

Surface Phenomena of Molecular Clusters by Molecular Dynamics Method *

Shigeo MARUYAMA † Sohei MATSUMOTO † Akihiro OGITA †

Abstract

Liquid droplets of water and argon surrounded by their vapor have been simulated by the molecular dynamics method. To explore the surface phenomena of clusters, each molecule is classified into 'liquid', 'surface', or 'vapor' with respect to the number of neighbor molecules. The contribution of a 'surface' molecule of the water cluster to the far infrared spectrum is almost the same as that of the 'liquid' molecule. Hence, the liquid-vapor interface is viewed as geometrically and temporally varying boundary of 'liquid' molecules with only a single layer of 'surface' molecules that might have different characteristics from the 'liquid' molecules. The time scale of the 'phase change' of each molecule is estimated for the argon cluster by observing the instantaneous kinetic and potential energies of each molecule. To compare the feature of clusters with macroscopic droplets, the temperature dependence of the surface tension of the argon cluster is estimated.

KEYWORDS: *Molecular dynamics method, Cluster, Surface tension, Infrared spectrum, Water, Argon*

Nomenclature

c = speed of light, $= 2.997925 \times 10^8 \text{m/s}$
 \hbar = Planck constant, $= h/2\pi$
 $= 1.05459 \times 10^{-34} \text{J}\cdot\text{s}$
 I = power spectrum of dipole moment, $\text{C}^2\text{m}^2\text{s}$
 k_B = Boltzmann constant, $= 1.38066 \times 10^{-16} \text{J/K}$
 L = size of the control volume, \AA
 m = mass of molecule, kg
 n = refractive index
 N = number of molecules
 $N(r)$ = number density of molecules, $1/\text{m}^3$
 N_n = number of neighbor molecules
 p = pressure, MPa
 r = distance of molecules or radius, \AA
 R_e = equimolar radius, \AA
 T = temperature, K

v = velocity, m/s
 $\alpha(\omega)$ = absorption cross section per molecule, \AA^2
 ε = energy scale of the potential, J
 $\phi(r)$ = potential function
 ρ = density, kg/m^3
 μ = electric dipole moment, $\text{C}\cdot\text{m}$
 σ = length scale of potential, \AA
 or surface tension, N/m
 ω = angular frequency of light, rad/s

Sub/Superscripts

l = of liquid
 v = of vapor
 s = at saturated condition

1 Introduction

* Received: October 1, 1993

† Department of Mechanical Engineering, The University of Tokyo (7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan, Tel (03)3812-2111, Fax (03)5800-6983)

The behavior of molecules on a liquid-vapor interface is the key to understand the surface phenomena such as the surface tension, evaporation and condensation, closely related to the phase change heat transfer. However, the physical mechanism of surface phenomena based on the kinetics of molecules is only poorly understood. The molecular dynamics simulation of a cluster of molecules up to a few thousands molecules is now possible. Two important applications of this simulation technique can be addressed. One is simulating the large enough system to reproduce the macroscopic property of droplets. Another is to study the property of very small clusters that are out of the range of experimental treatments. The former will be a strong tool to investigate the yet unknown or uncertain physical properties of macroscopic system. The latter is important in homogeneous and inhomogeneous nucleation phenomena encountered in phase change heat transfer theories. It is suspected that when the droplet becomes certainly small, the surface phenomena cannot be expressed simply by extrapolating the macroscopic properties.

Thus, clusters of water and argon surrounded by their vapor have been simulated by the molecular dynamics method. A water cluster of 512 molecules expressed by the ST2 potential and the Lennard-Jones argon systems of 864 molecules at various temperatures have been realized in a sufficiently large cubic box with periodic boundary conditions. To explore the surface phenomena of clusters, each molecule is classified into 'liquid', 'surface', or 'vapor' with respect to the number of neighbor molecules. Three-dimensional and slice view of molecules confirm this classification. Contributions of molecules in each regime to the far infrared spectrum of water cluster are compared. The time scale of the 'phase change' of each molecule is estimated for the argon cluster by observing the instantaneous kinetic and potential energies of each molecule. To compare the feature of clusters with macroscopic droplets, the temperature

dependence of the surface tension of argon clusters is estimated.

2 Description of Calculations

2.1 Formulation of Water Cluster and Far Infrared Spectra

The technique to formulate the water cluster and to calculate the far infrared spectra is basically the same as the previous reports for CO spectra [1] and for water spectra [2]. The molecular dynamics simulation with 512 water molecules expressed by the ST2 potential [3] has been performed in a cubic region with periodic boundary condition. This potential models a rigid water molecule with an oxygen atom at the center of a regular tetrahedron of two hydrogen atoms and two negative static charges (imaginary). The parameters are reproduced in Table 1.

