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## Temperature and Supersaturation Dependent Nucleation Rates of Water by Molecular Cluster Model Calculations

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### ABSTRACT

The homogeneous nucleation process for water has been the subject of great interest, despite the fact that water droplet formation in the atmosphere occurs by heterogeneous nucleation. This is because the homogeneous nucleation process is the simplest of the nucleation processes to treat, both theoretically and experimentally, and because it is strongly dependent on, and hence can be used to illuminate, the molecular interactions and processes that are important for heterogeneous nucleation and aerosol hydration. Using a microphysical approach to nucleation, we present an extensive study of water nucleation rates for wide ranges of both temperature and supersaturation ratio. Based on the fundamental molecular properties of clusters instead of bulk properties, the microphysical approach is demonstrated to predict good agreement with measured nucleation rates over this broad range of conditions. Predicted critical sizes for nucleation are found to be relatively small, and are in the molecular cluster size regime rather than in a size regime that should be characterized by bulk values. Estimated sticking coefficient values cover the range of  $\sim 0.9$  to  $\sim 0.2$  for the temperature range considered, whereas sticking coefficient values corresponding to Becker-Doring theory suffer an unreasonably large three-orders of magnitude decrease for temperature increase from 220 K to 285 K.

### 1. Introduction

The hydration of various molecular species (embryonic stage of heterogeneous nucleation) is at the center of numerous atmospheric and environmental problems. This process occurs on the molecular scale and depends on the interactions associated with the specific molecules involved. A proper understanding of this microphysical process must involve a model which correctly accounts for the detailed molecular interactions which bind water molecules to the growing cluster. A molecular level nucleation theory has been developed and needs to be tested against accurate experimental data. The simplest nucleation process available for such a test is, of course, homogeneous nucleation of liquid water from vapor. There exist ample homogeneous nucleation data (Madonna et al. 1961; Allen and Kassner 1969; Wagner and Strey 1981; Miller et al. 1983) published for the atmospheric science community. Here, we report on the successful comparison of nucleation rates calculated via microphysical (molecular limit) methods with experiment and with those obtained from the macrophysical (bulk limit) approach, namely the classical Becker-Doring theory. This theory is known to fit water homogeneous nucle-

ation well (Pruppacher and Klett 1980), and is most frequently used for studying the nucleation rates for water.

Nucleation (phase transition) rates are sensitive to the variation of temperature and humidity (supersaturation ratio) in both homogeneous (Abraham 1974; Zetlemoyer 1969; Defay et al. 1966) and heterogeneous nucleation. Foreign nuclei (ions, molecules, soluble or insoluble particles) can serve to lower the critical supersaturation in the case of heterogeneous nucleation. In the case of heterogeneous nucleation involving hydrated ions (Castleman Jr. 1979; Castleman Jr. and Tang 1980; Chan and Mohnen 1980b; Briant and Burton 1976; and Salk (Suck) et al. 1981, 1982), it is known that ion nucleation occurs at much higher saturation ratios similar to the homogeneous nucleation process for water (Chan and Mohnen 1980a; Salk (Suck) et al. 1982). Nucleation on particles can occur at much lower supersaturations. For nucleation on planar, water-insoluble substrates, theory and experiment show reasonable agreement for critical supersaturations ( $S-1$ ) between 0.7% and 10% (Mahata and Alofs 1975; Hidy 1984). When the foreign nucleus is soluble, the vapor to liquid transformation is made complicated by the dissolution process. The particle becomes a solution droplet below 100% relative humidity, and droplet growth above 100% relative humidity becomes an activation process governed by the Kohler equation (Pruppacher and Klett 1980) rather

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than a nucleation process. The processes embodied in homogeneous nucleation theory also play a role in aerosol hydration. In their study of aerosol formation McMurry and Friedlander (1979) considered competing homogeneous and heterogeneous condensation processes. McGraw and Marlow (1983) have recently developed a generalized multistate kinetics theory of nucleation in the presence of an aerosol by extending the classical Becker-Doring homogeneous nucleation theory to include monomer and cluster removal (scavenging) mechanisms. Under high humidity conditions, collision (interaction) between water vapor (monomers and clusters) and preexisting particles will cause the formation of hydrated clusters and hydrated aerosols. The phase change of water- to liquid- or solid-phase particles, i.e., gas-to-particle conversion, depends on the concentration of water monomers and clusters, sticking probability, and the barrier height of free energy change—the same processes treated in homogeneous nucleation.

