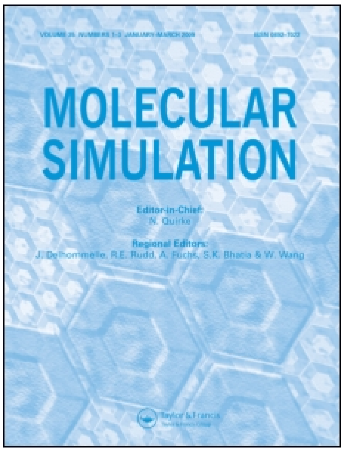

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Evaporation and Condensation at a Liquid Surface of Methanol

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EVAPORATION AND CONDENSATION AT A LIQUID SURFACE OF METHANOL

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Evaporation and condensation processes at a liquid surface of methanol were investigated at room temperature with a microcanonical molecular dynamics computer simulation technique. The condensation coefficient (the number ratio of condensed molecules to incident ones) was estimated by comparing two types of autocorrelation functions, and found to be less than unity, which is in qualitative agreement with experiments. A variety of complex dynamic phenomena were observed at the surface.

KEY WORDS: molecular dynamics, evaporation, condensation, liquid surface, methanol

INTRODUCTION

Evaporation and condensation processes play an important role in various fields of science and technology. Experimental and theoretical studies concerning the evaporation and condensation rates have a long history, but it is still difficult to obtain the absolute rate. One of the main difficulties exists in the fact that there is no clear physical pictures on molecular level about the dynamic processes at liquid surfaces. In this decade, there have been great progress in understanding of microscopic static structures of liquid surfaces, for both pure liquids and mixtures [1, 2], but only little is known about the dynamics.

Molecular dynamics (MD) computer simulations can provide a useful insight in this respect. Recently, we reported preliminary results of our MD simulation of liquid surface of pure methanol at room temperature [3]. The main concern in Ref. [3] is the unique evaporation process in which two methanol molecules are hydrogen-bonded and evaporate simultaneously; this dimer evaporation mechanism was experimentally suggested by Faubel and Kisters [4] for associating fluids such as carboxylic acids, and we believe that Ref. [3] is the first evidence by computer simulations.

Also in Ref. [3], we calculated the condensation coefficient α_c, defined as the number ratio of the condensed molecules to the incident ones, by counting the events directly, and found that α_c is less than unity ($\simeq 80\%$). This is in qualitative agreement with recent experiments by Fujikawa and Maerefat [5] by means of a shock tube.

When we look more closely into the events of evaporation and condensation at a methanol surface, however, we can see that there are various complicated dynamical behaviors. These are certainly ascribed to the special surface properties of associating fluids due to hydrogen bondings, but explanations from the view point of statistical physics are still to be developed. In this report, we briefly describe the method of liquid surface simulation, and show some of interesting phenomena observed at the surface. Also we present a new way to determine α_c with less arbitrariness by defining two different escaping rates in terms of number auto-correlation functions. The resulting α_c agrees with the value from direct counting.

SIMULATION METHOD

The program for the simulation is similar to what we used before [6] to examine static properties (surface tension, average molecular orientation, etc.) of methanol liquid surface. The main features of the program are (1) a microcanonical ensemble (*NVE*-constant) molecular dynamics, (2) a rectangular prism as the unit cell, (2) the periodic boundary conditions for all three dimensions, (3) the Ewald summation technique for Coulombic interactions, (4) rigid molecules with site-site interactions, (5) the leap-frog algorithm with quaternions for numerical integration of the classical equations of motion, and (6) Jorgensen's TIPS (OPLS) potential parameters for the molecular interactions of methanol [7].

In this work, the total number of molecules is 864. The time step is 0.5 fs ($=0.5 \times 10^{-15}$ s), and the short range interactions in real space are truncated at