Table 1 ST2 potential parameters

Distance of O and H	r_{OH}	0.8 [Å]
Charges	q	0.3776×10^{-19} [C]
Energy parameter	ϵ	5.2605×10^{-22} [J]
Length parameter	σ	3.10 [Å]
Near threshold	D_1	2.0160 [Å]
Far threshold	D_2	3.1287 [Å]

The initial configuration of molecules shown in Fig. 1 is a cubic ice (diamond lattice) at the center of the calculation domain that is 4 times larger in length ($L = 99.3\text{Å}$) than the cubic ice. Using the predictor-corrector method 50,000 steps have been calculated (the time step was 1 femto second). Initial 10,000 steps were used for numerical evaporation of the ice with the temperature control at 270K and following 40,000 steps of relaxation process gave the equilibrium condition. For the calculation of the far infrared spectrum 2,500 steps of equilibrium system are used. Here, positions of molecules are adjusted every step so that the center of gravity of whole cluster is always kept at the center of the calculation cell.

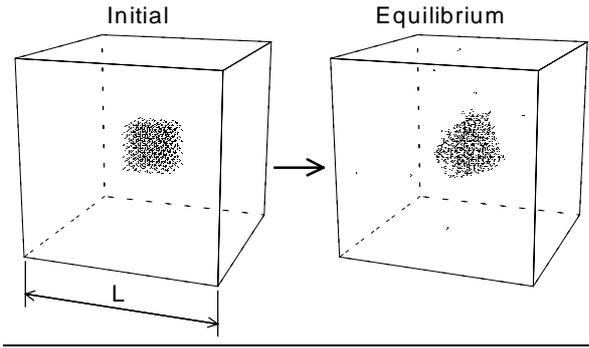


Figure 1 Generation of a water cluster by the molecular dynamics method

The absorption spectrum represented by the absorption cross section per molecule $\alpha(\omega)$ for light of frequency ω is derived as follows from the quantum mechanical perturbation theory [4,5]. Assuming that light interferes only to the permanent electric dipole moment, $\alpha(\omega)$ is expressed as

$$\alpha(\omega) = \frac{\pi\omega \{1 - \exp(-\hbar\omega/k_B T)\}}{3\varepsilon_0 \hbar mc N} I(\omega), \quad (1)$$

where T , c , and n are system temperature, speed of light, and refractive index which is assumed to be unity, respectively. The transition rate $I(\omega)$ is expressed as

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\omega t) dt \langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle_0 \quad (2)$$

with the electric dipole moment $\mu(t)$. Here, $\langle \rangle_0$ denotes the ensemble average in the equilibrium system.

For the classical equilibrium system the absorption cross section tends to the following equation as the classical limit of $\hbar\omega/k_B T \rightarrow 0$.

$$\alpha(\omega) = \frac{\pi\omega^2}{3\varepsilon_0 k_B T n c N} I(\omega) \quad (3)$$

The ensemble average $\langle \mu(0) \cdot \mu(t) \rangle_0$ is equivalent to the autocorrelation, and $I(\omega)$ reduces to the power spectrum of the electric dipole moment of the system.

2.2 Formulation of Argon Clusters

The molecular dynamics simulations have been performed for 864 argon atoms enclosed in a cubic region with the periodic boundaries. Argon

atoms are expressed by the following 12-6 Lennard-Jones potential.

$$\phi(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}, \quad (4)$$

where parameters of the potential are $\sigma = 3.40 \text{ \AA}$, $\varepsilon = 1.67 \times 10^{-21} \text{ J}$. The simple Verlet method is employed to integrate the classical equation of motion with the time step of 0.01 ps.

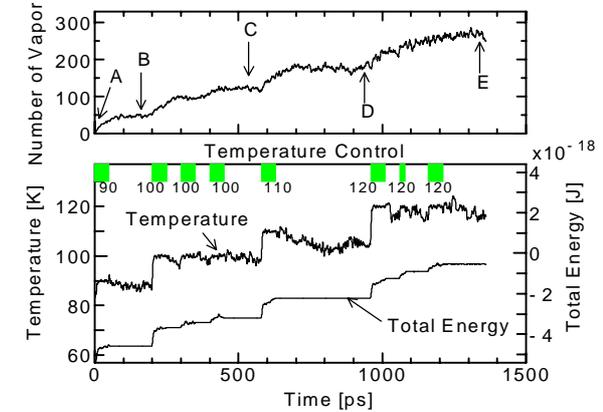
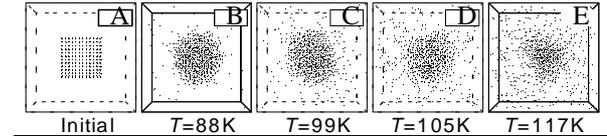


Figure 2 Procedure to generate argon clusters at various temperatures

A f.c.c. crystal of argon is placed in a cubic cell as shown in Fig. 2(A) with randomly directed velocity $v = \sqrt{3k_B T/m}$ for the aimed temperature T . The numerical evaporation process is shown in Fig. 2. For initial 50 ps the velocity scaling for the temperature control at $T = 90 \text{ K}$ is imposed each 40 step, which is related to the fluctuation of total energy and almost constant temperature in Fig. 2. After the period of temperature control, about 50 ps is needed for the relaxation, which involved the small increase of potential energy and decrease of temperature. We decide that the system becomes equilibrium when the temperature and the number of 'vapor' atoms (see section 3 for definition) are settled to almost constant values. Then, 100 ps of simulation is stored for further calculations.

