Physics Faculty Research & Creative Works   Physics

01 Jan 1982

A Study of the Critical Cluster Size for Water Monolayer Clusters on a Model AgI Basal Substrate

Richard C. Ward

Barbara N. Hale
Missouri University of Science and Technology, bhale@mst.edu

Sergio Terrazas

A study of the critical cluster size for water monolayer clusters on a model AgI basal substrate[a]

Richard C. Ward, Barbara N. Hale, and Sergio Terrazas

Department of Physics and Graduate Center for Cloud Physics Research, University of Missouri-Rolla, Rolla, Missouri 65401

We present a formalism and estimate a critical cluster size for water monolayer formation on a (rigid) model AgI basal substrate. The formalism is modified from that developed for vapor clusters [B. N. Hale and R. C. Ward, J. Stat. Phys. **28**, 487 (1982)] and uses a Metropolis Monte Carlo method developed by Squire and Hoover [J. Chem. Phys. **50**, 701 (1969)] to determine (Helmholtz) free energy differences for clusters containing n and $n - 1$ molecules. Calculations for clusters of $n = 1, 2, 3, 4, 6$, and 24 water molecules on a model AgI basal face at 265 K are used in a statistical mechanical formalism which assumes that the adsorbed clusters form a mixture of noninteracting ideal gases; the adsorbed monomer concentration is related to the vapor concentration at the same temperature. At water saturation and 265 K a critical cluster size of $n^* \simeq 3$ molecules and a steady state nucleation rate (for monolayer formation) of 10^{23} cm^{-2} s^{-1} is predicted. The implications of this for ice nucleation on the model AgI substrate under atmospheric conditions are discussed.

I. INTRODUCTION

The motivation for this work is to study the critical size of embryos of the new phase (liquid or solid) forming on a substrate exposed to the vapor. The critical cluster has equal probability of gaining or losing one molecule and within the framework of steady state nucleation rate theory can be used to estimate the nucleation rate.[1,2] Recently, a technique,[3] originally developed by Bennett,[4] has been applied to an estimate of the critical cluster size n^* for the homogeneous nucleation of argon from the vapor at 60 K—modeled with the Lennard-Jones 6-12 potential. In the present work we use a second technique developed by Squire and Hoover[5,6] to approximate the critical cluster size for the nucleation of a water monolayer on a model substrate. A H$_2$O-substrate potential[7,8] and the H$_2$O-H$_2$O central force potentials of Stillinger and Rahman[9] are used to model the equilibrium properties of small monolayer water clusters on the (iodine exposed) basal face of hexagonal AgI. The water molecules are assumed to be rigid but otherwise are allowed to translate and rotate in a fully three dimensional system as they adsorb on the rigid AgI surface. The statistical mechanical formalism assumes that the adsorbed clusters form a mixture of noninteracting ideal gases with each gas consisting of clusters with n molecules. The canonical partition function for the adsorbed cluster includes the H$_2$O-AgI interaction potential energy.[10] The monomer concentration on the substrate is related to the monomer concentration in the vapor and areal concentrations of adsorbed clusters are written in terms of the adsorbed monomer concentration. The application of this method to water monolayer formation on the model AgI substrate predicts a critical cluster size of three molecules at 265 K and water saturation. (In this case, water saturation implies a water vapor concentration at equilibrium with a liquid water surface at 265 K.) The corresponding

steady state nucleation rate for water monolayer formation on the model substrate is $\simeq 10^{23}$ cm^{-2} s^{-1}.

The formalism for obtaining the adsorbed cluster concentrations and the critical cluster size is given in Sec. II. The model system and the Monte Carlo technique are described in Sec. III and the results of the calculations at 265 K and water saturation are presented in Sec. IV. Comments and conclusions are given in Sec. V.

II. FORMALISM FOR ESTIMATING CRITICAL CLUSTER SIZE

In the classical steady state nucleation rate formalism, the nucleation rate J for heterogeneous nucleation is given by[11]

$$J = \left\{ \sum_{n=1}^{n > n^*} \left[\frac{1}{\Gamma_n N_n^s / A} \right] \right\}^{-1}, \tag{1}$$

where Γ_n is the rate at which particles attach to a cluster of size n and N_n^s is the number of clusters of n molecules on the substrate in the area A. To obtain an expression for N_n^s we assume: (i) that the adsorbed clusters form a mixture of noninteracting ideal gases with each gas consisting of clusters of n molecules; (ii) that the number of clusters of n molecules on the rigid substrate N_n^s is given by

