Development of a Water Cluster Evaporation Model using Molecular Dynamics

Arnaud Borner, Zheng Li, Deborah A. Levin.

Department of Aerospace Engineering, The Pennsylvania State University, University Park, PA 16802

Abstract. A Monte Carlo simulation using the SPC potential model has been used to determine the potential energy and constant volume heat capacity of water dimers and trimers. It was found that the potential energy almost follows a linear trend versus temperature. The heat capacity fluctuates around 10 cal/mol/K and reaches a maximum around 220 K for the dimer and 240 K for the trimer. The Molecular Dynamics simulation has been used to evaporate water dimers and trimers. The cumulative evaporation probabilities were calculated for temperatures ranging from 240 K to 300 K. The cluster evaporation rates were calculated using Weerashinge's equation, and they were compared with the UDT rates. Both values were found to be in good agreement. Finally, vibrational frequencies were computed.

INTRODUCTION

The study of evaporation is important because it helps predict the condensation phenomenon. Condensation in free expansion plumes has been studied for the past several decades and has a number of important aerospace applications. Expansion plumes from thrusters in rarefied flows regime can condensate and generate problems for spacecrafts, such as solar panels contamination or optical systems contamination. Condesation flows have been studied in numerical and experimental approaches for many years. Recent interest has grown in developing a particle based direct simulation Monte Carlo (DSMC) method [1] capable of modelling homogeneous condensation in the translational and rarefied flow regimes. DSMC has been used extensively and succesfully to model the processes of cluster formation and evolution in supersonic jets [2]. Molecular dynamics (MD) simulations can be used to investigate the kinetics of clusters formation and calculate many key parameters for argon or water clusters. In this work, we propose first to use a Monte Carlo Canonical Ensemble (MCCE) simulation to calculate the potential energy and heat capacity of water dimers and trimers at different temperatures. Then, a MD simulation models the evaporation of water dimers and trimers and calculates the evaporation rate, which can be compared to the value calculated using the Unimolecular Dissociation Theory (UDT) [3].

CALCULATION OF WATER DIMER AND TRIMER HEAT CAPACITIES

A Molecular Dynamics study of $(H_2O)_{n=2,3,4,6,8}$ clusters was conducted by Guvenc and Anderson [4]. Melting temperature was plotted as a function of cluster size, and the ones for the dimer and the tetramer closely ressemble the bulk melting temperature, while those for the other sizes were considerably lower. Pedulla and Jordan [5] studied the melting behavior of $(H_2O)_6$ and $(H_2O)_8$ water clusters. The location and sharpness of the melting transition were investigated for different potential models. It was found that the position of the peak in the heat capacity curve was quite sensitive to the specific model potential.

The interactions among water molecules are dominated by dipole interactions. One effective way to describe such interactions is to consider three point charges, one on each atom. The SPC model[6] consists of a triangular water model with an OH distance of 1 Å (compared to the true bond length of 0.9584 Å), with point charges on the oxygen and hydrogen positions of -0.82 and +0.41 e (electronic charge units), respectively. The corresponding potential is a combination of Lennard-Jones interactions between the the oxygen atoms of each water molecule,

$$U^{\mathrm{LJ}}(r) = 4\varepsilon^{\mathrm{LJ}}\left[\left(\frac{\sigma^{\mathrm{LJ}}}{r}\right)^{12} - \left(\frac{\sigma^{\mathrm{LJ}}}{r}\right)^{6}\right] \tag{1}$$

with the parameters of $\sigma^{LJ} = 3.166$ Å, $\varepsilon^{LJ} = 0.65$ kJ/mol and the Coulomb potential between all the atoms,

$$U_{ij}^{\text{Coulomb}}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{2}$$

where q_i, q_j are the charges of O or H atoms and ε_0 is the permittivity of free space.