The ultimate objective of nucleation study lies in the prediction or measurement of nucleation rates. Most nucleation studies have been based on classical theories (Becker and Doring 1935; Volmer and Weber 1926; Zeldovich 1942; Abraham 1974) which assume macroscopic (bulk) properties in the assessment of formation energy for the nucleation embryos. The assignment of bulk properties to the crucially important and intrinsically microscopic nucleation embryos was questionable. For this reason, workers in this field (Lothe and Pound 1962 1966; Kikuchi 1971) developed statistical mechanical theories in order to append some microphysical terms (translational and rotational cluster energies) onto the classical approach. This hybridization has been often questioned (Reiss et al. 1968; Kikuchi 1969; Reiss 1970; Katz and Blander 1972; Reiss 1977). One way to circumvent the uncertainty of the hybridization is the development of a nucleation theory which is based on the molecular properties of the nucleating material instead of its bulk properties. The terms missing from the classical energy of formation are automatically included, and the need for "replacement" terms is precluded (Pruppacher and Klett 1980). On a computational side, Monte Carlo (Kistenmacher et al. 1974) and molecular dynamics (Briant and Burton 1974, 1976) methods have been employed to explore water cluster properties relevant to nucleation on a molecular scale. These methods (any truly molecular method) require the use of an intermolecular interaction potential suitable for an arbitrary poly-molecular aggregate, which was not available. Approximate fitted potentials were employed, and the results are therefore limited by the accuracy of the potential used. The errors introduced into water cluster results through the use of such fitted pairwise additive potentials has been graphically demonstrated (Salk et al. 1986a). Hale and Plummer (Hale and Plummer 1974a,

1974b; Plummer and Hale 1972; Plummer et al. 1976) employed a grand canonical statistical mechanics method to study the formation energy  $\Delta\Phi$  and nucleation of water clusters. Again, a realistic intermolecular interaction for water was not available. For this reason necessary information for the binding energies and vibrational frequencies of the clusters was drawn from the measured values of bulk ice force constants and the CNDO/INDO (Pople and Beveridge 1970) theory in order to construct an approximate cluster partition function. This work was self-criticized by pointing out that the resulting energy of formation incorrectly increases with temperature and that "A number of approximations have been made in our evaluation of  $\Delta\Phi$  and we view this work as an indication of the possibilities of such an approach rather than as a rigorous determination of  $\Delta\Phi$ " (Plummer and Hale 1972). Since then the failure of the quantum mechanical methods (CNDO/INDO) for water has been discussed (Thiel 1978; Salk et al. 1986b). Our present study greatly differs from the works of other researchers described above; our goal has been to pursue the objective of a molecular based nucleation model in a self-consistent manner. Thus, necessary information for the evaluation of partition functions will be deduced only from one source, namely our quantum mechanical treatment of I-MNDO (Salk et al. 1986b). This yielded the prerequisite potential surface. The importance of the application of this quantum mechanical approach and its implications to real atmospheric and environmental problems, e.g., gas-to-particle conversion and hydrated aerosols, has been discussed (Salk et al. 1986a). Next, a statistical mechanical treatment for clusters, designed to use this fundamental quantum mechanically derived information, was developed (Salk and Lutrus 1987; Lutrus and Salk 1987). Here we use these tools to calculate water cluster properties and homogeneous nucleation rates. While vapor-to-liquid homogeneous nucleation does not occur naturally in the atmosphere it does provide a needed test of our molecular-based nucleation theory.