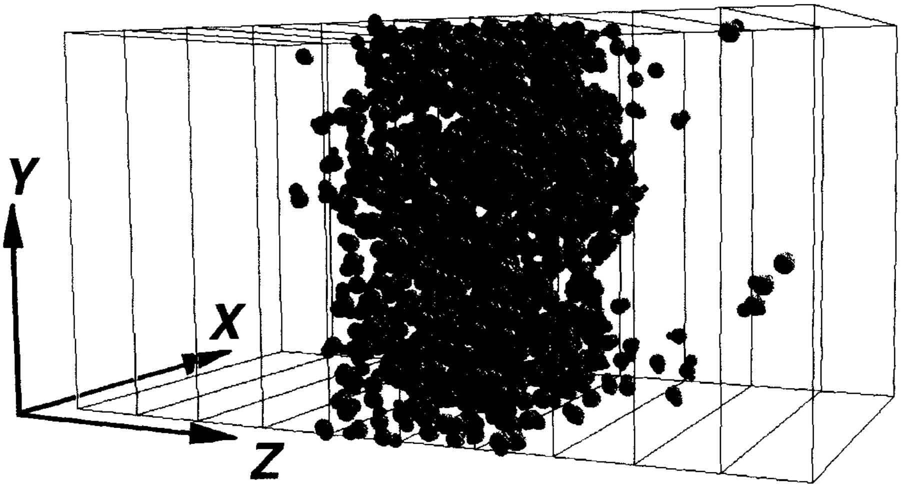

Figure 1 A snapshot of the simulated interfacial system of methanol. The unit cell contains 864 methanol molecules, most of which make a thick liquid film. The grids are drawn 10 Å apart. In this snapshot, each molecule is expressed by a space filling model with three sites (O, H, and the methyl group).

14 Å. Initially, we make a thick liquid layer (slab) of methanol at the center of the cell (51.0 Å × 51.0 Å × 100 Å) and start the simulation. After equilibrating the system to $T \simeq 300\,\mathrm{K}$ by repeatedly rescaling the linear and angular velocities of each molecule, we accumulate the configurational data for 300 ps. A typical configuration is shown in Figure 1; the liquid layer is about 20 Å of thickness, on both sides of which are flying several molecules, making the vapor phase. The average number of the vapor molecules is about 10 in this simulation, and we can sometimes observe hydrogen-bonded dimers and trimers, as reported in Ref. [3]. Since the temperature is low enough, the liquid layer is stable during the whole simulation without an external field.

DATA ANALYSIS AND DISCUSSION

In the total of 300 ps configurations, we observed more than 100 events of evaporation and condensation processes. The most interesting cases of dimer evaporation were already reported in Ref. [1]; hence, we show here other examples, which may be less amazing but are relevant for understanding the dynamics because of their abundance. Figure 2 depicts typical dynamic processes of a molecule. It takes about 5 ps to gather energy of excitation to vaporize itself (at $\simeq 30$ ps in Figure 2), and takes a similar time to relax (or dissipate) the extra energy to condense (at $\simeq 90$ ps). Reflection at the surface also takes place (at $\simeq 67$ ps); the molecule comes very close to the surface, but there is no energy relaxation and the molecule is bounced.

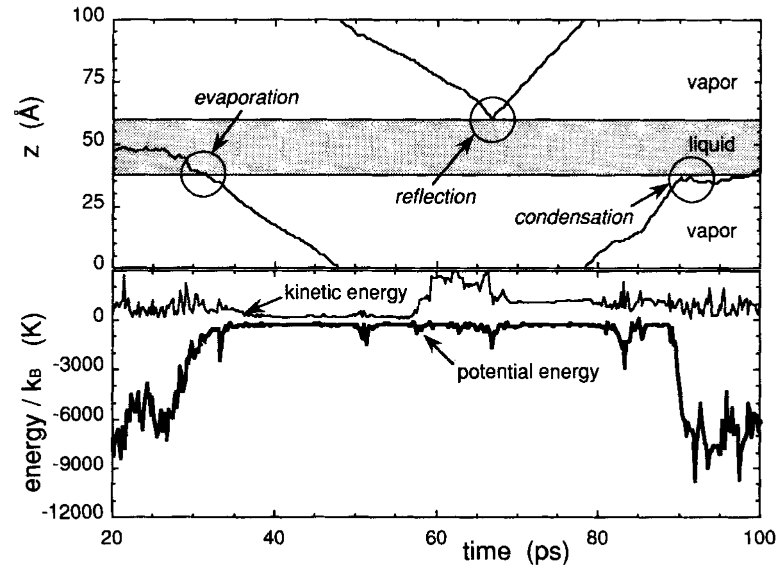

Figure 2 An example of dynamic behavior of a methanol molecule to show three typical phenomena at a liquid surface. (Top) Surface normal component of the center-of-mass trajectory is plotted as a function of time. The shown phase boundary is the Gibbs dividing surface determined from the time-averaged density profile. (Bottom) Kinetic (translational + rotational) and potential energies of the same molecule are plotted as a function of time. The energies are shown in the unit of absolute temperature.

We drew a similar figure for each molecule and counted the number of incident molecules, which collide with the surface from the vapor side, and the number of condensed molecules to estimate the condensation coefficient α_c. Analyzing 120 ps data [3], we observed 23 cases of condensation out of 28 incident molecules, and reported $\alpha_c = 23/28 \simeq 80\%$.

