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# Temperature dependence of homogeneous nucleation rates for water: Near equivalence of the empirical fit of Wölk and Strey, and the scaled nucleation model

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It is pointed out that the temperature fitting function of Wölk and Strey [J. Phys. Chem. **105**, 11683 (2001)], recently shown to convert the Becker–Döring [Ann. Phys. (Leipzig) **24**, 719 (1935)] nucleation rate into an expression in agreement with much of the experimental water nucleation rate data, also converts the Becker–Döring rate into a form nearly equivalent with the scaled nucleation rate model,  $J_{\text{scaled}} = J_{\text{oc}} \exp[-16\pi\Omega^3(T_c/T-1)^3/3(\ln S)^2]$ . In the latter expression  $J_{\text{oc}}$  is the inverse thermal wavelength cubed/sec, evaluated at  $T_c$ . © 2005 American Institute of Physics.  
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For some time it has been known that the classical nucleation rate expression of Becker and Döring,<sup>1</sup>

$$J_{\text{BD}} = \left[ \frac{P_o}{kT} \right]^2 \left( \frac{2\sigma}{\pi m} \right)^{1/2} \frac{S^2}{\rho_{\text{liquid}}} \exp \left[ - \frac{16\pi}{3} \frac{\left( \frac{\sigma}{kT} \right)^3}{(\rho_{\text{liquid}} \ln S)^2} \right], \quad (1)$$

tends to underestimate the experimental nucleation rate  $J$  at low temperatures and overestimate  $J$  at high temperatures, generally giving agreement at one temperature in the range where the data exist.<sup>2–6</sup> In Eq. (1)  $P_o$ ,  $\sigma$ ,  $S$ ,  $T$ ,  $m$ ,  $\rho_{\text{liquid}}$ , and  $k$  are the equilibrium vapor pressure, liquid surface tension, supersaturation ratio ( $P/P_o$ ), temperature, molecular mass, liquid number density, and Boltzmann constant, respectively. Most of the more successful approaches to improving the temperature dependence of the classical steady state homogeneous nucleation rate have focused on the free energy of formation of the critical cluster which appears in the exponent.<sup>7–13</sup> Some time ago we noted<sup>14</sup> that a scaled model for  $J$ ,<sup>15,16</sup>

$$J_{\text{scaled}} = J_{\text{oc}} \exp \left[ - \frac{16\pi\Omega^3 \left( \frac{T_c}{T} - 1 \right)^3}{3(\ln S)^2} \right], \quad (2)$$

fits the temperature dependence of the homogeneous nucleation rate data for toluene<sup>5</sup> and nonane.<sup>3</sup> Besides the temperature scaling of the energy of formation,  $J_{\text{scaled}}$  differs from  $J_{\text{BD}}$  in its nonclassical prefactor  $J_{\text{oc}}$ , which (to first order) is independent of  $S$  and  $T$ .  $J_{\text{oc}}$  is well approximated by one event per thermal wavelength cubed per second (evaluated at  $T_c$ ).  $\Omega$  is the excess surface entropy per molecule (divided by  $k$ ), and as estimated from experimental surface tension, is about 2 for normal liquids and about 1.5 for polar liquids. This scaled model did not agree with the first extensive set of water data, taken by Miller *et al.*<sup>17</sup> at low nucleation rates ( $\approx 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$ ). Schmitt repeated this data recently obtaining the same nucleation rates at larger  $S$ ,

suggesting contamination at the lower rates.<sup>18</sup> However, in 1993, Viisanen, Strey, and Reiss<sup>19</sup> reported expansion chamber data for water at high nucleation rates ( $10^6$ – $10^9 \text{ cm}^{-3} \text{ sec}^{-1}$ ) and it was shown that these water data fit the temperature dependence of Eq. (2) with  $\Omega_{\text{water}} = 1.47$ .<sup>20</sup>

Recently, Wölk and Strey<sup>21</sup> repeated the 1993 H<sub>2</sub>O nucleation rate experiments and reported a similar body of data for D<sub>2</sub>O. In addition to investigating the isotope effect, Wölk and Strey analyzed the data's temperature dependence and presented an empirical fitting function for H<sub>2</sub>O and D<sub>2</sub>O which brings the classical expression of Becker and Döring into close agreement with experiment:

$$J_{\text{exp}} = J_{\text{BD}} \exp \left[ A + \frac{B}{T} \right]. \quad (3)$$

For water, Wölk found  $A = -27.56$  and  $B = 6500 \text{ K}$ . The fitting functions gave excellent agreement with the H<sub>2</sub>O and D<sub>2</sub>O data for a wide range of nucleation rates, temperature, and supersaturation ratio  $S$ . Subsequently, Wölk, Strey, Heath, and Wyslouzil<sup>22</sup> tested the fitting function on a wider set of data and found that Eq. (3) provided a good description for most of the available water data. The purpose of the present note is to point out that the empirical fitting function in Eq. (3) converts the classical Becker–Döring expression into a form nearly equivalent to the scaled model of Eq. (2).