The primary objectives of the present study are threefold: (1) comparison of our molecular cluster model (microphysical) approach with the classical theory, (2) comparison of predicted nucleation rates with experimental observation (Miller 1976; Miller et al. 1983; Wagner and Strey 1981; Hagen and Kassner 1984) for wide ranges of temperature and supersaturation ratio, and (3) deduction of temperature dependent sticking coefficient by making comparisons between theory and experiment (Miller 1976). Our objective is to compare our results with the classical theory of capillarity approximation to show that we obtain physically reasonable trends, and with experiment to show that we obtain good nucleation rate results. Classical theory is chosen since it fits water nucleation data surprisingly well (Pruppacher and Klett 1980), it is

simple to use, and illuminates trends in the data. The real strength of our theory is that it is based on a firmer microphysical foundation (interaction potential and statistical-mechanical treatment) that can be applied to heterogeneous nucleation and aerosol hydration. We seek not only homogeneous nucleation rates, but also information concerning binding energies important for studying the hydration processes of atmospherically important aerosols and heterogeneous nucleation processes involving water, including sticking coefficients. The contents of this paper are arranged as follows: in the next two sections (2 and 3), we present a statistical mechanical expression of the formation energy of clusters (or droplets) that is cast into a form readily useful for the molecular level treatment of clusters (droplets) for the homogeneous nucleation process. For convenience, our treatment will be designated as the "molecular cluster model" approach for nucleation. In section 4, we report computed results for formation energies, barrier heights, critical sizes, sticking coefficients, and nucleation rates. Section 5 is devoted to a summary of findings obtained from the present molecular cluster model approach.

This paper develops a new method for predicting the properties of small water clusters with sufficient accuracy to be useful in problems relevant to atmospheric science. The refinement of this method for application to heterogeneous nucleation is presented elsewhere (Salk and Lutrus 1988). The model has also been successfully applied to studies of the properties of a simple periodic system, linear-chain ice crystals (Choe et al. 1988).

## 2. Statistical mechanical treatment for homomolecular clusters

Earlier, we presented a statistical mechanical description of hydrated ion clusters [Salk (Suck) et al. 1981]. Here we discuss only homomolecular cluster systems. For a system of gas in which the concentration of monomer (e.g., water vapor) is dominant, the growth or decay process of homomolecular clusters can be written



where  $A_i$  represents the homomolecular cluster composed of  $i$  number of monomers.

The law of mass action for the process above is written

$$N_i/(N_{i-1}N_1) = q_i/(q_{i-1}q_1). \quad (2.2)$$

Here  $N_i$  is the total number of the homomolecular cluster  $A_i$ , and  $q_i$ , its partition function,  $N_1$  the total number of monomer and  $q_1$ , the partition function of the monomer. Applying successive substitution, the expression (2.2) leads to

$$N_i = N_1^i q_i / q_1^i. \quad (2.3)$$

The partition function of the cluster can be written in the product form,

$$q_i = \xi_i \xi_i^e. \quad (2.4)$$

Here  $\xi_i^e$  is the ground state electronic partition function and  $\xi_i$  is the partition function which represents translational, rotational and vibrational motions;  $\xi_i$  can be approximated by the product of translational ( $\xi^t$ ), rotational ( $\xi^r$ ), and vibrational ( $\xi^v$ ) partition functions,

$$\xi_i = \xi_i^t \xi_i^r \xi_i^v, \quad (2.5)$$

in the case of weak coupling. Likewise, for monomer, we write

$$q_1 = \xi_1 \xi_1^e. \quad (2.6)$$

Denoting  $E_i$  and  $E_1$  as the total electronic ground state energies of the cluster  $A_i$  and monomer  $A_1$  respectively, the substitution of (2.4) and (2.6) into (2.3) above yields

$$N_i = N_1^i (\xi_i / \xi_1^i) \exp(-\Delta E_i / kT). \quad (2.7)$$

Here  $k$  is the Boltzmann constant and  $T$ , the absolute temperature;  $\Delta E_i$  is the total binding energy or stabilization energy of the homomolecular cluster of size  $i$  at 0 K. It is given by

$$\Delta E_i = E_i - iE_1, \quad (2.8)$$

or

$$\Delta E_i = \sum_{j=1}^i \delta E_{j-1,j}. \quad (2.9)$$

Here  $\delta E_{j-1,j}$  is the difference in the total binding energy between the clusters of sizes  $j-1$  and  $j$ ,

$$\delta E_{j-1,j} = \Delta E_j - \Delta E_{j-1}. \quad (2.10)$$

We rewrite (2.7)

$$N_i = N_1 \exp[-\{\Delta E_i - kT \ln \xi_i + ikT \ln \xi_1 - (i-1)kT \ln N_1\} / kT]. \quad (2.11)$$