Table 2 Survey of simulations of argon clusters (N=864, L=80.9[Å]).

Label	T [K]	R_e [Å]	ρ_l [kg/m ³]	ρ_v [kg/m ³]	p_l [MPa]	p_v [MPa]	σ [N/m]
88	87.7	20.8	1410	8.0	11.8	0.14	0.0121
99	98.9	20.2	1360	21.5	11.0	0.39	0.0107
105	104.9	19.5	1310	33.0	7.0	0.60	0.0063
117	117.2	17.8	1220	56.0	7.0	1.09	0.0053

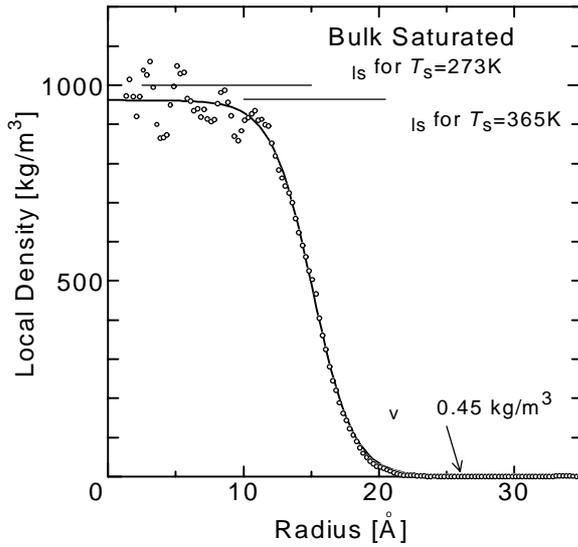


Figure 3 (a) Local density distribution (water, $T=270K$)

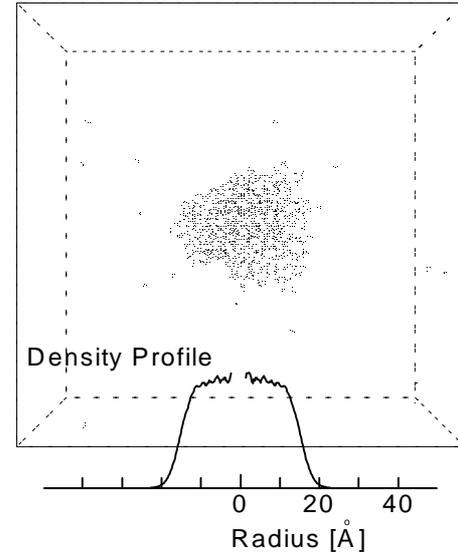


Figure 3 (b) Instantaneous 3-D view

For systems at different temperatures, once obtained equilibrium system is a good initial condition. Monitoring the temperature and number of vapor, we continue to control the temperature as shown in Fig. 2. As summarized in Table 2, 4 equilibrium cases at different temperatures were stored in order to study the effect of temperature.

3 Interface of 'Liquid' and 'Vapor'

Fig. 3(a) shows the calculated local density distribution of the water cluster. The local density at a distance r from the center is measured as the average number of molecules in a spherical shell with a small width about the radius r divided by the volume of the shell. The least squares fit of tanh form function shown in the figure well represents the numerical data. The numerical data largely scatter near the center of the cluster because the number of molecules in the control

shell is less. The density at the central region is 962 kg/m³ compared with 999.78 kg/m³ for saturated liquid density at 273 K. The density of vapor ρ_v at the outer region is about 0.45 kg/m³ compared with 0.00485 kg/m³ for saturated bulk density at $T = 273$ K. Both densities are close to the saturated condition at about 365 K, where $\rho_{ls} = 964$ kg/m³ and $\rho_{vs} = 0.46$ kg/m³. The differences of these densities might due to the size effect of the droplet. The surface region in which the density is smoothly changing has a width of about 10 Å. Fig. 3(b) compares the density profile with the 3-dimensional snapshot of molecules at the equilibrium state.

Fig. 4(a) is a zoom up view of Fig. 3(b) in contrast to Fig. 4(b) that is a 4 Å thick slice of Fig. 4(a) at the center of the cell. With this size of the cluster, the instantaneous geometry seems far from spherical. Another interesting point is that the surface of liquid and vapor looks very sharp and discontinuous. The smooth change of the local

density as a function of radius shown in Fig. 3(a) is thus due to the spatial and time averaging.