For cluster-monomer interactions, the initial separations between molecules inside a cluster affects the cluster potential energy. Since those initial positions are randomly generated, there will be a lot of different possible initial energies. Therefore a high number of initial configurations (between 400 and 4000) is chosen to reduce the statistical error. In order to prepare the initial position configurations for clusters, the Monte Carlo canonical ensemble simulation method is used. In this approach, a circular domain is setup with a known radius, R_i, which depends on the cluster size, i, and is typically 2.8 Å. The initial molecules (for example, 2 molecules for a dimer) then are randomly put in the spherical domain and one of the molecules is moved a small distance from its original point . The system potential energy is calculated based on the SPC model and designated as, U_o. The system is allowed to evolve for a large number of steps and for each time step, one of the molecules is randomly moved in the sphere and the new energy U_n is calculated. The move is accepted with probability, $P_a = \min(1, \exp(-[U_n - U_o])/kT)$, where T is the temperature and k is Boltzmann's constant. After 10,000 steps, the system is assumed to be in equilibrium and an the configuration with the lowest energy is saved to a file every 100 steps. The so-called 'baby steps', which are typically 0.43 Å ensure a higher number of configurations are accepted. The molecule is also rotated with a small angle, which is typically 1ř change compared to the angle at the previous step. The system is run for 1,000,000 timesteps in total. Six of those independents Monte Carlo cycles were computed at every temperature, the difference being the initial seed used for the random number generator.

The potential energy of the system is calculated by summing the SPC potential due to each molecule in the cluster. Then it is normalized by dividing by the number of molecules in the cluster. The constant volume heat capacity is computed as $C_v = \frac{<U^2> - <U>^2}{3RT^2} + 3R$, where R is the ideal gas constant. The standard deviations are based on the 6 independent cycles at each temperature. Figure 1 (left) shows the the potential energy of a water molecule in a dimer as a function of the ensemble temperature. It can be seen that the potential energy increases with the temperaure, almost with a linear trend. Figure 1 (right) shows the constant volume heat capacity as a function of the temperature. Even though the value of C_v fluctuates with respect to the temperature, the general trend that can be seen from this plot is that there is a peak around 220 K. This point where the heat capacity reaches its maximum is known as the melting point. This value is relatively close to the one found by Guvenc and Anderson [4], 275 K, for a dimer. The heat capacity fluctuates around 10 $\frac{cal}{mol-K}$, while the one measured for liquid water at 300 K is about 18 $\frac{cal}{mol-K}$. The results for the water trimer are shown in Figure 2. The same linear trend as for the dimer can be seen again in the case of the trimer. The values of the potential energy are about double those of the dimer. The trend for the heat capacity of the trimer is also similar to the one of the dimer. The heat capacity fluctuates around 10 $\frac{cal}{mol-K}$ and is seen to have a melting point around 240 K.
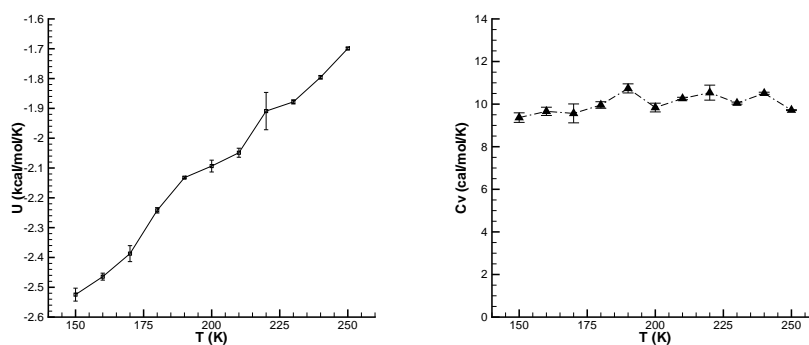
FIGURE 1. (Left) Potential energy of a water dimer cluster divided by the number of water monomers (2) for different cluster temperatures. The standard deviations are computed from six 2-million cycles of calculations. (Right) Constant volume heat capacity of a water molecule inside a dimer for different cluster temperatures (heat capacity per molecule).

Those results from MCCE simulations can now be used as starting points to Molecular Dynamics calculations which to study the evaporation of water clusters.
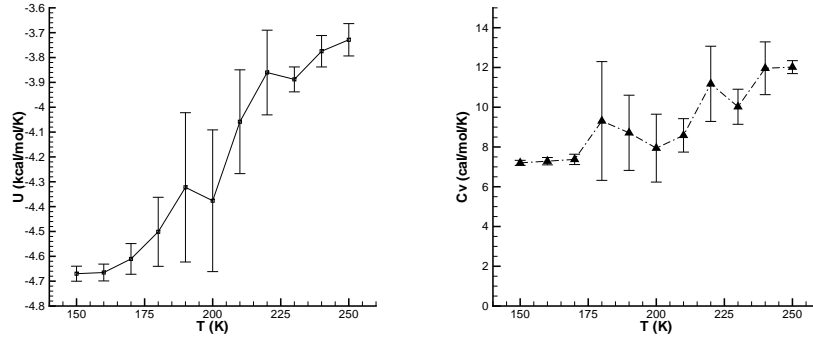
FIGURE 2. (Left) Potential energy of a water trimer cluster divided by the number of water monomers (3) for different cluster temperatures. The standard deviations are computed from six 1-million cycles calculations. (Right) Constant volume heat capacity of a water molecule inside a trimer for different cluster temperatures (heat capacity per molecule).