Dividing both sides of (2.11) above by the volume  $V$  and rewriting the resulting expression, we obtain the number concentration,

$$n_i = N_i/V = n_1 \exp[-\{\Delta E_i - kT(\ln(\xi_i/V) - i \ln(\xi_1/V)) - (i-1)kT \ln(N_1/V)\} / kT]. \quad (2.12)$$

We now introduce the equilibrium concentration  $n_1^0$  (at the saturation ratio  $S = 1$ ) and the equation of state for an ideal gas, in order to write

$$\begin{aligned} \ln(N_1/V) &= \ln(N_1/N_1^0) + \ln(N_1^0/V) \\ &= \ln S + \ln n_1^0, \end{aligned} \quad (2.13)$$

where  $N_1^0$  is the total number of monomers at  $S = 1$ . The substitution of (2.13) into (2.12) yields

$$n_i = n_1 \exp[-\{\Delta E_i - kT(\ln \xi_i' - i \ln \xi_1') - (i-1)kT(\ln S + \ln n_1^0)\}/kT], \quad (2.14)$$

where

$$\xi_i' = \xi_i/V. \quad (2.15)$$

We now cast (2.14) into the familiar form which defines the energy of formation  $\Delta\Phi_i$  (Abraham 1974),

$$n_i = n_1 \exp(-\Delta\Phi_i/kT). \quad (2.16)$$

Thus, we note that

$$\Delta\Phi_i = \Delta E_i - kT(\ln \xi_i' - i \ln \xi_1') - (i-1)kT(\ln S + \ln n_1^0), \quad (2.17)$$

or

$$\Delta\Phi_i = \Delta E_i - kT(\ln \xi_i' - i \ln \xi_1') - (i-1)kT \ln(P/kT). \quad (2.18)$$

Here  $P$  is the monomer partial or vapor pressure. The first term,  $\Delta E_i$  in (2.17) is the energy of formation of the cluster  $i$  from the  $i$  number of monomers at  $T = 0$  K. Thus, this total binding energy term is intrinsic in nature. The second term contains the change of free energy from monomer vapor to the cluster of size  $i$  due to change in the contribution of translational, rotational and internal (vibrational) degrees of freedom. The last term in (2.17) or (2.18) represents the influence of a thermodynamic intensive parameter, i.e., the partial pressure  $P$  or saturation ratio  $S$ .

### 3. Computational treatment of the energy of formation and nucleation rates for water clusters

The energy of formation  $\Delta\Phi_i$  (2.17) or (2.18) contains the contribution of the entropy and dynamic effects associated with translational, rotational, and vibrational motions. Here we discuss computation of the total binding energy  $\Delta E_i$ , and other terms that appear in (2.17). For the computation of  $\Delta E_i$  (for small water clusters up to  $i = 12$ ), we apply the effective Hamiltonian treatment discussed in the literature [Salk (Suck) and Lutrus 1987]. The empirical parameters and other details necessary for this treatment for water clusters were reported elsewhere [Salk (Suck) et al. 1986b].

The binding energy per bond is given by

$$B_i = \Delta E_i/n, \quad (3.1)$$

where  $n$  is the total number of bonds in the cluster. We find that the analytic relation

$$B_i = B_\infty(1 - i^{-\theta}) \quad (3.2)$$

fits reasonably the computed binding energies per bond

[Salk (Suck) and Lutrus 1987], with the choice of  $B_\infty = -13.4$  K cal/mol and  $\theta = 0.5$ . The value of  $B_\infty$  is the observed lattice energy of ice (Eisenber and Kauzmann 1969). The computed values values  $B_i$  are in excellent agreement with ab initio Hartree-Fock calculations (Tomoda and Kimura 1983). Using (3.1) and (3.2) above,  $\Delta E_i$  is then