$$N_n^s = [N_1^s / Z^s(1)]^n Z^s(n), \tag{2}$$

where $Z^s(n)$ is the canonical partition function for the n cluster on the substrate and includes the substrate cluster interaction potential energy; (iii) that $Z^s(n)$ is related to the configurational integral $Q^s(n)$ by

$$Z^s(n) = \Lambda^n \Lambda_R^n (V 8 \pi^2)^n \, Q^s(n)/n! \, . \tag{3}$$

The $\Lambda = (2 \pi m k T / h^2)^{3/2}$, $\Lambda_R = \Lambda (I_1 I_2 I_3 / 4 m^3)^{1/2}$, m is the mass of the water molecule, I_i is the ith principal moment of inertia of the rigid molecule, k is Boltzmann's constant and h is Plank's constant. The configurational integral is defined as

---

$$Q^s(n) = (V8\pi^2)^{-n} \int\int \cdots \int \exp[- U(\Omega_1, \Omega_2, \ldots, \Omega_n)/kT]$$

$$\times \prod_{i=1}^{n} d\bar{r}_i \sin\theta_i d\theta_i d\phi_i d\psi_i \ . \tag{4}$$

The U is the interaction potential, V is the volume, and $\Omega_i = (\bar{r}_i, \theta_i, \phi_i, \psi_i)$, where $\bar{r}_i$ is the center of mass position vector and θ_i, ϕ_i, and ψ_i are the Euler angles of the ith rigid H_2O molecule. Using the superscript v to designate the vapor state, we further assume

$$N_1^s = N_1^v Z^s(1)/Z^v(1) \ . \tag{5}$$

Thus, from Eqs. (2)-(5) and the definition $C(n)$ $\equiv \ln[Q^s(n)/Q^s(n-1)]$, we have,

$$N_n^s = N_1^s \exp - \left[-\sum_{i=2}^{n} C(i) + (n-1)\ln\frac{n}{N_1^v} + \ln\frac{n!}{n^{n-1}} \right] \tag{6}$$

$$\equiv N_1^s \exp - [\Delta w^s(n)] \ . \tag{7}$$

In deriving Eq. (6) we have used

$$C(1) \equiv \ln[Q^s(1)/Q^v(1)] = \ln Q^s(1) \ .$$

Values of $C(n)$ are calculated using the technique of Squire and Hoover[5,6] or the technique of Bennett.[4]

Finally, the critical cluster size can be estimated by approximating the derivative of $\Delta w^s(n)$ as the difference in the free energy of formation between the n and $n-1$ clusters

$$\frac{d\Delta w^s(n)}{dn} \cong \Delta w^s(n) - \Delta w^s(n-1) = -C(n) + \ln\frac{n}{N_1^v} \ . \tag{8}$$

In the continuous variable theory, the critical cluster size n^* is the value of n for which $d\Delta w^s(n)/dn = 0$. Using the supersaturation ratio, $S = N_1^v/N_1^{v0}$ (where N_1^{v0} is the number of water monomers at equilibrium with a surface of liquid water), we obtain the following formula estimating the critical cluster size $n = n^*$:

$$C(n^*) = \ln\frac{n/V}{N_1^{v0}/V} - \ln S \ . \tag{9}$$

The n/V is the density used in the Monte Carlo simulation of the n cluster and in the present calculations is held fixed for all cluster sizes.

III. THE MODEL SYSTEM AND THE TECHNIQUES USED TO OBTAIN $C(n)$

The model sytem under study is a monolayer cluster of n water molecules on the iodine exposed basal AgI substrate. The water molecules interact via the Stillinger–Rahman[9] central force pair potentials. We assume the molecules are rigid with an OH distance of 0.96 Å, and an HOH angle of 104.45°. The H_2O-basal AgI potential is that developed by Hale and Kiefer[7] with the effective substrate ion charge equal to ±0.4 e; e is the electronic charge. The substrate is rigid and a linear interpolation of the substrate potential from four grids is used.[8] This greatly increases the speed of the calculations.

The water molecules are constrained to a half sphere as shown in Fig. 1. This example shows $n = 24$ molecules at temperature $T = 265$ K after 225 000 Monte Carlo steps. The radius of the constraining volume for each
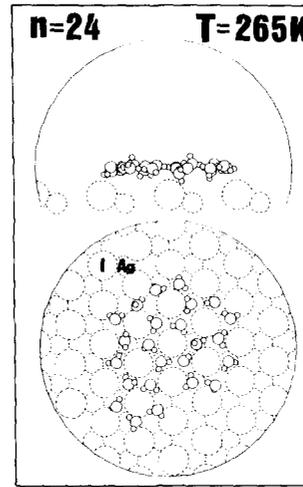

FIG. 1. Snapshot of a monolayer cluster with 24 water molecules on the model basal AgI substrate at $T = 265$ K after 225 000 Monte Carlo steps. The constraining volume (a half sphere) has a radius of 15 Å.

n cluster is determined by the constant density n/V $= 3.4 \times 10^{21}$ molecules/cm^3. The corresponding constraining volume per molecule is $\simeq 10V_b$, where V_b is the volume per molecule in the bulk liquid. The constraining volume has a negligible effect on the Metropolis Monte Carlo averages calculated for total cluster binding energies.