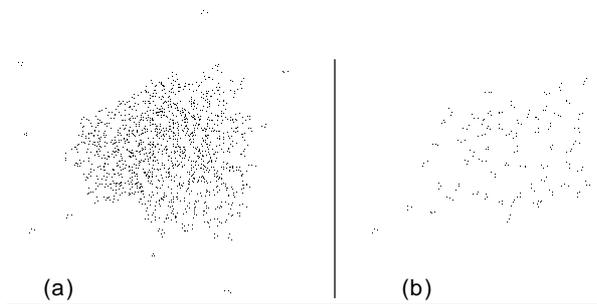


Figure 4 Slice view of the water cluster

We then tried to extract some distinct features of motion of molecules near the surface. We speculated that at least one layer of molecules at the edge of the cluster should have some special property of 'surface'. Thus, we classified molecules into three phases 'vapor', 'liquid', or 'surface' through the instantaneous properties of each molecule. For this purpose, several properties of each molecule have been tried such as absolute force acting on the molecule or the potential energy of the molecule. Finally, we chose the physically simplest property, the number of neighbor molecules. Neighbor molecules are determined as the molecules within the distance of 1.4σ (length scale of the potential) from the molecule of interest. The number of neighbor molecules N_n counted for each molecule is averaged for 2.5 ps. Here, we have roughly optimized the distance and the integration time with the following classification and confirmation procedures.

The histogram of N_n plotted in Fig. 5 shows distinguishable three peaks. The first peak at $N_n = 0$ clearly relates to molecules outside the cluster core, which usually have no neighbor molecules. It is expected that surface molecules have less number of neighbor molecules compared with those at the central region of the cluster. We decide that molecules with $N_n \leq 1$ are 'vapor' molecules, $2 \leq N_n \leq 8$ are 'surface', and $N_n \geq 9$ are 'liquid'. Thus, each molecule is classified into 'vapor', 'surface', or 'liquid'. To confirm this classification, 'surface' molecules are shown in

solid symbol in Fig. 4(b). It is clear that this classification is successful and that the averaging time 2.5 ps is short enough so that most of molecules are kept at the same phase.

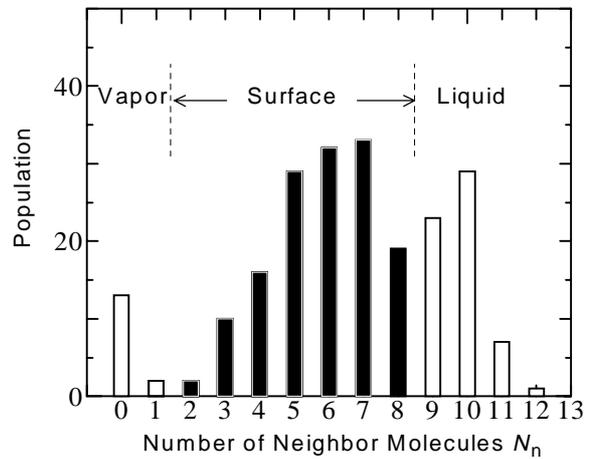


Figure 5 Histogram of the number of neighbor molecules (water cluster)

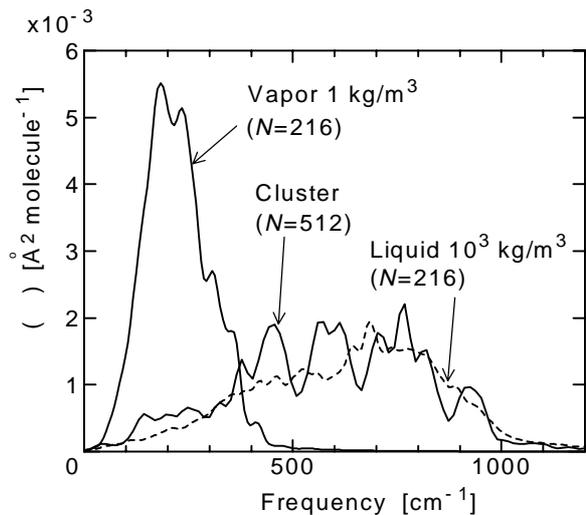


Figure 6 Far infrared spectra of water cluster

4 Far Infrared Spectra of Water Cluster

Fig. 6 shows the far infrared spectra calculated for the water cluster compared with the bulk vapor and bulk liquid phase spectra in our previous report [2]. The lower frequency peak at about 200 cm^{-1} of vapor phase spectrum relates to the free rotation of molecules. The liquid phase spectrum is made up with principal peak of libration motion at the frequency range of 600 to

1000 cm^{-1} , and a small peak at about 300 to 500 cm^{-1} which is assigned to the stretching motion of hydrogen bonding, O-H...O [6]. The spectrum for the cluster is similar to the liquid case except for a little broadening to the lower frequency region and a trace of the lower frequency peak related to the vapor phase.