$$\Delta E_i = nB_\infty(1 - i^{-\theta}). \quad (3.3)$$

Assuming that the intramolecular vibrational frequencies of the molecular clusters are close to those of the monomer (isolated molecule), we write for the second term in (2.18),

$$F_i^{v'} = -kT(\ln \xi_i^{v'} - i \ln \xi_1^{v'}) = -kT \ln \xi_i^{v'}, \quad (3.4)$$

where  $\xi_i^{v'}$  denotes the partition function for the intermolecular vibrational motion. The intermolecular normal mode vibrational frequencies are obtained by using the potential energy surface generated from the effective Hamiltonian method. Note that the weak coupling (between the various types of contributing motions) approximation used to develop Eq. (2.5) is most valid for small cluster sizes and low temperatures. At high temperatures the critical size increases, more degrees of freedom are activated, and anharmonicity becomes more significant, leading to coupling between the vibrational and rotational degrees of freedom. For this reason small cluster information is used to formulate an analytic expression for  $F_i^{v'}$ . Using the computed values of the vibrational frequencies for small clusters, we find that predicted values for (3.4) are closely fit by the expression,

$$F_i^{v'} = (i-1)[Ak - kT \ln\{1 - \exp(-B/T)\}], \quad (3.5)$$

with  $A = 1.55 \times 10^3$  K and  $B = 2.0$  K. This analytic relation exhibits proper asymptotic behavior, correctly converging to the limit of  $\xi_i^{v'} = \infty$  for  $T \rightarrow \infty$ , and of  $\xi_i^{v'} = 0$  for  $T \rightarrow 0$ . It approaches the computed value of  $F_i^{v'}$  for small clusters (e.g.,  $i = 2$ ). The predicted intermolecular normal mode vibrational frequencies for  $i = 2$  were reported elsewhere [Salk (Suck) et al. 1986b].

The rotational partition function (Abraham 1974) is computed from

$$\xi_i^r = \sqrt{\pi I_x I_y I_z} (8\pi^2 kT/h^2)^{3/2} / \eta. \quad (3.6)$$

Here  $h$  is the Planck constant,  $\eta$ , the symmetry number, and  $I_x$ ,  $I_y$  and  $I_z$  are the components of principal moments of inertia. The principal moments of inertia were computed by using the predicted equilibrium geometries of the water clusters. For large droplets (clusters) we assume that the moments of inertia are to be the same as those of spherical clusters. Indeed, the computed rotational partition functions for various structures of  $i > 6$  are found to be close to those of spherical

clusters. Thus the partition function for the spherical clusters is written

$$\xi_i^t = \sqrt{\pi} (8\pi^2 kT/h^2)^{3/2} \left[ \frac{2}{5} m \left( \frac{3m}{4\pi\rho} \right)^{2/3} \right]^{3/2} i^{5/2}, \quad (3.7)$$

where  $\rho$  is the mass density of the water droplet (computed values for  $\rho$  based on equilibrium geometries approximately  $1 \text{ g cm}^{-3}$  for sufficiently large clusters) and  $m$ , the mass of monomer.

The translational partition function is simply

$$\xi_i^t = V(2\pi mkT/h^2)^{3/2} i^{3/2}. \quad (3.8)$$

The ultimate goal of nucleation study is to evaluate the nucleation (droplet formation) rate at which gas-to-particle phase transition occurs. The nucleation rate  $J$  is given by (Abraham 1974)

$$J = \alpha \exp(-\Delta\Phi_{i^*}/kT). \quad (3.9)$$

Here  $i^*$  is the critical cluster size for which  $\Delta\Phi$  reaches a maximum;  $\alpha$  the prefactor,

$$\alpha = \beta\sigma F n_1 Z, \quad (3.10)$$

where  $\beta$  is the sticking coefficient;  $\sigma$ , the geometrical cross section of a critical size cluster;  $F = n_1 \sqrt{8kT/\pi m}$  is the monomer flux; and  $n_1$ , the concentration of monomer. Here  $Z$  is the Zeldovitch factor (Abraham 1974),

$$Z = \left( \frac{-\partial^2 \Delta\Phi_i / \partial i^2}{2\pi kT} \right)_{i=i^*}^{1/2}. \quad (3.11)$$