The technique of Squire and Hoover[5] is used to obtain values of $C(n)$. In this technique, a Monte Carlo average is performed on an ensemble consisting of the water molecule cluster and the rigid substrate with the interaction potential of one water molecule (the probe molecule) reduced by a factor $0 \leq \lambda \leq 1$. Thus the total interaction potential energy of the system is:

$$U = U_0 + \lambda \Delta U \ , \tag{10}$$

where U_0 is the potential energy of the $n-1$ molecules on the substrate and ΔU is the interaction potential energy of the probe molecule. Squire and Hoover[5] and Abraham et al.[6] show that $C(n)$ can be obtained from

$$C(n) = -\int_0^1 \frac{\langle \Delta U(\lambda) \rangle}{kT} d\lambda \ , \tag{11}$$

where $\langle \Delta U(\lambda) \rangle$ is a Metropolis Monte Carlo average[12] of $\Delta U(\lambda)$ for a cluster of n molecules with total interaction potential U given by Eq. (10). Both references point out the advantages of modifying this integration to reduce errors from the large fluctuations in $\langle \Delta U(\lambda) \rangle$ as λ approaches 0. For a substrate potential which is the sum of Lennard-Jones r^{-12} terms one expects $U(r) \simeq r^{-9}$ as $r \to 0$. In this case the limit $\langle \Delta U \rangle \lambda^{2/3} = $ constant as $\lambda \to 0$ and we use the following reformulation of Eq. (11):

$$C(n) = -3\int_0^1 \lambda^{2/3} \frac{\langle \Delta U(\lambda) \rangle}{kT} d(\lambda^{1/3}) \ . \tag{12}$$

Figure 2 shows a plot of $\lambda^{2/3}\langle \Delta U \rangle$ vs $\lambda^{1/3}$ for $n = 6$ at $T = 265$ K. This is a typical plot of the function for values of $n \leq 24$. The uncertainties are obtained from the root mean square standard deviations over 50 000 Monte Carlo step intervals. The fluctuations in the Monte Carlo averages for $\langle \Delta U \rangle$ become larger as λ approaches zero. In addition, as n becomes larger ($n > 24$) the positive contribution to the integral grows in
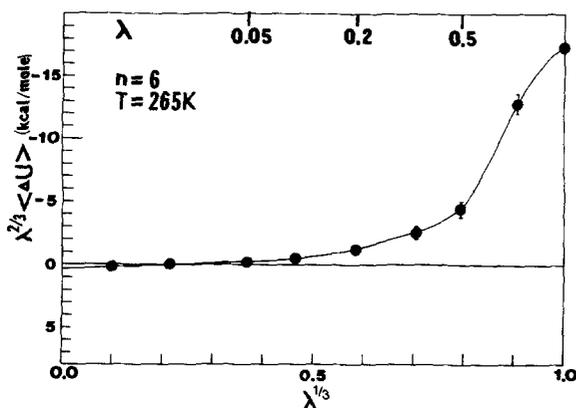
FIG. 2. Plot of $\lambda^{2/3} \langle \Delta U \rangle$ vs $\lambda^{1/3}$ for a monolayer cluster of $n = 6$ water molecules on the model AgI basal substrate at 265 K. $C(6)$ is $-3/(kT)$ times the area under the curve drawn through the data points ($\blacklozenge$).

magnitude and an accurate result for $C(n)$ requires extensive Monte Carlo averaging. For the cluster sizes used in these calculations, however, the positive contribution is $\leq 2.0\%$ of the total area.

The technique of Bennett[4] is used to check the value of C obtained for $n = 6$ molecules. The application of this technique has been discussed.[5] It differs from that of Squire and Hoover in that two ensembles of particles are required; one ensemble uses $\lambda = 1$ and the other ensemble uses a value of $\lambda = 0.1$. The C value obtained from the Bennett technique is $-3/(kT)$ times the area under the curve in Fig. 2 from $\lambda = 1$ to $\lambda = 0.1$. To obtain the correct value of C one must add the contribution from the area under the curve below $\lambda = 0.1$. Note that in the case of $n = 6$ the latter area is approximately zero and the correction to the Bennett technique result is negligible.