The scaled nucleation model was initially intended to incorporate a scaled surface tension form,  $\sigma = \sigma_o(1 - T/T_c)$ , into the classical model and derive a scaling law for onset supersaturation ratios,  $\ln S_{\text{onset}} \approx 0.53\Omega^{3/2}(T_c/T-1)^{3/2}$ .<sup>15</sup> This scaling law can be derived directly from Eq. (2). At the time, however, the approximation was made that the kinetic prefactor of the classical nucleation rate had a weak temperature dependence.<sup>15</sup> The agreement of the scaling law with onset data for a wide range of substances was thus surprising, given the temperature dependence of  $[P_o/kT]^2$  in the kinetic prefactor of the classical model. In search of the reason for the success of the scaling law (and motivated by Dillmann's treatment of small cluster size effects<sup>8</sup>), we calculated the

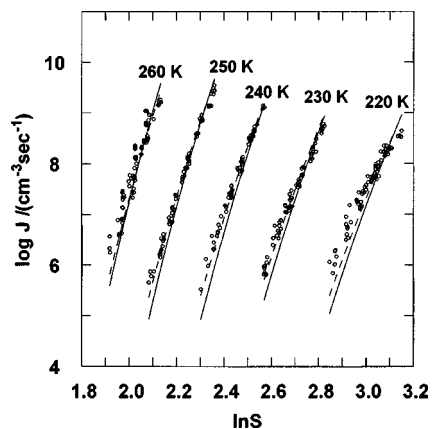


FIG. 1. Comparison of the empirical fit of Wölk and Strey (dashed line) and the scaled model (solid line) predictions with the experimental data of Wölk and Strey.

free energy of formation of the critical cluster by summing Fisher droplet model free energy differences over discrete cluster sizes.<sup>14</sup> This summation (together with the scaled surface tension) produced the scaled model temperature dependence. The discrete summation technique was also applied to TIP4P potential<sup>23</sup> water clusters using Monte Carlo generated cluster free energy differences.<sup>20,24</sup> These model studies indicated that small cluster discrete size effects can produce a term in the energy of formation which is of the form  $W(T_c/T-1)$  and which can cancel in part the strong exponential temperature dependence of  $[P_o/kT]^2$  in the classical model kinetic prefactor. Inspection of Wölk and Strey's fitting function (which has a similar  $T$  dependence) motivated the present comparison of the two models.

In Fig. 1 is a comparison of the predictions of  $J_{BD} \exp[A+B/T]$  (dashed line) and of  $J_{scaled}$  (solid line) together with the water data of Wölk and Strey (circles). The models are nearly identical at high temperatures and at the lower temperatures differ by less than a factor of 6 at low nucleation rates. Over the entire temperature range, the two models appear to agree with each other about as well as either model agrees with the data.

Another direct comparison of  $J_{BD} \exp[A+B/T]$  and  $J_{scaled}$  for all the  $(T_i, S_i)$  data points of Wölk and Strey (each pair corresponds to an experimental nucleation rate  $J_i$ ) is shown in Fig. 2. If the models were identical, all the points would lie on the dashed line. One can also see in this figure that the major discrepancies between the fitting function and the scaled model occur at the smallest nucleation rates where the two models differ by less than a factor of 6.

To analyze the empirical fitting function in Eq. (3) with  $A=-27.56$  and  $B=6500$  K we transform it into the following form:

$$\left[ \frac{J_{exp}}{J_{BD}} \right] = \exp \left[ 10.05 \left( \frac{T_c}{T} - 1 \right) - 17.5 \right]. \quad (4)$$

The temperature dependent term,  $10.05(T_c/T-1)$ , can be seen to largely cancel the square of the monomer concentration factor  $[P_o/kT]^2$  in the kinetic prefactor of  $J_{BD}$ ,

