

Dynamic Processes at a Liquid Surface of Methanol

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Using a molecular dynamics computer simulation technique, evaporation and condensation processes of liquid methanol are studied at room temperature. We observe evaporation of a hydrogen-bonded dimer, which was experimentally suggested. The condensation coefficient (the number ratio of condensed molecules to incident ones) seems to be less than unity as several groups predicted. Since various modes of dynamic processes at the surface are found, more careful analyses and theoretical consideration are necessary.

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An understanding of evaporation and condensation processes on the molecular level is very important in many fields of science and technology. For decades, various experimental techniques (liquid jets, pressure measurements, shock wave tubes, etc.) have been applied to measure the absolute value of the evaporation or condensation rate, but none of them are free of difficulties in conducting the experiments (e.g., surface contamination) or in interpreting the obtained results (e.g., secondary effects such as the surface temperature drop). In particular, the problem of whether the condensation coefficient α_c of associating fluids is unity or not is still quite controversial [1,2]. Here α_c is defined as the number ratio of the condensed molecules to the incident ones; $\alpha_c = 1$ means that all of the molecules colliding with the surface are trapped and immediately condensed. Most of the experimental results support $\alpha_c \approx 1$ for simple liquids such as carbon tetrachloride. For associating liquids (water, alcohols, etc.) and polar fluids (e.g., chloroform), however, there is a wide range of experimental estimations, from $\alpha_c \approx 0.001$ to $\alpha_c = 1$. Also there are various theoretical explanations, one of which is the well-known transition state theory [3], but the applicability to these phenomena is still to be confirmed. Considering the above-mentioned experimental difficulties, computer simulations seem to be one of the best ways to investigate the phenomena in more detail.

Another interesting topic relating to the dynamics at liquid surfaces is the molecular process of evaporation. Faubel and Kisters [4] recently reported some results of their molecular beam experiments of carboxylic acid evaporation, and suggested a special mechanism ("surface-tension model") for hydrogen-bonded dimer evaporation. They mentioned that computer simulations would be suitable to examine the evaporation mechanism on the molecular level.

In this Letter, we briefly describe our results of molecular dynamics (MD) computer simulation concerning the dynamic properties of an associating liquid surface. We

have chosen methanol as our first target, because we already examined static properties of methanol surfaces. In a previous report [5], we found that methanol molecules have very strong orientational ordering at the surface due to their hydrophobic methyl group. In other words, methanol molecules near the surface are trying to maintain as many hydrogen bonds as possible. Therefore, if one of the hydrogen bonds is kept during the evaporation process, we can expect to find dimer evaporation phenomena, though the dimer is not as stable as in the case of carboxylic acid; carboxylic acid dimers can have a double hydrogen bond.

Analyzing the simulation data we have, in fact, observed several cases of dimer evaporation, but the evaporation-condensation processes have turned out to be much more complicated than expected.

A microcanonical ensemble (*NVE*-constant) MD method was adopted. The computer program is similar to what we used before [5] to examine static properties of a liquid-vapor interface of pure methanol: periodic boundary conditions for all three dimensions, the Ewald summation technique for the Coulombic interactions, and the leap-frog algorithm with quaternions for numerical integration of the classical equations of motion. The time step is 0.5 fs ($=0.5 \times 10^{-15}$ s). The short-range potential is truncated at 14 Å. The intermolecular potential is Jorgensen's OPLS (TIPS) for methanol [6].

The total number of molecules is 864. The unit cell is a rectangular prism (51.5 Å \times 51.5 Å \times 100 Å), in the center of which we initially made a thick layer (slab) of the liquid [5]. Since the temperature is low enough, the liquid layer is stable without external fields during the whole simulation. We have estimated the temperature from the total kinetic energy of the system, and adjusted it to be 300 K during the equilibrating process of 40 000 steps, or 20 ps.

Data accumulation is still continuing, but we report here some preliminary results from our 120 ps ($=240\,000$ steps) calculation.