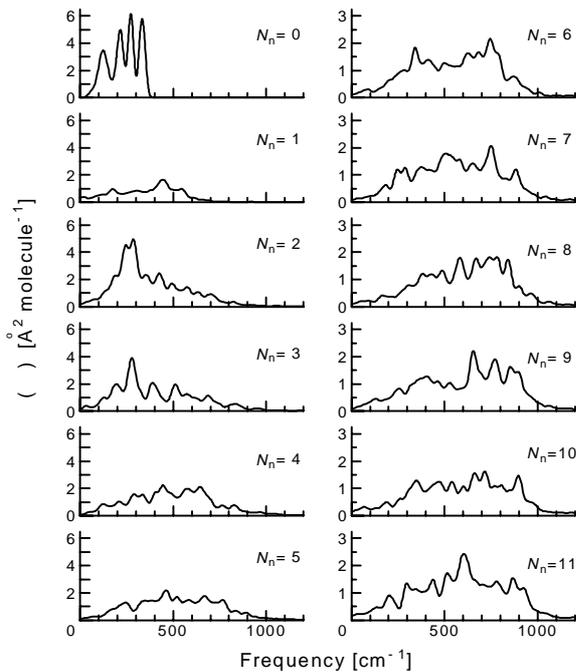


Figure 7 Far infrared spectra for each N_n

Since the difference of cluster and liquid phase cases has been so small although the former should have so many surface molecules, the more detailed examinations of the effect of the number of neighbor molecules are achieved as shown in Fig. 7. Molecules of each N_n are grouped to separately calculate the contribution to the spectrum. Each spectrum is noisy due to the less number of molecules. Here, only cases with N_n up to 3 are significantly different from the spectrum of liquid phase. This means that the far infrared spectra of the 'surface' molecules are principally the same as the core 'liquid' or the bulk liquid cases. This result further implies that the motion of 'surface' molecules are approximately the same as the inner core. We conclude that a water cluster of this size range has a very sharp interface

between vapor and liquid without any molecules with an intermediate property. The gradual change of properties such as the density must be explained by the spatial and temporal averaging effect of the fluctuating interface geometry.

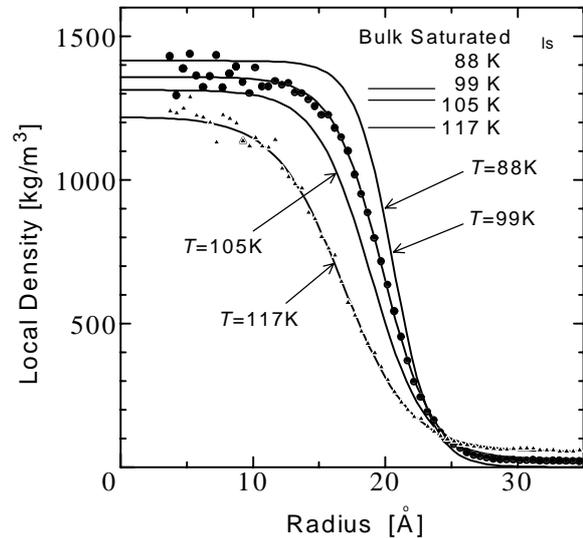


Figure 8 Local density distributions of argon clusters. Calculated points are shown only for $T=99\text{K}$ and $T=117\text{K}$ for clarity.

5 Phase Change of Molecules

Water is known as an extremely special material in the sense of physical properties because water molecules have the strong permanent dipole moment and exhibit hydrogen bonding. Thus, we have adopted the much simpler argon clusters for further studies of kinetics of molecules at the surface. The local density distributions calculated with the same technique as for the water cluster are plotted in Fig. 8 for various temperatures. Here, tanh form functions are used for curve fittings. The overall shapes of the distribution are similar to the water cluster. With the increase of temperature the core liquid density decreases and the vapor density increases. Asymptotic values of liquid and vapor densities read from this figure are listed in Table 2. In contrast to the case of water cluster, liquid and vapor densities compare well to the saturated bulk properties.

Fig. 9 shows the histogram of the number of neighbor molecules N_n for the argon cluster at $T = 99\text{K}$. The same feature as the case of water cluster is clear. In this case, the integration time was 4.0 ps. Classifications here are that molecules with $N_n \leq 1$ are 'vapor' molecules, $2 \leq N_n \leq 7$ are 'surface', and $N_n \geq 8$ are 'liquid'.