MOLECULAR DYNAMICS CLUSTER EVAPORATION MODEL

MD is a computer simulation technique which allows one to predict the time evolution of a system interacting particles, e.g. atoms or molecules. Usually, each real atom is modeled as a point-sized particle that interacts with other particles through a defined potential. Here, the traditional Lennard-Jones 6-12 is chosen again[7].

Initial clusters configurations were generated using the MCCE code. However, this method only provides atomic positions, and for the MD trajectory calculation every molecule has to be given an initial velocity, i.e. an initial kinetic energy. It is usual to chose random velocities, with the magnitudes conforming to the required temperature, corrected so that there is no overall momentum for the cluster. However, in this case, each O and H atom is treated separately in the MD simulation and it is not possible to assign random velocities to them because of the rigid bond assumption. The solution is therefore to distribute the total kinetic energy of the cluster randomly among the molecules. The total kinetic energy of a cluster is defined by $E_{c,kin} = 3nk_BT_c$, where n is the cluster size, k_B is the Boltzmann constant and T_c is the cluster temperature. The kinetic energy of the cluster can be separated into the contribution that comes from the translation of the cluster and the other one from the rotation of the cluster. Both modes are assumed to be equal to half of $E_{c,kin}$. Note that this model does not take into account vibrations of the molecules. For each water molecule, it is possible to calculate the center of mass velocity from the translational part of the kinetic energy since,

$$E_{c,kin,trans}^i = \frac{m_{H_2O}}{2} \sum_{k=1}^{3} v_{CM,k}^{2,i} \qquad (3)$$

where the superscript i represent the ith molecule in the cluster, "CM" is the center of mass of the water molecule and m_{H_2O} is the mass of a water molecule. The rotational part of the kinetic energy is used to calculate the angular velocity of each water molecule in the cluster since, $E_{c,kin,rot}^i = \frac{1}{2}\omega \mathbf{I} \omega$, where ω is the angular velocity vector of a water molecule about its center of mass and $\mathbf{I}$ is the inertia tensor. The coefficients of the inertia tensor are calculated from the position of the O and H atoms in the center of mass frame and the mass of those atoms. Finally, it is possible to calculate the velocity of each atom by using the following equation, $\mathbf{v_i} = \mathbf{v_{CM}} + \omega \times \mathbf{r_{i,CM}}$, where $\mathbf{r_{i,CM}}$ is the position of the ith atom in the cluster in the center of mass of the corresponding water molecule frame. The last step in assigning the cluster an initial kinetic energy is to set the cluster center of mass velocity to zero to ensure the cluster stays at fixed location until evaporation occurs. The cluster internal energy is $E_{c,int} = E_{c,kin} + E_{c,pot}$, where $E_{c,pot}$ is the cluster potential energy, $E_{c,pot} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} U_{i,j}$, where $U_{i,j}$ is the potential between molecules i and j inside the cluster coming from the SPC model. A single cluster is used in the MD evaporation simulation for each case of fixed internal energy. A typical time step of 10^{-15} s is chosen in this work.

