This paper (N11) is a welcome contribution to the study of heterogeneous ice nucleation. The authors endeavors to clarify thereasons for the dichotomy that prevails in the literature regarding the treatment of heterogeneous nucleation of ice, namely interpretations based either on stochasticity or on singularity. They do this by constructing a "soccer-ball" model and exercise the model with a variety of assumptions about the population of nucleating particles. The paper does attain its purpose up to a point, but there is more to be said.

The underlying physics of ice nucleation is viewed in this paper the same way as in the modified singular description, VS66(Vali and Stansbury 1966; Vali 1994), even if it clothed in different colors and one of the authors' conclusion seems to be stating the opposite. In the foregoing, I will try to draw out the parallels and the differences.

The three major components of heterogeneous ice nucleation incorporated into both the VS66 and N11 descriptions are: (i) nucleation sites exist with specific properties that influence or determine ice nucleation on them, (ii) nucleation rate on the site is the expression of the probability per unit time that nucleation will take place, and (iii) the nucleation rate is a function which rises sharply with increasing supercooling. There is agreement on (ii). The crucial point to examine is how important are the relative contributions of (i) and of (iii) to observed freezing temperatures. Various other consequences follow from this point regarding the interpretations of experiments.

In VS66the dominant differences among sites are assumed to arise, in general,from (i), as is illustrated in Fig. 1. The bottom panel shows the nucleation rate for four sites. The rate rises within a relatively narrow temperature range compared to the difference in their position along the temperature axis. That position is defined by a “characteristic temperature”,the temperature at which the nucleation rate on a site reaches some arbitrary, fixed, value (as illustrated in Fig 12 of Vali and Stansbury 1966). In the N11 model, the rate for each site is given by $j_{het}(T,\theta_i)$based on CNT. Looking at one example in Zobrist (2007) this rate rises many orders of magnitude in just a few Kelvin. This is also to be expected from the rate for homogeneous nucleation. The magnitude of site-specific effects in N11 can be gauged from the differences induced by altering the width of the distribution of contact angles σ_θ. While not specifically stated in the paper, that spread can be deduced to be large for σ_θ> 0.1 from the fact that in panels c and d of Fig. 4 of N11 temperatures many degrees higher than the -21°C corresponding to σ_θ = 0 are considered in order to see anything but instantaneous freezing. So, it appears that there is no disagreement here between VS66 and N11. This assertion can be readily tested by the authors of N11 by plotting as a function *T*numerical values of $j_{het}(T,\mu_\theta - \sigma_\theta)$, $j_{het}(T,\mu_\theta)$and $j_{het}(T,\mu_\theta + \sigma_\theta)$for σ_θ> 0.1, or forother selected values of θ.

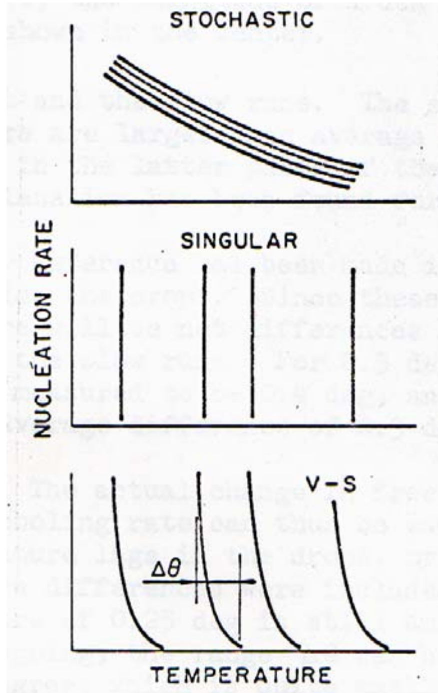

Figure 1. Contrasting forms of the nucleation rate for four different sites as viewed in the stochastic, singular and VS66 models (from Vali G.: The characteristics of freezing nuclei. *Proc. Seventh Conf. Cond. and Ice Nuclei*, Prague and Vienna, 387-393, 1969).

The next point to examine is how different is the use of the contact angle to specify properties of a site from the characteristic temperature used in VS66. In my view, there is no fundamental difference since the contact angle serves in N11 to specify the properties of the sites by assigning a given $j_{het}(T,\theta_i)$ function to it. The characteristic temperature does the same by specifying a temperature at which $j_{het}(T,k,l,m)$ has a specific (threshold) value. The function is denoted here with *k*,*l* and *m* as unspecified factors meant to reflect the ice nucleation potential of the site. Those factors can be different for various types of sites (steps, dislocations, inclusions, inhomogeneities of any kind); usually these factors are not known.In practical terms, the characteristic temperature is close to the observable temperature of freezing on a site, independently of the assumed form of the $j_{het}(T,k,l,m)$ function, while $j_{het}(T,\theta_i)$ is a more abstract description. In all, whether the properties of a site are specified by the contact angle (N11) or by the characteristic temperature (VS66) there is a unique nucleation rate function attached to that site. This is also stated in point 3 of page 3166 of N11, using the word "characterize".

