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Homogeneous nucleation rate for water

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Homogeneous nucleation rate data for water extending over an exceptionally large domain of rate (J), supersaturation ratio (S), and temperature (T) was recently published. Because it spans a large J-S-T surface, this data constitutes a good test of nucleation theory. Here classical nucleation theory is used to analyze this data. By adjusting only the sticking coefficient, we are able to obtain a good fit between theory and experiment. It was necessary to include an increase in the water molecular density associated with the finite water compressibility.

I. INTRODUCTION

A knowledge of the nucleation process is a key element in the understanding of many natural and industrial processes. Nucleation plays a prominant role in a wide variety of engineering processes, wherever condensation, boiling, crystalization, sublimation, and catalytic processes occur. In the biological sciences nucleation and the mathematical methods developed to treat it have far reaching application towards the development of teeth and bone, arteriosclerosis, arthritis, and formation of kidney and gallstones,[1] the onset of anomalous heart activity,[2] and the polymerization of hemoglobin and sickle cell anemia.[3] Freezing nucleation influences the damage to living cells in freezing weather. In the atmosphere nucleation influences precipitation in clouds and the formation of certain aerosols of concern in air pollution chemistry. In spite of its role in environmental, biological, and industrial processes, nucleation still remains only poorly understood. In the three-dimensional world many of these transitions, like melting and freezing, occur so rapidly that little is known about the underlying mechanisms. The precursor fluctuations are so rare as to be unobservable and the intermediate states are so unstable that they do not exist in equilibrium to any appreciable extent.[4]

Since the innovative work of Wilson,[5] the expansion cloud chamber has been developed and used by numerous investigators to study homogeneous nucleation. In particular, Kassner and his co-workers developed numerous advances in expansion chamber technology and applied them to a variety of nucleation and condensation phenomena.[6–12] In a recent paper[13] we presented experimental homogeneous nucleation rate data for water which was taken in an expansion cloud chamber. This data was presented in detailed tabular form and with an empirical expression that gave the nucleation rate as an analytic function of supersaturation and temperature. A notable feature of this data was that it extends over an exceptionally large J-S-T (nucleation rate-supersaturation ratio-temperature) surface. Since the data covers such a large portion of the J-S-T surface, it provides a severe test of homogeneous nucleation theory. Here we show that classical nucleation theory, with a suitably flexible sticking coefficient, can give a good fit to this broad set of experimental data.

II. CLASSICAL NUCLEATION THEORY

The classical nucleation rate is given by

$$J = C^* \Gamma A^* \alpha Z, \qquad (1)$$

where C^* is the concentration and A^* is the surface area of critical sized nucleation embryos, Γ is the flux of water molecules to the cluster surface, α is the sticking coefficient, and Z is the Zeldovich factor which accounts for nonequilibrium effects in the embryo concentration. The critical sized cluster is one for which the free energy of formation

$$\Delta G = -NkT \ln S + A\sigma$$

reaches a maximum value. N denotes the number of water molecules in the cluster, k is Boltzmann's constant, T is absolute temperature, S is the supersaturation ratio, A and σ are the cluster's surface area and surface tension, respectively.

For the surface tension σ we use the results developed by Sinanoglù[14] in his study of microscopic surface tension of water down to molecular dimensions

$$\sigma = \sigma_b(T)[1 + C(T)/N^{2/3}],$$

where $\sigma_b = 118.44\ \text{dyn cm}^{-1} - (0.155\ \text{dyn cm}^{-1}\ \text{K}^{-1})\,T$ is the bulk water surface tension, $C = 1.302\,(T/298)^{0.0311} - 1$ is a microphysical correction factor, and N is the number of water molecules in the cluster. N can be related to the cluster's surface area by equating two expressions for the water molecular density n_l:

$$n_l = [1 + 2\sigma k_c/(A/4\pi)^{1/2}]\,n_b(T) \qquad (2)$$

$$= N/[(4\pi/3)(A/4\pi)^{3/2}]. \qquad (3)$$

$(A/4\pi)^{1/2}$ is just the cluster radius. k_c denotes the (temperature dependent) compressibility for bulk water and $n_b(T)$ is the temperature dependent bulk water molecular density.

Equation (2) accounts for the increase in density due to the increased pressure in the small droplet as given by the Laplace equation.