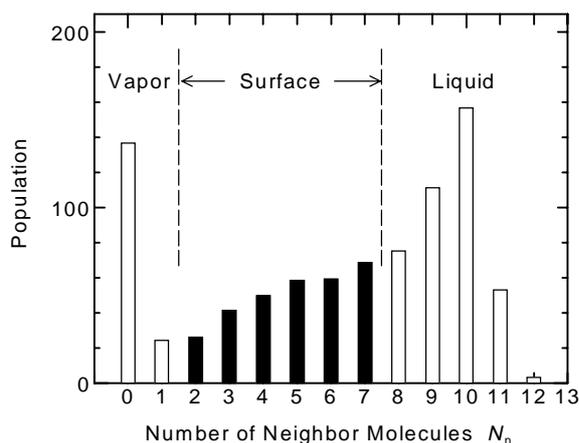


Figure 9 Histogram of N_n for argon cluster ($T=99\text{K}$)

The result of classifications is visually demonstrated in Fig. 10, which is the slice view of Fig. 2(C) with the thickness of 3 \AA . Marked molecules are arbitrary selected representatives for the convenience of the following discussions in Fig. 11.

The time histories of the instantaneous number of neighbors N_n , kinetic energy (temperature), and potential energy of these 6 molecules are compared in Fig. 11. Molecule #1 is always in the cluster core and labeled 'liquid' for whole 100 ps. On the other hand, molecule #2 is 'vapor' for whole 100 ps. Molecule #3 hovers near the surface for a while and finally enters into the core. Molecules #4 and #5 change their phase, 'liquid' to 'vapor' and 'vapor' to 'liquid', respectively. Finally, molecule #6 is special. It exhibits small oscillatory changes of N_n and potential energy during the middle of the observation period. It is confirmed from the 3-D animation that this molecule is a part of a dimer and the vibrational

motion between the partner molecule results in these phenomena.

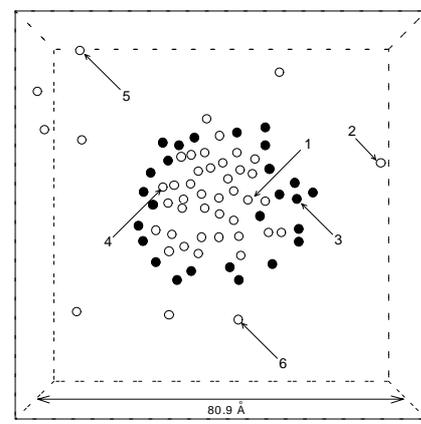


Figure 10 Slice view and selected molecules

The variation of potential energy well correlates to that of the number of neighbor molecules, simply because neighbor molecules within 1.4σ have large negative contribution to the potential of each molecule. Spikes in kinetic and potential energies at the same time represent collisions. The rate of collisions is clearly contrasted in #1 of 'liquid' and #2 of 'vapor'.

Time scales of the phase change phenomena can be roughly estimated from #4 and #5 molecules. Molecule #4 which is 'liquid' at $t=0$ spends about 50 ps as 'surface' gradually gaining the potential energy before the vaporization. On the other hand, molecule #5 condenses to the 'surface' and spends about 50 ps for the gradual loss of potential energy.

Other molecules in Fig. 10 have been similarly examined. Out of 73 molecules in Fig. 10, 10 molecules show phase change characteristics similar to #4 or #5, and 35 molecules are similar to #3. Many of these examples show that the life time of 'surface' regime of a molecule is typically 50 ps.

6 Surface Tension of Argon Clusters

For a liquid droplet of radius R_c , the surface tension σ is defined by the well known Laplace's equation