However, there are various other types of dynamical behaviors, which make it very difficult to determine the exact moment of condensation. Figure 3 shows an example; the incident molecule remains near the surface for more than 10 ps, (from 116 ps to 127 ps) but this might not be condensation because its potential energy is close to zero. With many cases similar to this, it is hard to estimate α_c without arbitrariness from the direct counting. Certainly, we need to look into more detail (instantaneous molecular orientation, energy transfer from/to the surrounding molecules, etc.) to make up a better criterion of condensation, and we will do it in future works.

In this article, however, we develop other way of estimating α_c than direct counting, it uses two types of autocorrelation functions for the number of vapor molecules, and is believed to be much less arbitrary than the direct counting because we need not care about the dynamics of each molecule.

Let V_v be the vapor region, and consider the following discrete function $\sigma_i(t)$ for each molecule at time t:

$$\sigma_i(t) = \begin{cases} 1 & \text{if } i\text{-th molecule} \in V_v \text{ at } t, \\ 0 & \text{if } i\text{-th molecule} \notin V_v \text{ at } t. \end{cases} \tag{1}$$

Then, we can construct two autocorrelation functions for $\{\sigma_i(t)\}$:

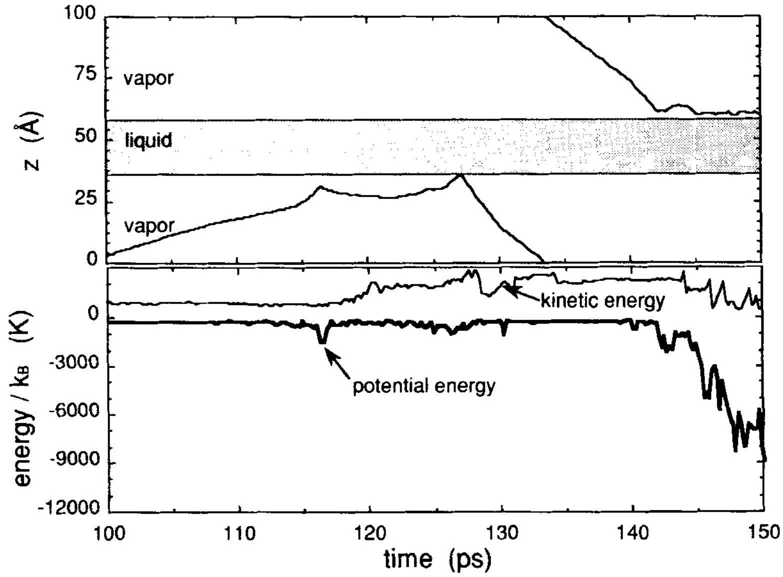

Figure 3 Similar to Figure 2 for another molecule. In this case, it is hard to determine the exact moment of reflection.

$$C_1(t) \equiv \left\langle \sum_i \sigma_i(t_0)\sigma_i(t_0+t) \right\rangle_{t_0} \tag{2}$$

and

$$C_2(t) \equiv \left\langle \sum_i \sigma_i(t_0)\sigma_i(t_0+\Delta t)\sigma_i(t_0+2\Delta t)\cdots\sigma_i(t_0+t) \right\rangle_{t_0}, \tag{3}$$

where $\langle\cdots\rangle_{t_0}$ represents the ensemble average with respect to t_0 and Δt is the time step of simulation, or the time interval of saving the configurational data. The two functions, $C_1(t)$ and $C_2(t)$, are different. $C_2(t)$ is the average number of molecules which exist in the region V_v continuously during the period of t, while $C_1(t)$ is the number of molecules which are in V_v at both 0 and t irrespective of their whereabouts at the intermediate time. It is ideal to take $\Delta t \rightarrow 0$ limit in Equation 3, but the result of $C_2(t)$ does not depend much on Δt as long as we put the boundary of V_v well apart from the surface (inside the bulk vapor phase) because the main cause for the difference of $C_1(t)$ and $C_2(t)$ is the reflection of molecules at the surface.

To demonstrate the difference of $C_1(t)$ and $C_2(t)$, let us consider the case where a reflective wall exists outside of V_v. The value of $C_1(0) = C_2(0)$ represents the average number of molecules in V_v, and both functions should have the same initial decay because they are similarly counting the number of molecules escaping at the boundary of V_v. However, $C_1(t)$ counts the molecules which are reflected by the wall and $C_2(t)$ does not. Thus, $C_2(t)$ decreases monotonically and always $C_2(t) \leq C_1(t)$ at later time. Whether $C_1(t)$ is monotonic or not depends on the "elasticity" of the wall as well as the initial configuration of molecules, although we can expect it is also monotonic in most cases.