The functional form chosen for the sticking coefficient is

$$\alpha = \exp(v_1 + v_2 Sp_e/p + v_3 N),$$

subject to the constraint that $\alpha \leqslant 1$. We expected α to depend upon T, Sp_e/p, and N. The Sp_e/p term was put in to allow α

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to decrease with the rate at which new molecules had to be incorporated into the embryo thereby releasing latent heat, proportional to Sp_e, and increase with the total gas pressure p, the rate at which collisions with the inert carrier gas carried away this energy. This term also carries the temperature dependency through p_e. The v's are adjustable.

The adjustable parameters (v_i's) are varied to minimize

$$\Delta^2 = \sum_{T,S} (\ln J_{\text{theory}} - \ln J_{\text{exp}})^2 . \tag{4}$$

J_{theory} denotes the theoretical nucleation rate [Eq. (1)] and J_{exp} the corresponding experimental value. Here we used the empirical nucleation rate formula $J(S,T)$ given by Miller *et al.*[13] to represent the data since it is a smooth function and it deletes the small anomalous "knees" present in the raw data at low nucleation rates which are known to be due to trace impurities which nucleate the system.[12] The summation runs over all values chosen for temperature and supersaturation ratio. Here temperature runs from 230 to 290 K, and supersaturations are used such that at each temperature the nucleation rate covers the approximate range from 1 to 10^6 cm^{-3} s.$^{-1}$

Due to the size dependencies in σ and A an analytic expression for J was not found. Instead J must be calculated numerically. The critical size is found by numerically solving

$$d\Delta G/dN = 0 \tag{5}$$

for N using values of A and dA/dN from the numerical solution of Eqs. (2) and (3). The IMSL[15] routine ZREAL1 was used for these numerical solutions. Standard linear least squares methods can be used to minimize Δ^2 in Eq. (4) to find the v's.

III. RESULTS

The final solution for the parameters is

$$v_1 = -11.929, \; v_2 = -0.034\,564, \; v_3 = 0.039\,176.$$

The quality of the fit to experiment is shown in Fig. 1. The classical theory with a parametrized α fits the experimental data in precisely the same manner as Miller's[13,16] empirical $J(S,T)$ function. The theory was fit to the Miller data (O) Also shown are the data (+) of Wagner and Strey,[17] who studied nucleation at much higher rates. When the parametrized theory is extrapolated to these high nucleation rate regimes the fit to the Wagner and Strey data is reasonably good, except that the fit does not follow the knees in their data which occur just above 10^6 cm^{-3} s.$^{-1}$ Note that the theory was not adjusted to fit the Wagner and Strey data, but rather only the Miller data.

Figure 1 also shows the results of fitting the same data without including the water compressibility effects, i.e., k_c is set to zero. The fit fails badly at low temperatures. The reason is that when $k_c = 0$, the surface tension σ decreases (tending to increase J), while the water molecular density n_l also decreases (tending to lower J). The density effect dominates and lowers J overall. Because the sticking coefficient is constrained, $\alpha \leqslant 1$, it cannot increase enough to compensate for the overall lowering of J. The water compressibility effect clearly needs to be accounted for.

We now discuss the properties of the physical parameters in the theory. Figure 2 shows the behavior of the molecular density n as a function of embryo size for selected temperatures (n_b is the bulk water molecular density). We find that the microscopic n everywhere exceeds the bulk value, more so at the colder temperatures and smaller cluster sizes. The dependence of the critical cluster size upon S for selected temperatures is shown in Fig .3. Also plotted are the critical sizes N_1 corresponding to size independent bulk values for σ and n_l. N and N_1 show the same characteristics of decreasing with increasing S or T, but N always lies below N_1. Note that the molecular density and the critical cluster size, i.e., Figs. 2 and 3, are not dependent on the sticking coefficient, our only adjustable physical parameter. Figure 2 also shows the dependence of sticking coefficient α upon cluster size N at selected temperatures. α ranges from 0.93×10^{-6} to 0.41×10^{-4} over the span of conditions stud-