$$\sigma = \frac{(p_l - p_v)R_c}{2}, \quad (5)$$

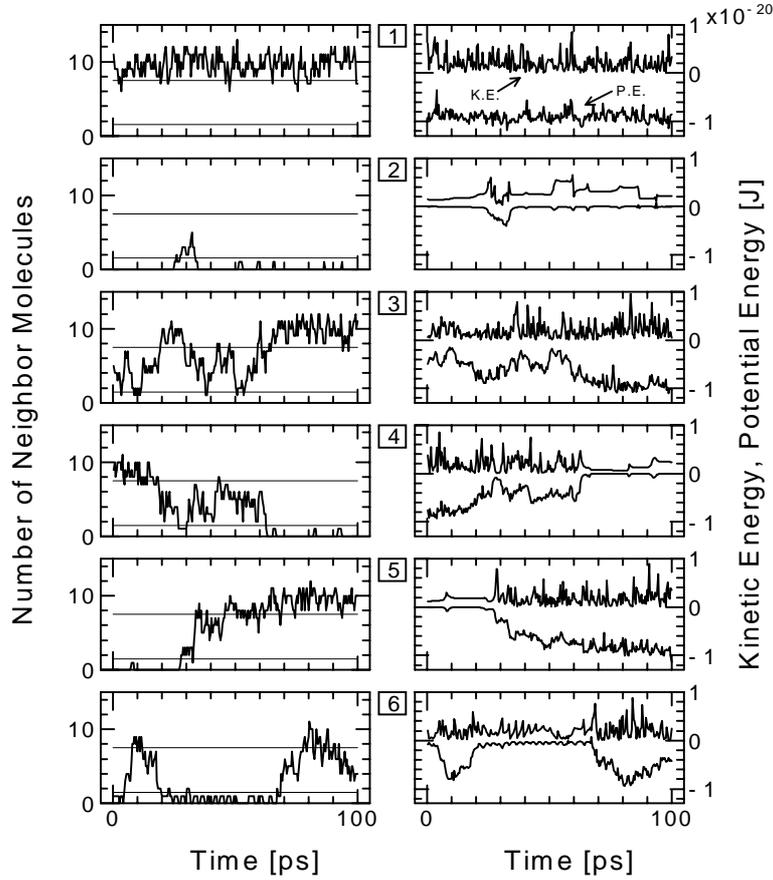


Figure 11 Traces of potential and kinetic energies compared with N_n

where p_l and p_v are the pressure of liquid and vapor, respectively. However, at this size range, even the definition of the radius of a cluster is not straightforward.

Here, the simplest equimolar radius R_c is defined as follows

$$mN = \frac{4\pi}{3} R_c^3 \rho_l + \left\{ L^3 - \frac{4\pi}{3} R_c^3 \right\} \rho_v, \quad (6)$$

where ρ_l , ρ_v , N , and L are liquid density, vapor density, number of molecules, and unit length of the cell, respectively. This R_c means the radius of a hypothetical sphere of uniform density ρ_l in the cubic cell of density ρ_v .

The estimation of the pressure distribution is more difficult and result in a considerable error. We have followed the technique of Thompson *et*

al. [7] and used the following spherical extension of Irving-Kirkwood's formula to calculate the normal pressure distribution.

$$p(r) = k_B T N(r) - \frac{1}{4\pi r^2} \sum_k f_k, \quad (7)$$

where $N(r)$ is the number density distribution. A control spherical surface of radius r from the center of the cluster is defined. The sum over k is over the normal component f_k of forces acting across the control surface between a pair of molecules i and j . The sign of f_k is defined as positive for repulsive force and negative for attractive force. Using the vector $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, and the potential $\phi(r_{ij})$, the normal pressure is expressed as

$$p(r) = k_B T N(r) - \frac{1}{4} \frac{1}{r^3} \sum_k \left| \mathbf{r} \cdot \mathbf{r}_{ij} \right| \frac{1}{r_{ij}} \frac{d\phi(r_{ij})}{dr_{ij}}. (8)$$

Terms in Eq. (8) are plotted in Fig. 12. The kinetic term $k_B T N(r)$ denoted as K in Fig. 12 is simply proportional to the density profile shown in Fig. 8. The second term of Eq. (8) represents the contribution of the internal force field and denoted as IF in Fig. 12. The internal force is further divided into attractive force denoted as AF and repulsive force denoted as RF. Calculated results are shown as the range of the standard deviations for RF, AF, and K.

We need the pressure of liquid p_l that is asymptotic value of $p(r)$ as $r \rightarrow 0$ and of vapor p_v for the calculation of surface tension. Since the scatter of data is very large when $r \rightarrow 0$ due to less number of molecule pairs, the estimation of p_l is very difficult. We fit tanh function to RF and AF to obtain the asymptotic values.

Estimated values of p_l and p_v are listed in Table 2. The dependency of p_v on temperature is compared with the saturated bulk vapor pressure in Fig. 13. Even with this size of cluster the vapor pressure is almost the same as the bulk.

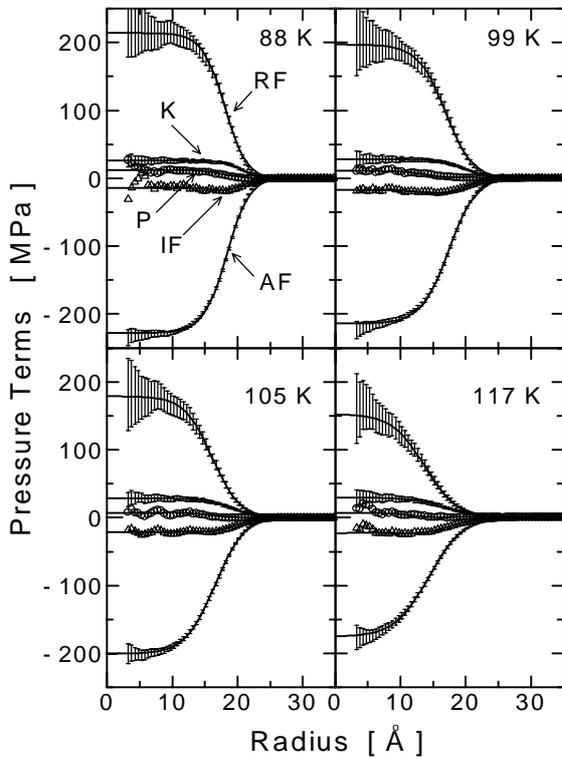


Figure 12 Pressure terms of argon clusters
[P: normal pressure (=K+IF), K: kinetic term, IF: internal force term (=AF+RF), RF: repulsive force term, AF: attractive force term]