The insertion of (3.3), (3.5), (3.7), and (3.8) into (2.17) leads to the final form of the energy of formation,

$$\begin{aligned} \Delta\Phi_i = & nB_\infty(1 - i^{-\theta}) - kT \{ \ln(ai^{3/2}) - i \ln a \} \\ & - kT \{ \ln(bi^{5/2}) - i \ln \xi_i^t \} \\ & + (i-1)[Ak + kT \ln \{ 1 - \exp(-B/T) \}] \\ & - (i-1)kT(\ln S + \ln n_1^0), \end{aligned} \quad (3.12)$$

with  $n = i - 1$ ,  $a = (2\pi mkT/h^2)^{3/2}$  and  $b = \sqrt{\pi} (8\pi^2 kT/h^2)^{3/2} [2/5 m (3m/4\pi\rho)^{2/3}]^{3/2}$ .

The substitution of (3.12) into (3.11) yields the microscopic expression for the Zeldovitch factor,

$$Z = \frac{\sqrt{-(1/4)B_\infty(i^{*-3/2} + 3i^{*-5/2}) - 4kTi^{*-2}}}{2\pi kT}. \quad (3.13)$$

#### 4. Analysis of formation energies, nucleation rates, and sticking coefficients

In Fig. 1 we show the dimensionless formation energy,  $\Delta\Phi/kT$  for water clusters (using Eq. (3.12)) as a function of cluster size at varying temperatures for a fixed supersaturation ratio of  $S = 5$ . Despite a great discrep-

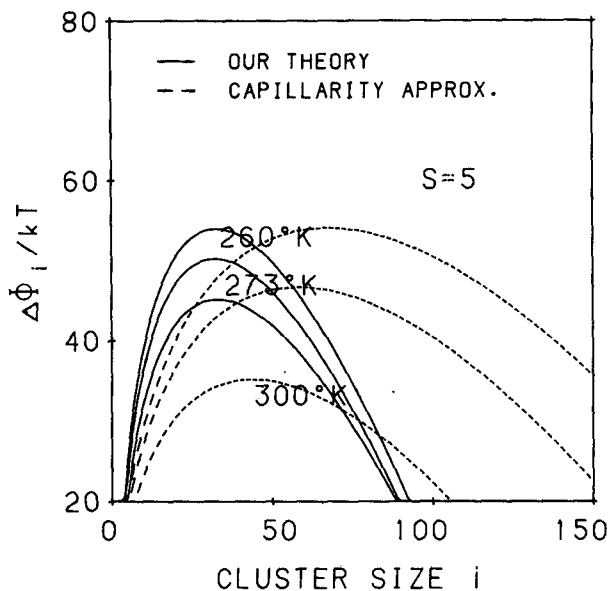


FIG. 1. Dimensionless formation energy vs cluster size at various temperatures and at a supersaturation ratio of  $S = 5$ .

ancy in the expression for the formation energy between our molecular cluster model approach and the classical capillarity approximation (Abraham 1974), we find agreement in the trend of decreasing barrier height with increasing temperature for a fixed saturation ratio, although there exist differences in the magnitudes of barrier height between the two theories. This decreasing trend with temperature is an important condition to test the validity of a theory. The decreasing trend in barrier height is the cause of the increase in observed nucleation rates with temperature (Miller et al. 1976, 1983; Wagner and Strey 1981). In Fig. 2 we show the variation of the dimensionless formation energy with supersaturation ratio at a fixed temperature of 300 K. Again, the two theories agree in the trend of decreasing barrier height and critical cluster size as supersaturation ratio increases, but not in their magnitudes. Note that the predicted critical size of clusters tends to converge to the classical limit. On the other hand, for fixed supersaturation ratio,  $S$ , and fixed monomer concentration, both theories show the propensity to decrease barrier height with increasing temperature. Also, critical cluster size is found to decrease with  $S$  in both theories.