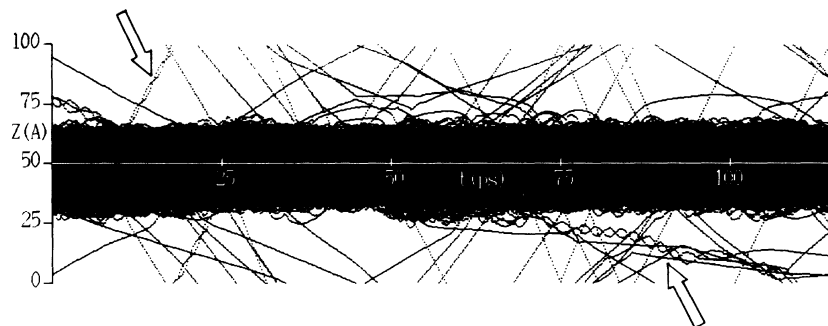


FIG. 1. Surface normal component of the trajectory plotted as a function of time and superimposed for all molecules. The dark area at the center corresponds to the liquid slab. Two pairs of intertwined trajectories corresponding to the hydrogen-bonded dimers in the vapor phase are indicated by arrows.

The difficulty of this kind of computer simulation for investigating dynamic processes exists in the fact that the vapor density is so low at normal temperatures (i.e., near the triple point) that evaporation and condensation are expected to be very rare phenomena. In our simulation, the vapor pressure at the vapor-liquid equilibrium is almost 10 times higher than the experimental value at room temperature; the phase behavior of TIPS methanol is unknown yet, but the critical temperature must be lower than real methanol. It is also probable that the relatively thin liquid slab, the thickness of which is about 25 Å, resulted in truncation of the potential tail and caused the high vapor pressure. Fortunately, this made it possible for us to observe 32 cases of evaporation and condensation processes during the rather short simulation of 120 ps.

Figure 1 is the superimposition of the surface normal component of the trajectory of each molecule (the center of mass). Most of the molecules exist in the center part, which corresponds to the liquid phase, but several trajectories are seen in the outside region, or the vapor phase. The vaporized molecules, shown as the trajectories going from the liquid phase to the vapor, have to return to the liquid phase due to the periodic boundary condition.

The complexity of the trajectories in the vapor phase apparently reflects the various mechanisms of dynamic processes near the liquid surface. One can see in the figure several examples of condensation, evaporation, and reflection of molecules at the surface.

The most remarkable observation is the dimer evaporation shown as two intertwined trajectories. During the period 10–24 ps, one can see an almost freely flying dimer pair (shown by the left arrow in Fig. 1); notice the periodic boundary condition. On the other hand, the dimer generated at the time of about 70 ps interacted with a third molecule during the flight and the pair was destroyed at around 90 ps at 20 Å from the liquid surface (shown by the right arrow in Fig. 1). We believe that these are the first evidence of dimer evaporation on the molecular level.

Data analysis is still in progress, but we show several

examples of the molecular energy excitation and relaxation process. Figure 2 shows the energies of each molecule of the dimer pair from the period 10–24 ps. During the free flight, the potential energy is almost constant; the value of about -3000 K (-25 kJ/mol) suggests that a very strong hydrogen bond exists between the dimer molecules. The kinetic energy of each molecule oscillates during the flight because the translational and rotational modes of the dimer overlap; the phases of the kinetic energy oscillation of the two molecules differ by π so that the total kinetic energy of the dimer is almost constant.