To study the evaporation process, a simple cluster is assumed to be at the center of a thermal box isolated without energy exchange with the walls. Before the evaporation process occurs, the cluster constantly experiences internal energy exchange between kinetic energy, $E_{c,kin}$ and potential energy, $E_{c,pot}$, modes related to intermolecular

TABLE 1. Water dimer and trimer dissociation energies

Cluster size	H_2O E_{evap} MD, eV	H_2O E_{evap} Borner[8], eV
2	0.091	0.153
3	0.135	0.354

interactions. The cluster binding energy, $E_{b,n}$, is defined as the absolute value of the cluster internal potential energy. The dissociation energy of a single molecule evaporated from a cluster, $E_{d,n}$, can be defined as the difference in the cluster energy before and after the evaporation process, $E_{d,n} = E_{b,n} - E_{b,n-1}$. The binding energy can be simply sampled from the MD simulations. Table 1 shows the values of the dissociation energies for a dimer and a trimer calculated from MD simulations compared to the ones obtained by Borner *et al.* [8]

Evaporation of a molecule from the cluster occurs when its kinetic energy is greater than its internal, binding energy to the other molecules in the cluster. In the case of a dimer, since there is energy exchange between the two internal energy modes of potential and kinetic energies occuring during one internal vibrational period, dimer dissociation will certainly happen if the dimer internal energy is greater than the dissociation energy. In the case of a trimer, a molecule can only acquire part of the internal potential energy due to multimolecular interactions in the cluster: molecular evaporation is not a deterministic process. Figure 3 show the change in the cluster internal kinetic and potential energy during a typical evaporation case. It can be seen that the kinetic energy of the cluster typically decreases after the evaporation (the escaping molecule leaves with a positive kinetic energy), and the potential energy typically increases, showing an decrease in the cluster internal binding energy (due to a decrease in the cluster size). In the case of a dimer, the potential energy after evaporation is zero since there are two isolated molecules with no interactions. It is also interesting to note that the potential energy of the cluster is typically negative since it represents a stable bound state. The total internal energy has been conserved to within 0.5%. The cluster evaporation process depends on the cluster total internal energy but also on the distribution of internal energy among the cluster molecules. Therefore, multiple trajectories need to be run for the same temperature. At each temperature, the most probable configuration is given by the MCCE simulations and 1000 different trajectories are run. Once a molecule moves away from the cluster, the evaporation is recorded and the next trajectory is initialized. It was observed that in most of the cases the evaporation process is unimolecular, therefore multiple molecule simultaneous evaporation is neglected in this work. It is almost impossible to observe the evaporation process in all trajectories in an affordable computation time, especially at low temperatures. Therefore, the MD evaporation process is better expressed as the cumulative evaporation probability, which is definded as the ratio of the number of evaporated trajectories divided by the total number of trajectories. Zhong [7] showed that the difference between the cumulative evaporation probabilities obtained for 1000 or 20000 trajectories is negligible, so we used 1000 trajectories in this work to save computational time. MD evaporation simulation results are displayed on Figure 4. The temperature range used in this study is 240 K to 300 K. Since it appeared that no (or minimal) evaporation occured for temperatures lower than 240 K for dimers and 250 K for trimers. It can be seen that as the cluster temperature increases, the cumulative evaporation probability also increases.
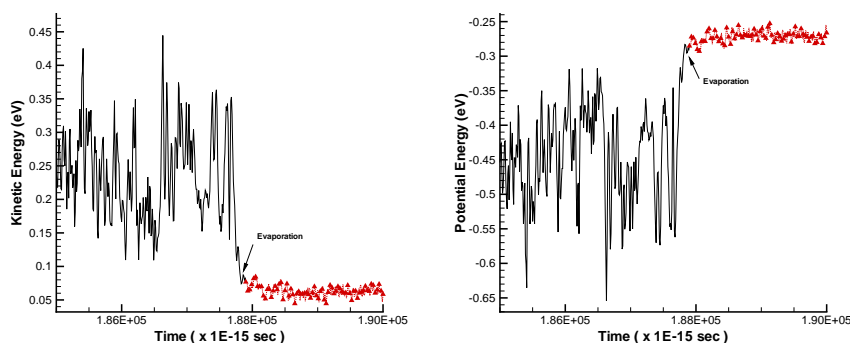
FIGURE 3. (Left) Change in kinetic energy of a trimer with an internal energy of -0.208 eV during an evaporation process. (Right) Change in potential energy of a trimer with an internal energy of -0.208 eV during an evaporation process.
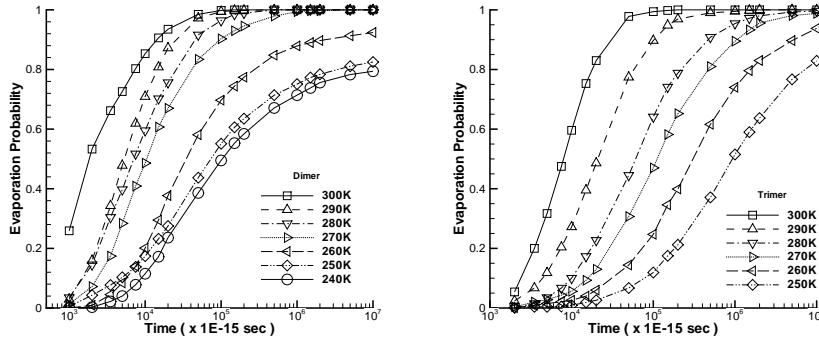
FIGURE 4. (Left) Cumulative evaporation probabilities for various cluster temperatures for a dimer. (Right) Cumulative evaporation probabilities for various cluster temperatures for a trimer.
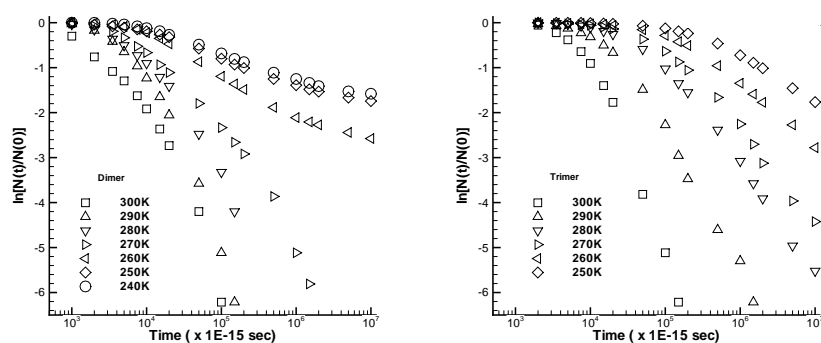
Weerashinge and Amar [9] proposed a simple relationship to describe the cluster evaporation process for the number of unevaporated clusters at time t, N(t), as $N(t) = N(0) \exp(-k_e t)$, where N(0) is the total number of trajectories and k_e is the cluster evaporation rate constant. Rearranging the previous equation as $\ln\left(\frac{N(t)}{N(0)}\right) = -k_e t$, we can get the cluster evaporation by plotting $ln[N(t)/N(0)]$ versus time. Figure 5 show plots for the cluster evaporation rates following Eq. (13) for dimer and trimer. It is interesting to note that there is period of lag time on the order of 10^{-11} before the evaporation actually occurs, especially at lower temperatures, which is consistent with the MD simulations results from Zhong [7]. It is possible to approximate a linear evaporation rate after this lag time, even though it should be noted that the evaporation rate can be a function of time - which is known as ther nonlinear effect. To validate those evaporation rates, the results can be compared to those from the UDT. Based on the UDT, the evaporation rate can be written as