The surface tension σ defined by the Laplace's equation is plotted on Fig. 13. The results of present calculations seem to agree well to the bulk physical property. However, considering the size effect of a droplet, we may need to expect to obtain less value of surface tension at this size range of $R_c \approx 20 \text{ \AA}$. The well-known experimental formula Tolman's equation predicts decrease of the surface tension for the smaller drops.

$$\frac{\sigma}{\sigma_0} = \frac{1}{1 + (2\delta / R_c)}, (9)$$

where σ_0 is the surface tension of macroscopic size and δ is the Tolman's length that is believed to be positive [7,8]. Further consideration of the effect of the droplet size is desired.

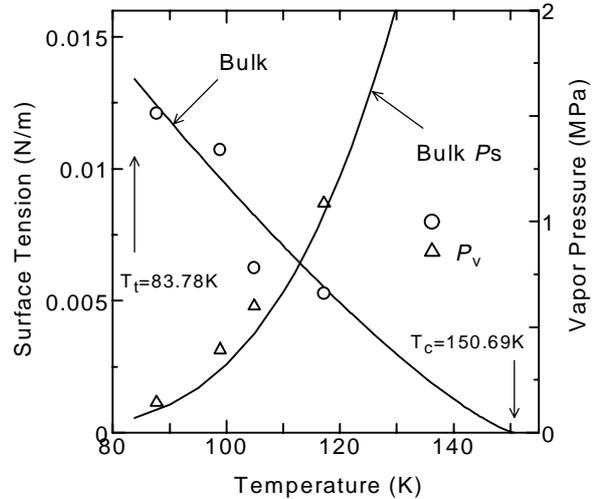


Figure 13 Surface tension and vapor pressure of argon clusters

7 Conclusions

Small clusters of 512 ST2 water molecules and 864 Lennard-Jones argon atoms surrounded by their vapor have been realized in a sufficiently large cubic box with periodic boundary conditions.

A simple classification of molecules into 'liquid', 'surface', or 'vapor' with respect to the number of neighbor molecules is demonstrated. From the observation of the 'surface' molecules it is found that the liquid-vapor interface is made up of about one layer of molecules, and its instantaneous geometry is far from spherical shape.

Far infrared spectrum of the water cluster is almost the same as that of bulk liquid water. Furthermore, it is confirmed that the contribution of a 'surface' molecule to the spectrum is almost the same as the 'liquid' molecule. This result implies that the kinetics of 'surface' molecules are not significantly different from those of 'liquid' molecules.

The history of instantaneous kinetic and potential energies of each molecule demonstrated that the life time of a molecule behaving as 'surface' is about 50 ps. During the evaporation and condensation processes, each molecule spends about the same period of time as 'surface'.

The surface tension estimated for argon clusters reproduces the order of magnitude and temperature dependence of bulk physical property.

Acknowledgments

We thank Professor Masahiro Shoji and Professor Susumu Kotake for extended and fruitful discussions. Part of this work is supported

by the research grand (No. 04002476) of the Ministry of Education, Japan.

References

- [1] Matsumoto, S., Maruyama, S., and Shoji, M., "Calculation of Infrared Spectra by Molecular Dynamics Method," *Transport Phenomena Science and Technology*, Ed. B.-X. Wang, Higher Education Press, Beijing, (1992), 575-580.
- [2] Matsumoto, S. and Maruyama, S., "Far Infrared Spectrum of Water by Molecular Dynamics Method," *2nd JSME-KSME Thermal Engng. Conf.*, Kitakyushu, (1992), 3.61-3.64.
- [3] Stillinger, F. H. and Rahman, A., "Improved Simulation of Liquid Water by Molecular Dynamics," *J. Chem. Phys.*, **60**-4 (1974), 1545-1557.
- [4] Gordon, R. G., "Correlation Functions for Molecular Motion," *Advan. Magn. Reson.*, **3** (1968), 1-42.
- [5] Berens, P. H. and Wilson, K. R., "Molecular Dynamics and Spectra. I. Diatomic Rotation and Vibration," *J. Chem. Phys.*, **74**-9 (1981), 4872-4884.
- [6] Guillot, B., "A Molecular Dynamics Study of the Far Infrared Spectrum of Liquid Water," *J. Chem. Phys.*, **95**-3 (1991), 1543-1551.
- [7] Thompson, S. M. *et al.*, "A Molecular Dynamics Study of Liquid Drops," *J. Chem. Phys.*, **81**-1 (1984), 530-542.
- [8] Nijmeijer, M. J. P. *et al.*, "Molecular Dynamics of the Surface Tension of a Drop," *J. Chem. Phys.*, **96**-1 (1992), 565-576.