A heterogeneous nucleation theory with explicit account of vapor adsorption

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In the classical picture of heterogeneous nucleation, spherical liquid caps appear on a surface at supersaturated conditions, and if these caps are larger than so called critical size, they grow spontaneously, whereas smaller caps will evaporate. In reality, vapor adsorption takes place already at subsaturated conditions, and depending on the substrate-vapor interactions, the adsorbed layer may consist of clusters centered on so called active sites. The extent of adsorption can be calculated using adsorption isotherms which give the average adsorption layer thickness as a function of vapor saturation ratio, provided that adsorption constants (characterizing the substrate-vapor interactions) are known. Here I propose a new theory that combines adsorption and heterogeneous nucleation so that it can be used to calculate both the adsorption layer thickness at subsaturated conditions, as well as the onset supersaturation for nucleation.

Consider spherical liquid caps with a contact angle Φ forming on a flat surface. The average number of monolayers in the liquid cap is denoted by $\Theta = (V/a)/d_v$, where V and a are the liquid cap volume, and its area of contact with the substrate, respectively, and d_v is the diameter of the vapor molecule (calculated assuming spherical shape). The adsorption is described using the FHH (Frenkel-Halsey-Hill) isotherm given by

$$\ln(S) = \frac{-A'}{\Theta_{av}^{B'}}$$

where S denotes the vapor saturation ratio, Θ_{av} is the average number of monolayers ($\Theta_{av} = \Theta Na/a_{tot}$) with N and a_{tot} the number of liquid caps on the substrate and the total surface area of the substrate, respectively, and A' and B' are adsorption parameters. The FHH equation describes adsorption equilibrium for the whole surface. With a single spherical cap, the curvature of the cap influences the equilibrium, and we can write

$$\ln(S) = \frac{-A}{\Theta^B} + \frac{2\sigma v}{kTR}$$

where σ is surface tension, v is volume of the condensed molecule, k is the Boltzmann constant, T is temperature, and R is radius of the spherical liquid cap. The radius can be expressed using the contact angle and the number of monolayers to rewrite the above equation as

$$\ln(S) = \frac{-A}{\Theta^B} + \frac{2\sigma v f(\Phi)}{3kTd_v\Theta}$$

where $f(\Phi)$ is a function of the contact angle only. If S is plotted as a function of Θ, it will show a maximum at some value above 1. The maximum denotes the critical supersaturation, at which point the spherical liquid caps will start growing spontaneously due to vapor condensation. In order to find the critical cap layer thickness Θ^* and the critical saturation ratio S^*, the derivative of $\ln(S)$ with respect to Θ is set to zero, giving

$$\Theta^* = \left(\frac{2\sigma v f(\Phi)}{3kTd_v AB}\right)^{1/(1-B)}$$

and

$$S^* = \exp\left(\frac{-A}{\Theta^{*B}}\right)\exp\left(\frac{2\sigma v f(\Phi)}{3kTd_v\Theta^*}\right)$$

Fig. 1 shows a comparison between the present theory and classical heterogeneous nucleation theory for gas-liquid nucleation of water on flat surfaces.
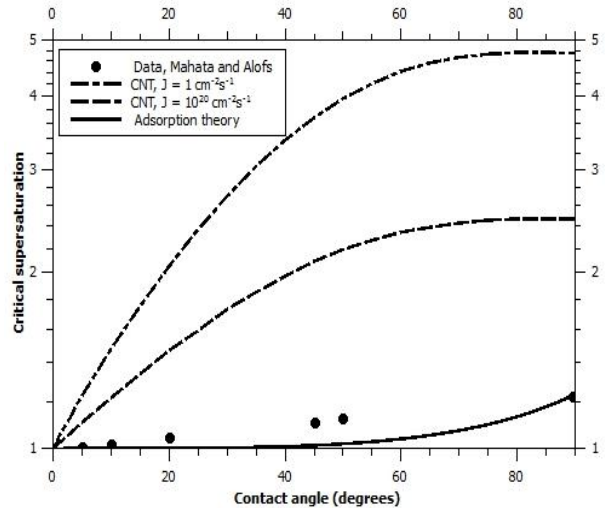

Figure 1. Critical supersaturation as a function of contact angle predicted with the current theory using $A = 3$, $B = 2$ (solid line) and classical heterogeneous nucleation theory (J = 1 cm^{-2}s^{-1}; dashed line; J = 10^{20} cm^{-2}s^{-1}, dash-dotted line), and experimental data by Mahata and Alofs (J. Atmos. Sci. 32, 116, 1975) (circles).