$$k_{UDT} = n^{2/3} \omega \exp\left(-\frac{E_d}{kT_c}\right), \tag{4}$$

where n is the cluster size, ω is the vibrational frequency of an water molecule within the cluster, E_d is the cluster dissociation energy, and T_c is the cluster temperature. The dissociation energies were obtained from the MD simulation and summarized in the previous section. A vibrational frequency of $2.68 \times 10^{12} s^{-1}$ is proposed by Okada and Hara [10], independent of the cluster size. The vibrational frequency of a water molecule inside s cluster can also be calculated from the MD simulations. The distance between all the molecules is recorded and can be fitted with a sinusoidal trend, giving directly a frequency in the case of a dimer. In the case of a trimer, the three values obtained have to be averaged. Values of $3.1 \times 10^{12} s^{-1}$ for the dimer and $4.5 \times 10^{12} s^{-1}$ for the trimer are calculated. Eq.(14) shows that the UDT evaporation rate is proportional to the number of molecules on the cluster surface, as indicated by the term $n^{2/3}$; it also increases exponentially with the cluster temperature. Figure 6 show that the cluster evaporation rates at various temperatures for dimers and trimers are well described by the UDT rate equation, within the statistical accuracy of the simulations, as found by Zhong [7] for argon clusters. The best fit for the UDT evaporation rate is found to be for a value of ω of $5 \times 10^{11} s^{-1}$.