IV. RESULTS

Values of $C(n)$ for $n = 1, 2, 3, 4, 6$, and 24 water molecule clusters on the model AgI basal substrate are obtained at $T = 265$ K using the technique of Squire and Hoover. The results are shown in Fig. 3 where $C(n)$ is plotted vs $n^{-1/2}$. We plot $C(n)$ in this manner in order to compare the results to a model for $\Delta w^s(n)$ discussed below. The uncertainties on this curve indicate the range of $C(n)$ obtained from the maximum and minimum areas under the plot of $\lambda^{2/3} \langle \Delta U \rangle$ vs $\lambda^{1/3}$. The Bennett technique[4] ($n = 6$ and $\lambda = 0.1$) gives $C = 18 \pm 2$ and is consistent with the value $C = 17 \pm 1$ obtained using the technique of Squire and Hoover.

The solid line in Fig. 3 corresponds to $\ln[(n/V)/(N_1^{v0}/V)] = 10.5$, and its intersection with the data indicates an approximate value of $n^* = 3$ at $S = 1$ [see Eq. (9)]. A value of $P_0 = (N_1^{v0}/V)kT = 2.5$ mm Hg is used to determine N_1^{v0}/V.[13] Some preliminary calculations at $T = 298$ K and $S = 1$ also indicate a critical cluster size of $n^* \simeq 3$. Thus, at water saturation and for $265 \leq T \leq$ ≤ 298 K, the critical cluster size is small and apparently insensitive to temperature.

Using the values of $C(n)$ one can predict an approximate steady state nucleation rate for monolayer formation from Eqs. (1) and (6). To estimate N_1^s/A, we rewrite Eq. (5) as

$$N_1^s/A = S(N_1^{v0}/V)(V/A)_{n=1} \exp C(1) . \tag{13}$$

The ratio of the constraining volume to the constraining area V/A is 5.5×10^{-8} cm for $n = 1$, N_1^{v0}/V is 9.1×10^{16} cm^{-3}, and $C(1)$ is 10. Thus, for $S = 1$, Eq. (13) gives $N_1^s/A \simeq 10^{14}$ cm^{-2}. The rate at which molecules attach to the n cluster is $\Gamma_n = 2\pi\beta a_0 n^{1/2}(N_1^s/A)$, where $\beta N_1^s/A$ is the flux per unit length of (diffusing, adsorbed) H$_2$O monomers onto the cluster perimeter. The a_0 is approximated by $(\pi\rho_s)^{-1/2}$, where $\rho_s \simeq 10^{15}$ cm^{-2} is a typical molecular density in the monolayer clusters. Using a typical jump distance of $d = 3$ Å, a diffusion barrier of 2.5 kcal/mol,[7] and a typical (adsorbed) molecular vibrational frequency of 6×10^{12} s^{-1} a surface diffusion coefficient, $D_s = 4d\beta \simeq 5 \times 10^{-5}$ cm^{-2}s^{-1}, can be approximated. Substitution of these numbers and values of N_n^s [from Eq. (6)] into Eq. (1) give a steady state nucleation rate for monolayer formation on the model substrate of $J \simeq 10^{23}$ cm^{-2}s^{-1}. This large nucleation rate at water saturation ($S = 1$) indicates that the water monolayer forms rapidly and suggests that the nucleation of ice (or amorphous solid water) on the model substrate occurs after the deposition of one or more water layers.

It is interesting to estimate an effective line tension for the adsorbed clusters and to use the present results to estimate a value for the Helmholtz free energy per molecule in an adsorbed layer. A simple classical cluster model in two dimensions for $\Delta w^s(n)$ is $2\pi a_0 \gamma n^{1/2}/kT$ $- n \ln S + n(f^s - \mu)$ where γ is an effective line tension $e^{-\mu} = Z^v(1)/N_1^{v0}$ and f^s is the free energy per molecule in a large ($n \to \infty$) cluster. Using this model for $\Delta w^s(n)$ and Eq. (8) $C(n)$ is predicted to decrease linearly with $n^{-1/2}$ and to provide an estimate of f^s as $n \to \infty$. The present calculations give an effective line tension of $\simeq 10^{-5}$ erg/cm and a value of $\simeq -40 \pm 5$ for f^s. This approximate value for γ is consistent with line tensions obtained for
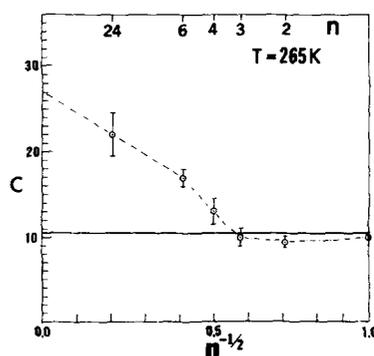

