent of moist air (i.e., a vapor/air mixture) with relative humidity χ_v at a total pressure of p_v with a dew point T_s is located at $x > 0$. Note that the relative humidity is defined as:

$$\chi_v = RH = \frac{p_i}{p_s(T_s)} \quad (1)$$

where p_i is the vapor partial pressure, and p_s is the saturated vapor partial pressure at T_s .

2.1. Changes in Gibbs free energy

As the environment temperature and pressure are constant (i.e., independent of time) during the onset of condensation process, we can use Gibbs free energy criterion to analyze the phase-change process. The criterion is given by $dG \leq 0$ where G is the Gibbs free energy defined as [26]:

$$G = U + pV - TS \quad (2)$$

with U being the internal energy and S the entropy. Thus, for onset of dropwise condensation under a constant atmospheric pressure and temperature, we have:

$$dG = G_l - G_v \leq 0 \quad (3)$$

where $G_l(p_l, T_l) = U_l + p_l V_l - T_l S_l$, $G_v(p_v, T_v) = U_v + p_v V_v - T_v S_v$, and the chemical potential μ is defined as $\mu = h - Ts$.

It is relevant to note that the chemical potential per unit mass is equal to the specific Gibbs function ($\mu = G/m = g$) for a pure substance. Since the temperature of subcooled vapor T_l is equal

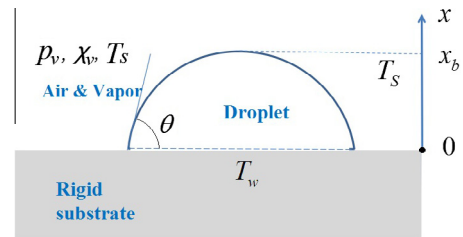


Fig. 1. Model of droplet condensation on a rigid surface.

to that of subcooled liquid T_v at thermal equilibrium, the change in Gibbs free energy between vapor and liquid is:

$$\Delta g = g_l - g_v = \mu_l - \mu_v^{air} = (h_l - h_v^{air}) - T_v(s_l - s_v^{air}) \quad (4)$$

where

$$\mu_v^{air} = h_v^{air} - T_v s_v^{air} \quad (5)$$

with μ_v^{air} being the chemical potential of water vapor in the surrounding air and T_v being the temperature of vapor at a position x . Note that we have assumed the water vapor being an ideal gas to obtain the chemical potential in Eq. (5). The first and second terms on the right-hand side of Eq. (4) can be written as:

$$h_l - h_v^{air} = h_{gf} + (c_{pl} - c_{pv})(T_v - T_s) + v_l(p_l - p_s(T_s)) \quad (6)$$

$$s_l - s_v^{air} = \frac{h_{gf}}{T_s} + (c_{pl} - c_{pv}) \ln \left(\frac{T_v}{T_s} \right) - R \ln \left(\frac{p_s(T_w)}{p_s(T_s)} \right) + R \ln(\chi_v) \quad (7)$$

where h_{gf} is the latent heat of water from vapor phase transform to liquid phase, v_l is specific volume of water, $p_s(T_s)$ and $p_s(T_w)$ are saturated partial pressures of water vapor in the surrounding air corresponding to temperature T_s and T_w respectively. p_l is the pressure inside liquid droplet depending on the location x , p_i is the partial pressure of water vapor in air, and R is the gas constant of the water vapor.

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