The paper by Herbert et al. (2014; H14) which appeared near-simultaneously with this article (V14) provides an opportunity to make some additional comments regarding the application of the nucleation rate in the interpretation of measurements of heterogeneous freezing nucleation.

To facilitate the discussion of the two papers it seems appropriate to first clarify differences in terminology and notation. "Apparent nucleation rate" used in H14 is equivalent to "freezing rate" in V14; to allow for both perspectives "rate function" will be used in the following. The slope parameter $\omega$ in V14 is denoted by $\lambda$ in H14 with a difference in sign: $\omega = -\lambda$. The notation for cooling rate is $w$ in V14 and $r$ in H14. In the following, the notation and terminology used in V14 is followed.

Data obtained with kaolinite KGa-1b in Mu11 is complemented in H14 with measurements using larger drop volumes, different cooling rates, and with freezing temperatures about 15°C higher. The combined data set is presented in H14 as an example for a single-component system, i.e. one that exhibits stochastic nucleation describable by a single nucleation rate function. This interpretation of observations is argued against in V14 so it is important to examine the new data and to re-visit the arguments presented in V14.

As a first characteristic of the stochastic system, the rate function is taken in H14 to be adequately described by an exponential formula. This is the same assumption as that of Bigg (1953) and is discussed in the Appendix of V14. It is not considered a requirement that this be a universal form of the rate function but the derivations of other characteristics are dependent on this form. H14 provides a quantitative prediction for the effect of variations in cooling rate. For cooling rate $w_2$ compared to a cooling rate $w_1$, an offset in freezing temperatures is expected for the same frozen fraction of the sample. The offset is given by

$$\Delta T = \xi \cdot \ln(w_1 / w_2) \tag{1}$$

with the value of $\xi$ equal to the inverse of the slope parameter $\omega$. This result also follows directly from Eq. (A3) of VS66. Another characteristic expected of a stochastic system is that at a fixed temperature the fraction of drops remaining liquid decreases exponentially, as in Eq. (3) of V14 or Eq. (13) of H14, and that the time constant of the decay rate is equal to the inverse of the rate constant determined for that temperature in an experiment at constant cooling (cf. Eq. A7 of VS66).

The foregoing set of conditions are shown in Mu11 and in H14 to have been satisfied by results obtained for kaolinite KGa-1b, as summarized in Figs. 4a and 4b of H14. The value $\omega = 1.1$ that was determined from the Mu11 data fits well the combined Mu11-H14 data set, the cooling-rate offset is as predicted (within the scatter of the data) and the decay rate of the constant-temperature test is close to prediction. In total, the case is quite convincing but some limitations and problems need to be mentioned. First, the slope parameter from the data in Mu11 is in itself an empirical result not a theoretical value. Second, the individual runs for the new data in H14 (the microliter samples, Fig 4a) have quite different slopes than the line fitted to the combined set. Thirdly, the data in their Fig. 4b is quite weak due, in part, to the small sample size, but

more importantly because of the shift of the first data point to near 1 min rather than zero. The temperature chosen for this experiment is close to (within <2°C) where all drops would freeze with steady cooling, i.e. where the freezing rate is high. In addition, the fit to the first 40% of the data would be very different than the overall fit shown in the figure. Finally, an important test of the validity of the stochastic description is to perform repeated tests with the same samples, as in V08 and WP13. Having such observations for KGa-1b would have been very useful.

The points raised above lead to some additional thoughts regarding the discussion of Section 5.3 in V14 about nucleating sites versus surfaces. As mentioned, repeated freezing of the same set of sample drops is a missing piece of the KGa-1b data. However, the large value of $\omega$ for this sample (=1.1) presents a difficult case for such observations because that steep slope will make the range of freezing temperatures for drops of the same size and same particle quite narrow. As a consequence of that, the spread in freezing temperatures for individual drops during the time sequence of repetitions is bound to be difficult to separate from the drop-to-drop variations of freezing temperatures in any one test. In other words, it may be difficult to identify chance variations due to the probability of nucleation (the nucleation rate) from uncertainties in the distribution of nucleating sites (the spectrum $k(T_c)$ of characteristic temperatures) such as detection errors and multiple sites per drop. This difficulty can be countered only to a limited degree by making the tests with large numbers of drops and with the use of suitable statistical analyses.

The problem just described is more general than the case of KGa-1b. As can be seen from Table 1 in V14, there are several other data sets with high values of $\omega$. Thus, it can be foreseen that to clarify the respective roles of sites versus surfaces (cf. Section 5.3 in V14) much further experimentation and a search for other lines of investigation will be required. As far as I can see, the distinction made in B12 and H14 between single-component and multiple-component systems hinges on the same issue: these authors consider as single-component systems those exhibiting no specific sites, versus multiple-component systems in which the existence of specific sites is ascribed to the presence of different materials in the INPs. In the end, that point of view can be reconciled with the notion of sites if the meaning of different materials is extended from different chemical composition to different surface properties (such as are envisaged to constitute sites) and is allowed to exist on the scales of ice embryos. It follows that a qualitative distinction between single-component and multiple-component systems, such as proposed in B12 and H14, does not necessarily indicate pure versus mixtures of materials of different composition. It is also evident that much more complete knowledge about nucleating sites is the only real progress that can provide solutions beyond the approach of characterizing sites, and their frequency of occurrence, by their observed freezing temperatures.

Cases at the other end of the range of $\omega$-values underscore the arguments made in the foregoing: the stochastic prediction of the cooling rate dependence fails for two data sets which have strong evidence for specific sites. Using subscripts 'obs' and 'st' for measured and predicted values respectively, for the V94 data we have $\xi_{obs}$ = 0.66 while

$\xi_{st} = 1/\omega_{obs} = 1/0.6 = 1.52$, and for the WP13 data $\xi_{obs} = 0.33$ while $\xi_{st} = 1/\omega_{obs} = =1/0.52 = 1.92$. For these cases, the stochastic model over-predicts the shifts in freezing temperatures by large factors. This is, of course, why these data would not qualify as single-component systems in the B12-H14 terminology.

Overall, the conclusions and recommendations stated in V14 are unchanged and reinforced. Effective descriptions of freezing nucleation can be constructed by giving primary role to specifying the spectrum of nucleating sites and by accounting for time-dependence on the basis of empirical results. While this approach seems counter-intuitive, knowing that embryo growth is essentially stochastic and that the manner surfaces aid embryo initiation is not well known, it is clear that the latter factor accounts for most observations of freezing nucleation. The analyses in H14 and in V14 both underscore the connection between the slope of the rate function and the cooling-rate dependence of freezing temperatures and also the rate of freezing at a steady temperature. This connection needs to be examined with careful experimentation.