Thus far we have examined the validity of many different aspects of the molecular cluster model, and compared them to the qualitatively reliable classical theory for water, i.e., the capillarity approximation. In all cases tested above, remarkably good agreement is found between the two vastly different theories, i.e., one based on microscopic (molecular) properties of clusters, and the other based on macroscopic (bulk) properties. This is quite encouraging in that it is now

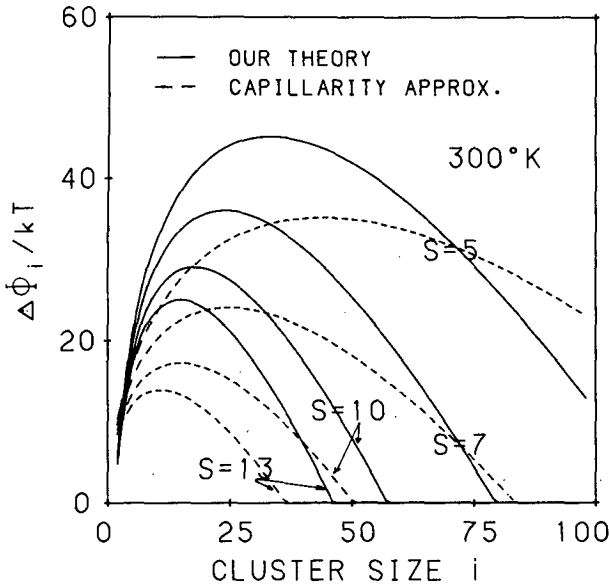


FIG. 2. Dimensionless formation energy vs critical size at various supersaturation ratios and at a given temperature of  $T = 300\text{ K}$ .

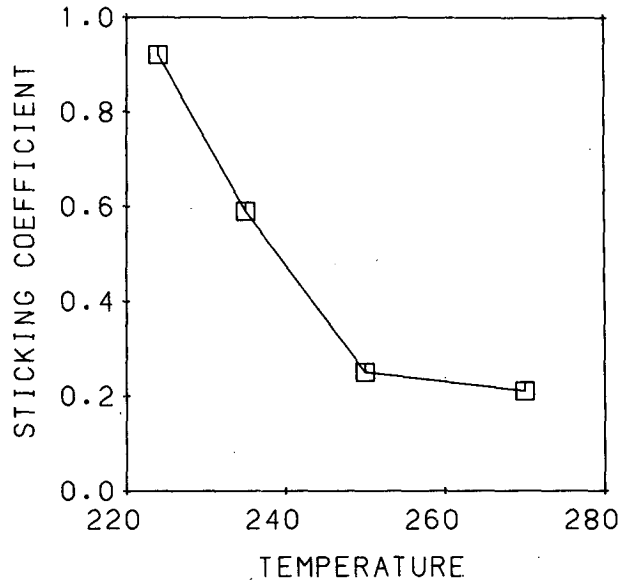


FIG. 4. Variation of sticking coefficient with temperature based on our molecular cluster model theory.

feasible to compute nucleation rates without the inclusion of commonly used bulk limit values, i.e., surface tension of bulk water instead of the more uncertain (unknown) surface tension of microclusters, which is not experimentally known.

In Fig. 3 we display the calculated nucleation rates ( $J$ ) from the molecular cluster model approach, and