SUMMARY

A Monte Carlo simulation using the SPC potential model has been used to determine the potential energy and constant volume heat capacity of water dimers and trimers. It was found that the potential energy almost follows a linear trend versus temperature. The heat capacity fluctuates around 10 cal/mol/K and reaches a maximum around 220 K for the dimer and 240 K for the trimer. The Molecular Dynamics simulation has been used to evaporate water dimers and trimers. The cumulative evaporation probabilities were calculated for temperatures ranging from 240 K to 300 K. The cluster evaporation rates were calculated using Weerashinge's equation, and they were compared with the UDT rates. Both values were found to be in good agreement. Finally, vibrational frequencies were computed.

FIGURE 5. (Left) Cluster evaporation rates from the MD simulations for a dimer. (Right) Cluster evaporation rates from the MD simulations for a trimer.
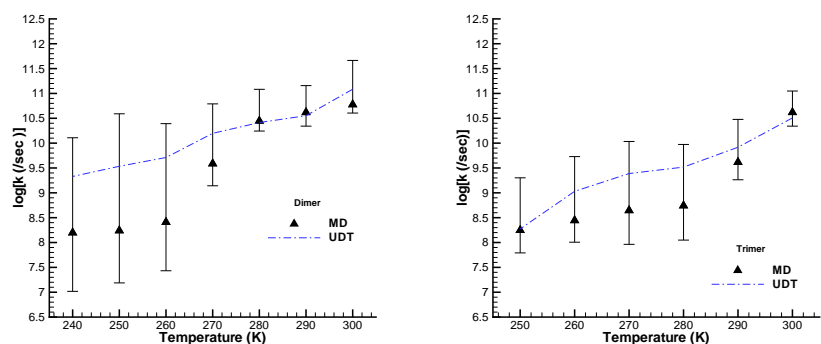
FIGURE 6. (Left) Comparison of cluster evaporation rates between MD simulation results and unimolecular theory for a dimer. (Right) Comparison of cluster evaporation rates between MD simulation results and unimolecular theory for a trimer.

REFERENCES

1. Bird, G. A., *Molecular Gas Dynamics and the Direct Simulation of Gas Flows*, (Clarendon, Oxford, 1994).
2. Zhong, J., Zeifman, M., Gimelshein, S., and Levin, D., "Direct Simulation Monte Carlo Modeling of Homogeneous Condesation in Supersonic Plumes", *AIAA Journal*, Vol. 43, No. 8, 2005, pp. 1784-1796.
3. Gilbert, R. G., and Smith, S. C., *Theory of Unimolecular and Recombination Reactions*, (Blackwell Scientific, Oxford, 1990).
4. Guvenc, Z.B., and Anderson, M.A., "A Molecular Dynamics Study of Small Water Clusters Comparing Two Flexible Models for Water," *Zeitschrift fur Physik D*, Vol. 36, 1996, pp. 171-183.
5. Pedulla, J.M., and Jordan, K.D., "Melting Behavior of the $(H_2O)_6$ and $(H_2O)_8$ Clusters," *Chemical Physics*, Vol. 239, 1998, pp. 593-601.
6. Berendsen, H.J.C., Psotma, J.P.M., van Gunsteren, W.F., and Hermans, J., "Interaction Models for Water in Relation to Protein Hydration", *Intermolecular Forces*, edited by B. Pullman, D. Reidel Publishing Co., Dordrecht, The Netherlands, 1981, p. 331-342.
7. Zhong, J., Moghe, N., Li, Z., and Levin, D.A., "A Unimolecular Evaportion Model for Simulating Argon Condensation Flows in Direct Simulation Monte Carlo," *Physics of Fluids*, Vol. 21, 2009-036101.
8. Borner, A., Li, Z., Levin, D.A., Jansen, R., Wysong, I., Gimelshein, S., and Zeifman, M., "Analysis of Kinetic Approach to Homogeneous Condensation in Water Expansions," 48th *AIAA Aerospace Science Meeting*, Orlando, FL, 2010.
9. Weerashinge, S., and Amar, F. G., "Absolute Classical Densities of States for Very Anharmonic Systems and Applications to the Evaporation of Rare Gas Clusters," *J. Chem. Phys.*, Vol. 98, No.4967, 1993.
10. Okada, Y., and Hara, Y., "Calculation of the Sticking Probability of a Water Molecule to a Water Cluster," *Earozoru Kenkyu*, Vol. 22, No.2, 2007, pp. 147-151.