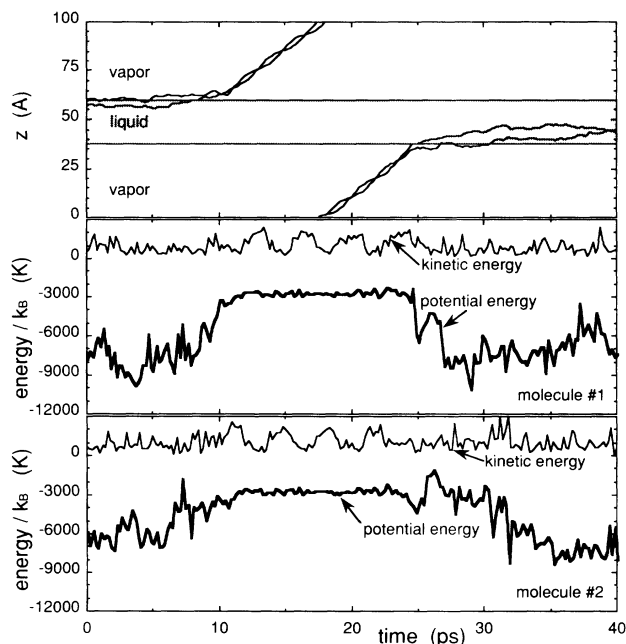


FIG. 2. (Top) Surface normal component of the trajectory for each molecule of a dimer pair as a function of time. The phase boundary shown is the Gibbs dividing surface determined from the averaged density profile of the 120 ps simulation data. (Middle and bottom) Kinetic and potential energies of each molecule of the dimer as a function of time. Energy is shown in the unit of absolute temperature.

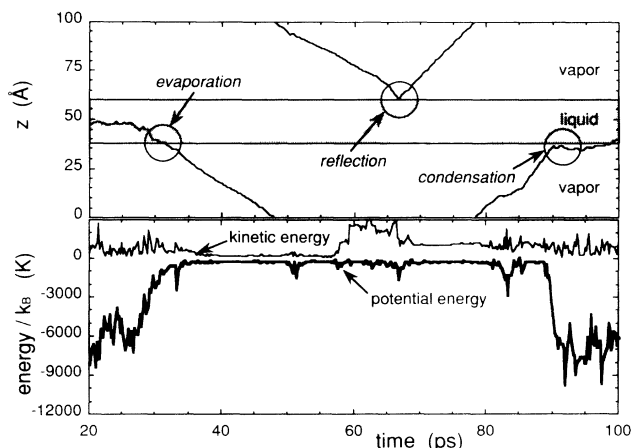


FIG. 3. Similar to Fig. 2 for evaporation, reflection, and condensation of a single molecule.

This suggests that the intermolecular vibration of the dimer is somehow "frozen," but further analysis is needed to understand the dimer evaporation mechanism. The other dimer pair (70–90 ps) is less stable; the potential energy of the pair oscillates around an average value of about -2000 K, which suggests that there remains intermolecular vibration.

A typical evaporation and condensation process of a single molecule is shown in Fig. 3. In many cases, it took 5–10 ps to gather excitation energy for evaporation and to relax extra energy for condensation. The figure also shows an example of reflection at the surface. The molecule came very near to the surface, but somehow the energy relaxation did not take place and the molecule bounced back. These complex behaviors (i.e., why energy relaxation or dissipation sometimes takes place and sometimes not) may be attributed to the strong orientational order of methanol molecules at the surface, but more detailed analyses are needed. During the "free flight" of single molecules in the vapor phase, the potential energy is close to zero as shown in Fig. 3. However, occasional interactions (or collisions) with other vapor molecules take place. Detailed data analyses, such as the mean free path, are in progress.

As for the condensation coefficient, we observed 23 cases of condensation out of 28 incident molecules. Simple calculation gives $\alpha_c = 23/28 \approx 80\%$. However, the phenomenon may be much more complicated; incident molecules sometimes cause local instability on the surface, and neighbor liquid molecules evaporate while the incident ones stick to the surface. In Fig. 4, we show sequential snapshots of the above-mentioned dimer evaporation. The dimer evaporates just after a trimer (shown as three intertwined trajectories at 0–10 ps in Fig. 1) collided with the surface. Large turbulence is seen at the place of the trimer collision (9.2 ps), and the dimer which was located only several angstroms from the collision spot evaporates. It is probable that a part of the