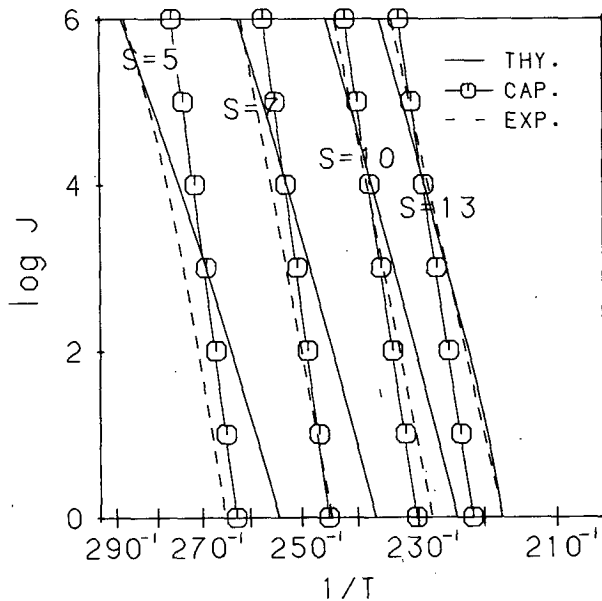


FIG. 3.  $\log J$  vs  $1/T$  at various supersaturation ratios. Solid lines are data from the present theory; solid lines with circles are from classical capillarity nucleation theory, and dashed lines are from experiment (Miller et al. 1983).

the capillarity approximation and the experimentally measured values using cloud chambers. The plotted experimental curve represents a conversion from the original data of nucleation rate vs temperature. The sticking coefficient was set to unity in both calculations. The nucleation rates are plotted in terms of  $\log J$  vs  $1/T$  for fixed supersaturation ratios. A remarkable linear relationship is found between  $\log J$  and  $1/T$  for all cases. Agreement between the two theories and experiment in the linear relationship occurred despite the strong temperature dependency of both the formation energy  $\Delta\Phi(T)$  and the prefactor  $\alpha(T)$  that appear in the nucleation rate equation (3.1).

Finally, in Fig. 4 we display estimated sticking coefficients as a function of temperature. Here  $\beta$  is obviously the ratio of observed nucleation rate to the computed value. The computed sticking coefficients should be regarded qualitative as they are obtained from the average of this ratio for a given domain of temperature at each supersaturation ratio. The salient feature is that the predicted sticking coefficient is found to decrease with temperature. Further, it shows a decrease from 0.9 to 0.2 for a temperature increase from  $225\text{ K}$  to  $270\text{ K}$ . On the other hand, the classical Becker-Doring theory predicts a somewhat unrealistic change, showing a three-order of magnitude decrease for the same range of temperature increase (Salk et al. 1988), although not shown here.

### 5. Summary

In the present study we have demonstrated by the example of water vapor-to-liquid nucleation that it is

feasible to compute nucleation rates without relying upon bulk properties (e.g., bulk surface tension) to describe the microscopic nucleation embryo water cluster  $(\text{H}_2\text{O})_i$ , containing  $i$  water molecules. For instance, note from Fig. 1 that even the capillarity approximation predicts a critical size  $l = 50$  for  $S = 5$  and  $T = 300$  K. This size cluster is too small to be described by bulk properties. Despite this concern, it is considered that the classical Becker–Doring theory, which employs the capillarity approximation for the formation energy of water, is qualitatively correct (in the temperature dependency of nucleation rates at a fixed supersaturation ratio).

From the present cluster model approach to nucleation, the following summary is in order:

1) a linear relationship is observed between  $\log J$  and  $1/T$  in experiment, in the present molecular cluster model theory, and in Becker–Doring theory. This provides a compact form for nucleation rate data presentation and analysis;

2) both the microscopic molecular cluster model and macroscopic Becker–Doring theories correctly yield decreasing nucleation barrier heights with increasing temperature for fixed supersaturation ratio, thus predicting consistency with the observed increase in nucleation rate with temperature; and

3) the present model predicts a realistic decrease in sticking coefficient with increasing temperature in contrast to the classical Becker–Doring theory.

Finally, in view of the satisfactory results obtained by the application of the present molecular cluster model to homogeneous nucleation theory, it is highly promising to apply the molecular level treatment to heterogeneous nucleation, and thereby properly take into account the molecular interaction between the surface defect sites (nucleation sites) of foreign particles and the nucleating water molecules (vapor). Such a study will soon be underway. In our molecular cluster model approach for nucleation, we have not introduced coupling between the vibrational and rotational degrees of freedom. Thus this can be regarded as a quasi-rigid model in that the vibrational degrees of freedom are introduced by satisfying the high and low temperature limits including the small cluster size limit. It will be of great interest to examine the effect of an anharmonicity correction particularly for computable small clusters (e.g., dimer) and a ro-vibrational coupling correction which is not readily computable.

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