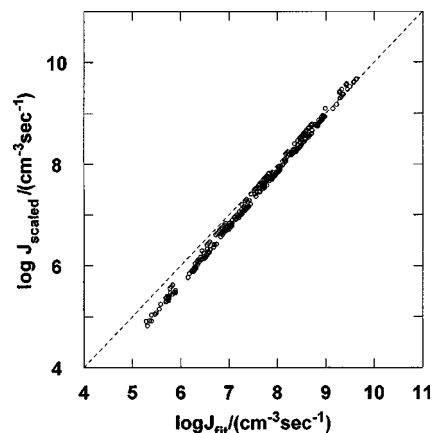


FIG. 2. The  $\ln(J_{scaled})$  vs  $\ln(J_{BDfit})$  for all the  $(S_i, T_i)$  data pairs of Wölk and Strey. [Each  $(S_i, T_i)$  corresponds to one experimental nucleation rate point  $J_i$ ]. The dashed line indicates where all circles should lie when  $\ln(J_{scaled}) = \ln(J_{BDfit})$ .

$$\left[ \frac{P_o}{kT\rho_{liquid}} \right]^2 = \left[ \frac{P_o}{P_c} \right]^2 \left[ \frac{P_c}{\rho_c kT} \frac{T_c}{T} \frac{\rho_c}{\rho_{liquid}} \right]^2 \approx \exp \left[ -2W_o \left( \frac{T_c}{T} - 1 \right) + 2 \ln \frac{\rho_c}{\rho_{liquid}} \right], \quad (5)$$

where  $W_o$  for water is about 7. Remaining discrepancies between the data and the classical model can be embedded in the temperature dependence of the liquid surface tension.

A plot such as Fig. 1 is useful because it explicitly demonstrates the dependence of  $\ln J_{exp}$  on both  $S$  and  $T$ . It is interesting to modify this standard plot slightly and plot  $\ln J_{exp}$  versus the  $\ln S$  scaled with a function of  $T$ . What function scales  $\ln S$  so that all the five temperature data sets in Fig. 1 collapse into one line of data? Following Binder and Stauffer<sup>25</sup> and Eq. (2), we plot  $\ln J_{exp}$  versus the following scaled  $\ln S$ ,

$$[\ln S]_{scaled} = C_o \frac{\ln S}{\left( \frac{T_c}{T} - 1 \right)^{3/2}}, \quad (6)$$

where  $C_o = (T_c/240-1)^{3/2}$  so that at  $T=240$  K, the  $[\ln S]_{scaled}$  coincides with  $\ln S$  in Fig. 1. One can see from Fig. 3 that

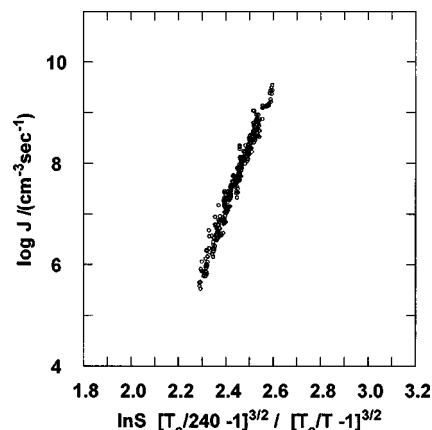


FIG. 3. The experimental nucleation rate of Wölk and Strey vs the scaled supersaturation function,  $C_o \ln S / (T_c/T-1)^{3/2}$ , where  $C_o = (T_c/240-1)^{3/2}$ .

when  $\ln S$  is so scaled all the data points collapse on a line, rather than falling along five separate lines as in Fig. 1. This representation of the data expresses the specific function of  $S$  and  $T$  upon which the experimental nucleation rate is dependent. That is,

$$J_{\text{experimental}} \approx J \left[ \frac{\ln S}{\left(\frac{T_c}{T} - 1\right)^{3/2}} \right]. \quad (7)$$

In summary, we have shown that the scaled model in Eq. (2) is nearly equivalent to the  $J_{\text{BD}} \exp[A+B/T]$  empirical fitting function of Wölk and Strey for water. The predictions of these two expressions differ only at the lowest water nucleation rates by less than a factor of 6 and agree about as well with each other as either does with the data over the temperature range of the data. It is also shown that the standard plot of Fig. 1 can be made to collapse into a single line of data if the  $\ln S$  of the abscissa is scaled by  $(T_c/T-1)^{3/2}$ . While the scaled model and the fitting function both predict the temperature dependence of the water data, the scaled model has some advantages. It is not restricted to water and it offers the experimentalist a way to check his/her data for consistency (or perhaps more usefully, inconsistency) with other substances.

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