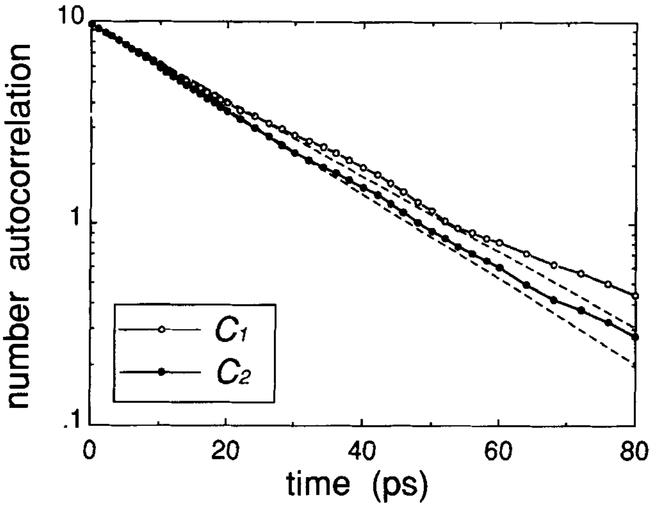

Figure 4 Two autocorrelation functions, defined in Equations (2) and (3), are plotted in the semi-logarithmic scale against time. The dashed lines are the results of least-square fitting to simple exponential functions.

The result of $C_1(t)$ and $C_2(t)$ for our simulation are plotted in semi-logarithmic scale in Figure 4. Both functions are monotonically decreasing with time, and $C_2(t) < C_1(t)$ as expected. In this calculation, we put the boundary of V_v inside the vapor phase, ca. 10 Å apart from the Gibbs dividing surface, so that the region of V_v is $0\text{ Å} \leq z \leq 26\text{ Å}$ and $72\text{ Å} \leq z \leq 100\text{ Å}$. The exact position of the region boundary should affect the intermediate behavior of $C_1(t)$, but little influence on the long time decay rate is expected. Since the liquid layer has a finite thickness (ca. 20 Å), the very long tail of $C_1(t)$ contains artifacts; it also counts molecules that were once condensed at a side of the liquid layer and evaporate again from the other side. From the self diffusion coefficient in the bulk liquid phase, however, the time necessary to cross the liquid layer is estimated to be more than 50 ps.

Both $C_1(t)$ and $C_2(t)$ are fitted fairly well to a single exponential function of t in the range of $0 < t < 25$ ps. The least square fitting gives

$$C_1(t) = C_0 \exp(-t/\tau_1), \qquad \tau_1 = 23.3\text{ ps}, \tag{4}$$

and

$$C_2(t) = C_0 \exp(-t/\tau_2), \qquad \tau_2 = 20.7\text{ ps}, \tag{5}$$

with $C_0 = 9.72$. Considering that C_0 is the average number of molecules in V_v (vapor phase) and that the surface area A is $2 \times 51.0 \times 51.0$ Å^2, we can estimate the apparent condensation rate, or collision rate, J_{coll} as

$$J_{\text{coll}} \equiv \frac{1}{A}\frac{dC_2}{dt}\bigg|_{t=0} = \frac{9.72/20.7}{2 \times 51.0 \times 51.0}\,\text{ps}^{-1}\,\text{Å}^{-2} = 1.50 \times 10^4\,\text{mol}\,\text{s}^{-1}\,\text{m}^{-2}, \tag{6}$$

and the real condensation rate J_{cnds} as

$$J_{\text{cnds}} \equiv -\frac{1}{A}\frac{dC_1}{dt}\bigg|_{t=0} = \frac{9.72/23.3}{2 \times 51.0 \times 51.0}\,\text{ps}^{-1}\,\text{Å}^{-2} = 1.33 \times 10^4\,\text{mol}\,\text{s}^{-1}\,\text{m}^{-2}. \tag{7}$$

Thus, from this autocorrelation analysis, we estimate

$$\alpha_c \equiv J_{\text{cnds}}/J_{\text{coll}} = 89\%. \tag{8}$$

This value is close to the result of direct counting, 80%, but with less arbitrariness about the definition of condensation.

A similar technique is applicable to the case where we choose the liquid region V_l instead of V_v. In this way, we would be able to estimate the passing rate at the liquid-side boundary of the surface layer. More generally, we can estimate the local diffusion near the surface by varying the boundary of the region, which is similar to the technique that was used to investigate the local diffusion around a molecule in bulk methanol [5]. The calculation is under way, and will be reported elsewhere.

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