FIG. 3. C vs $n^{-1/2}$ for $T = 265$ K. The uncertainties indicate the range in C obtained from the maximum and minimum areas under the curves indicated in Eq. (12). The solid line shows $\ln(n/N_1^{v0}) = 10.5$. Its intersections with the data for $C(n)$ locates an approximate value of $n^* = 3$. The dashed line for $n > 6$ indicates a possible straight line fit to the data for large clusters; the dot—dashed line guides the eye through the data points for small values of n.

other substances.[14] However, as can be seen in Fig. 3, γ (related to the slope of C vs $n^{-1/3}$) and f^* (related to the intercept at $n^{-1/3} = 0$) are subject to the uncertainties in C for large n. A more extensive study could improve these estimates or provide an argument for a revised classical model for $\Delta w^*(n)$. Since we have been primarily concerned with the critical cluster size (which we find to be small) we have not pursued extensive calculations of C for $n > 6$.

V. COMMENTS AND CONCLUSIONS

In this paper we have used the (Metropolis Monte Carlo) method of Squire and Hoover,[5] to calculate $\ln\{Q^*(n)/Q^*(n-1)\}$ for n molecule water cluster adsorbed on a model (rigid) AgI basal substrate at 265 K. Results for $n = 1, 2, 3, 4, 6$, and 24 are applied to a modified technique developed for vapor clusters,[3] and used to estimate a critical adsorbed cluster size $n^* = 3$ at 265 K and $S = 1$. Preliminary work at 298 K indicates that the critical cluster size is insensitive to temperature in the range $265 \leq T \leq 298$ K. However, from Eq. (9) and Fig. 3, one can see that the critical cluster size for monolayer formation is highly supersaturation dependent. At $S = 1$ and $T = 265$ K the predicted steady state nucleation rate for monolayer formation is $\simeq 10^{23}$ cm^{-2} s^{-1}, with a monomer concentration of $\simeq 10^{14}$ cm^{-2}. The large nucleation rate at water saturation implies that the adsorbed water monolayer forms rapidly and suggests that questions concerning ice nucleation on the model substrate should be addressed to the structure and stability of two or more water layers. We are presently studying two to eight water layers on the model substrate using periodic boundary conditions for the adsorbed

layers. Also in progress are studies of critical cluster size for water adsorbed on a featureless substrate and on the model AgI surface with modified lattice parameters. The long range goals of this work have been to examine the ice nucleating efficiency of substrates—with application to processes involved in atmospheric ice formation.

[1]N. H. Fletcher, *The Physics of Rainclouds* (Cambridge University, Cambridge, 1969), Chap. 3.

[2]J. J. Burton and C. L. Briant, in *Nucleation Phenomena*, edited by A. C. Zettlemoyer (Elsevier, New York, 1977), p. 131.

[3]B. N. Hale and R. C. Ward, J. Stat. Phys. **28**, 487 (1982).

[4]C. H. Bennett, J. Comput. Phys. **22**, 245 (1976).

[5]D. R. Squire and W. G. Hoover, J. Chem. Phys. **50**, 701 (1969).

[6]F. F. Abraham, M. R. Mruzik, and G. Marshall Pound, Faraday Discuss. Chem. Soc. **61**, 34 (1976); M. Mruzik, F. F. Abraham, and D. E. Schrieber, J. Chem. Phys. **64**, 481 (1976).

[7]B. N. Hale and J. Kiefer, J. Chem. Phys. **73**, 923 (1980).

[8]R. C. Ward, J. Holdman, and B. N. Hale, J. Chem. Phys. **77**, 3198 (1982).

[9]F. Stillinger and A. Rahman, J. Chem. Phys. **68**, 666 (1978).

[10]B. H. Hale and J. Kiefer, J. Stat. Phys. **12**, 437 (1975).

[11]F. F. Abraham, *Homogeneous Nucleation Theory* (Academic, New York, 1974), Chap. 5; N. Garcia and J. M. Soler Torroja, Phys. Rev. Lett. **47**, 186 (1981).

[12]N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[13]B. Smith, Department of Chemical Engineering, Washington, University, St. Louis, Missouri (private communication).

[14]Navascueś and P. Tarazone, J. Chem. Phys. **75**, 2441 (1981).