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Comment on "The dependence of homogeneous nucleation rate on supersaturation" [J. Chem. Phys. 141, 024307 (2014)]

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A recent article[1] discusses the failure of the classical nucleation theory (CNT) to account for a range of experimental observations of nucleation rates vs. supersaturation. Mis-estimations of the liquid drop parameters will obviously cause erroneous predictions for cluster free energies which will cause the temperature dependence of the nucleation rate to be in error. The author of Ref. 1 points out, correctly we believe, that nucleation rates at constant temperature but varying supersaturation will also be predicted incorrectly in the same situation.

The argument for this is based on the First Nucleation Theorem, which relates the nucleation rate J, the supersaturation ratio S, and the critical size n^* as

$$\left(\frac{\partial \ln J}{\partial \ln S}\right)_T = n^* + 1. \tag{1}$$

Incorrect free energy parameters in the liquid drop expansion will give an incorrect critical size and therefore an incorrect double logarithmic slope in Eq. (1). The nucleation rate will thus generally be predicted incorrectly, also in this case.

This conclusion can hardly be disputed. What this comment addresses is the comparison of numerically simulated cluster binding energies and the values derived from extrapolation of bulk properties and specifically what the difference between these two data sets imply for the critical size.

The theoretical results referenced in Ref. 1 are compared with experimental data on critical sizes derived from measurements of nucleation rates. For water the experimental data show a deviation from the values expected from CNT for n^* above approximately 40. The deviation is in the direction of a smaller experimental value than the predicted CNT value, by as much as one third.

This discrepancy is discussed with reference to the formation free energies of water clusters in the size range from $n = 1$ to 10,[2] and aluminum clusters of sizes 1–60.[3] The data for aluminum show large size-to-size fluctuations due to quantum size effects with a trend toward higher formation free energy. A similar shift is seen in water clusters. Density functional theory calculations of jellium metal clusters[4] gave similar results with a positive value for the curvature term, proportional to $N^{1/3}$, signifying a positive small-particle contribution to the surface energy additional to the bulk surface energy.

The trend observed in the theoretical results does not, however, seem to explain the observed mismatch between CNT predictions and experimental data. The simulated water data in Ref. 2 predict a *larger* critical size than CNT. The experimentally observed deviations reproduced in Fig. 1 show a *smaller* critical size, albeit in a different region than covered by the simulated data. A direct comparison is possible for water at the smallest critical sizes where experimental[5] and theoretical[2] data overlap. The experimental critical sizes were found to agree well with CNT. In contrast, the theoretical energies of Temelso *et al.*[2] find a critical size of about twice the CNT value for the example with $S = 100$ shown in Fig. 9 in Ref. 1.

The state-of-the-art calculations may then actually give a worse agreement with experiments than CNT. However, the picture is not absolutely clearcut. The opposite trend for the surface tension was found for gold clusters. Although gold has little relevance *per se* for nucleation studies, it qualifies as being one of the few cluster materials for which binding energies have been experimentally directly determined without recourse to modelling.[6] The ground state dissociation energies for a range of small cationic clusters were observed to exceed the bulk liquid drop values by typically 0.5 eV, corresponding to a significantly reduced effective surface tension. Of the measured values, $N = 7 - 27$, only one falls below the liquid drop value, and the amplitude of the size-to-size oscillation disappears rapidly for the sizes beyond 27, as judged by the mass abundance spectra in Refs. 7 and 8 and as expected for metallic clusters. Hence, the critical size is also most likely reduced for these clusters compared with the liquid drop parametrization. A smaller study on silver clusters with the same method showed less deviations from the liquid drop values.[9]

As also mentioned in Ref. 1, this stresses the importance of a better knowledge of the size dependence of the formation free energy. It seems that this situation can only be resolved with experiments that determine critical sizes *via* nucleation rates in parallel with experiments that determine the formation free energies for clusters of the same material. As pointed out by Vehkamäki and collaborators,[10] due consideration should be paid to the severe experimental difficulties in the determination of critical sizes.

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