The foregoing two paragraphs demonstrate, I believe, that the N11 model is actually an implementation of the VS66 model. It is a special case, with contact angle as the key parameter in place of the characteristic temperature. Is there an advantage to this? On the one hand, it is a useful to be more specific. On the other hand it does rely on an abstraction, the spherical cap model of embryo formation, which is known to have little validity for ice nucleation. But, this point doesn't need to be debated here. The assumptions in N11 regarding the sizes of sites, and linking sizes to the number of sites per particle, have no impact on this discussion either.

To underscore my main point, it may be useful to restate the results presented in N11 with the vocabulary of the VS66 model.The case of σ_θ =0and n_{site} = 1 implies that all of the particles (one per drop) are identical, namely have the same characteristic temperature. If such a set of drops are held at a temperature where the rate of nucleation is relatively low (say, well below the characteristic temperature) there will be a decrease in the number of drops with time as shown in Fig. 3 of N11. The slopes of the lines in the graph will depend on the temperature difference between the temperature of observation and the characteristic temperature. No such experiment has in fact been carried out so far, because it is close to impossible to produce identical particles and place them one in each drop of water. The closest approach to this is to repeat many times the freezing of one sample, and those tests (e.g. Vonnegut and Baldwin 1984;Shaw, Durant and Mi 2005; Vali, 2008) indeed yield results reflecting the stochastic nature of nucleation on a site, though some alteration of the particle or of the site with time cannot be ruled out. If the number of sites is increased but are assumed to be identical(σ_θ=0 is maintained) a minor difference will develop depending on whether the site sizes decrease in inverse proportion to the number (fixed total area), as in the N11 model, or if the sites remain the same size, as could be the case with each site located on a different particle. In the former case, since the nucleation rate is expressed per unit area the increase in number is cancelled by the decrease in size, leading to the same overall probability of freezing. In the latter case, the rate would increase in proportion to the number of sites and thus the slope of the line in Fig. 4a of N11 would increase. There would be no change from the stochastic pattern.

With a large range of characteristic temperatures (σ_θ= 0.5) and n_{site} = 1, each drop will freeze close to the characteristic temperature of the particle it contains. How close, will depend on the steepness of the nucleation rate function and on the rate of cooling. For the conditions represented in Fig 4d of N11, i.e. at a temperaturewhere all sites have a low nucleation rate (-1°C), this means that only a small fraction of the drops will freeze no matter how long one waits, as is the case in that figure. As n_{site} increases, the frozen fraction also increases because the likelihood that a site with a characteristic temperature closer to -1°C (a small contact angle) is present goes up and there will be continued increase in the number frozen as sites with somewhat lower characteristic temperatures (larger contact angle) may also have nucleation take place on them in a time-dependent fashion. All these rates remain low because the peak of the distribution of characteristic temperatures is near -21°C, so that the large spread in characteristic temperatures (large value of σ_θ) and a large number of sites per particle is needed to have any sites with appreciable probability of freezing near -1°C, if the assumption of Gaussian distribution of N11 is followed.Thus, the results shown in N11 are consistent with the expectations that flow from the ideas of VS66 for the appropriate conditions.

It follows from the aforesaid that the conclusion stated in the first three lines of Section 5 (page 3172) of N11 is incorrect. This also means that the descriptions‘transition’ and ‘bridging’ are somewhat misleading. The two elements, site characteristics and nucleation rate, are always present and are always part and parcel of heterogeneous nucleation. One or other feature may become dominant depending on the sample being examined and the experiment being performed.In other words, there are no two different types of heterogeneous ice nucleation, stochastic and singular, just a combination of the two. Experiments can reveal – or be designed to focus on – one or the other part of the picture but the two parts can never be separated. The results in N11 demonstrate this quite well by varying the magnitudes of the input parameters while leaving in place both of the processes involved.

The above criticisms notwithstanding, this paper is a good step toward due recognition of the two inseparable aspects of ice nucleation.Hopefully the comments here presented will be helpful too. Yet,it should not be forgotten that, in spite of having clear concepts about the processes of heterogeneous ice nucleation, our understanding of the factors that control heterogeneous ice nucleation, and our ability to predict nucleating potential as a function of substrate properties are very limited. Much remains to be discovered.