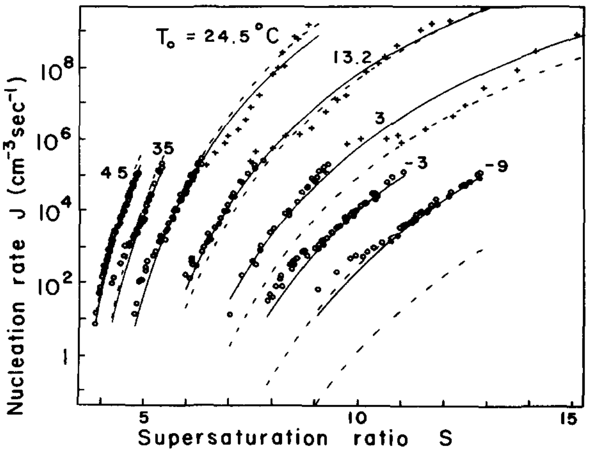

FIG. 1. Homogeneous nucleation rate vs supersaturation ratio. T_0 denotes the cloud chamber's initial temperature. (O)—data from Miller *et al.* (Ref 13). (+)— data from Wagner and Strey (Ref. 17). (———) — theory using the parametrization presented here. The theory was adjusted to fit the Miller data. (- - -)— theory using the method presented here, but with the compressibility of water set to zero.

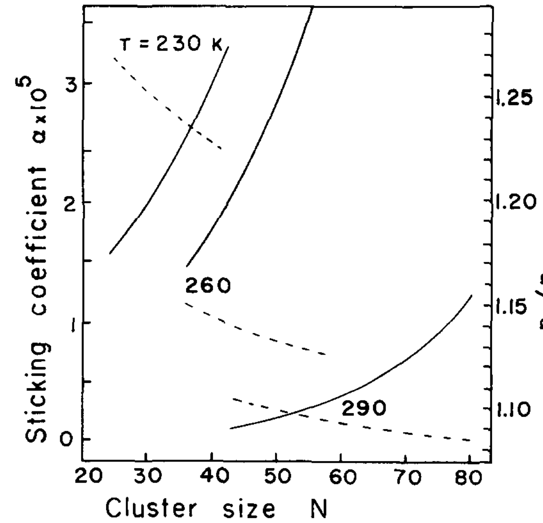

FIG. 2. (- - -)— water molecular density n_l vs cluster size N for selected temperatures. $n_b(T)$ is the bulk temperature dependent molecular density. (———) — sticking coefficient α vs cluster size N for selected temperatures.

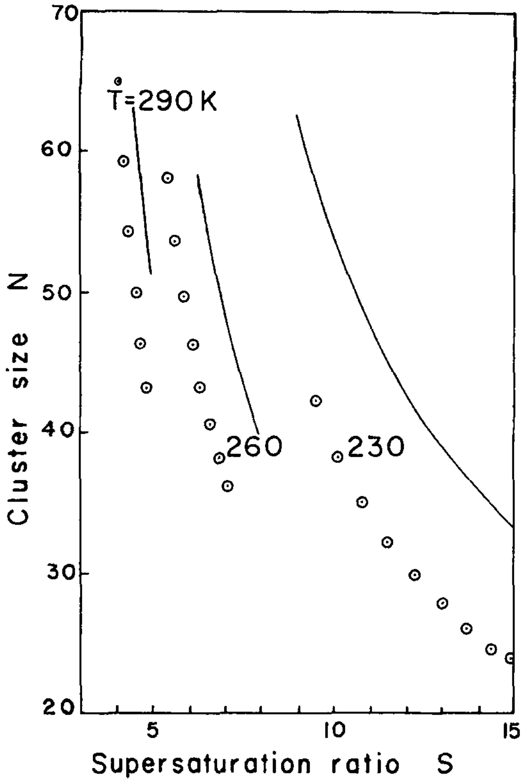

FIG. 3. (●)— critical cluster size N vs supersaturation ratio S for selected temperatures. (———) — critical cluster size derived from Eq. (5) with σ and n_l taking on their temperature dependent but size independent bulk values.

ied here. It has the properties that α decreases with increasing temperature, it decreases with increasing Sp_e/p and it increases with increasing N. It should be remembered that J is far more sensitive to σ and n_l than to α (since ΔG depends on σ and n_l but not on α) so the uncertainties in α determined from measured nucleation rates will be relatively large.

IV. CONCLUSIONS

Here we have shown that classical nucleation theory can be fit to our large volume of homogeneous nucleation rate data for water extending over a very broad range of temperature and supersaturation conditions. The fit yields physically reasonable values for the sticking coefficient when this parameter is allowed reasonable flexibilty. It is found necessary to account for the increase in water molecular density due to the finite compressibility of water.

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