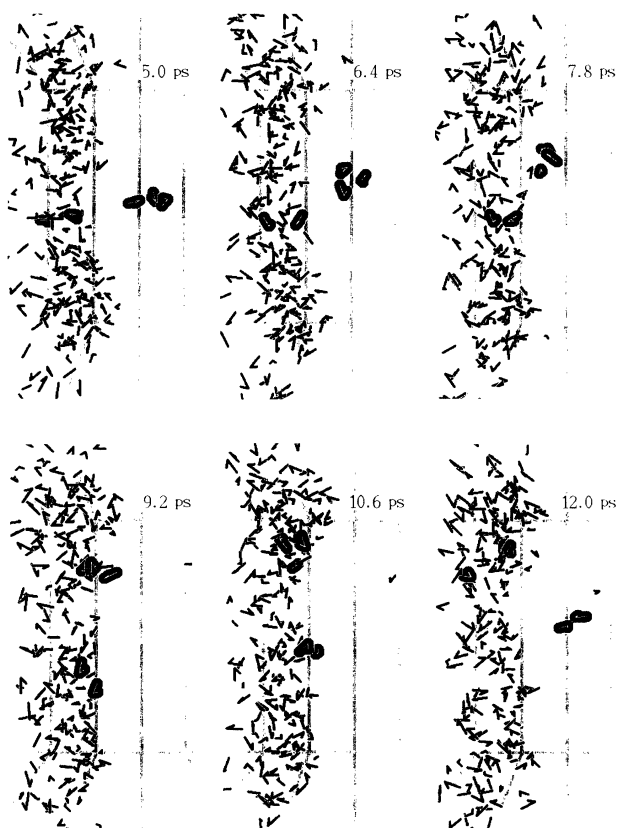


FIG. 4. Sequential snapshots of a methanol liquid surface. The time is shown on the top of each figure. One can see clearly a trimer collision (condensation) and a successive dimer evaporation. Molecules other than the trimer and the dimer are drawn as a wire model. The longitudinal lines in the background are 10 Å apart.

excess energy of the trimer was conveyed by the hydrogen bond network and spent to excite the dimer. Detailed investigation of the energy dissipation mechanism is apparently necessary to examine the condensation and evaporation rates.

We are grateful to Professor S. Fujikawa of Toyama Prefectural University for drawing our attention to this field. A part of the calculations were carried out at the Computer Center of the Institute for Molecular Science.

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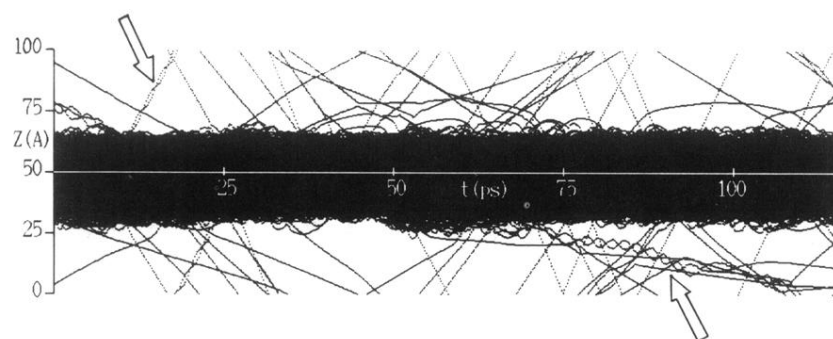


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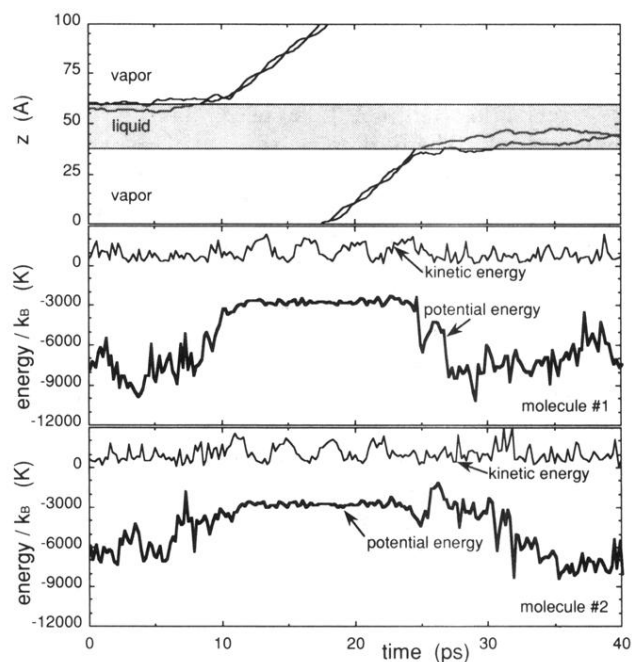


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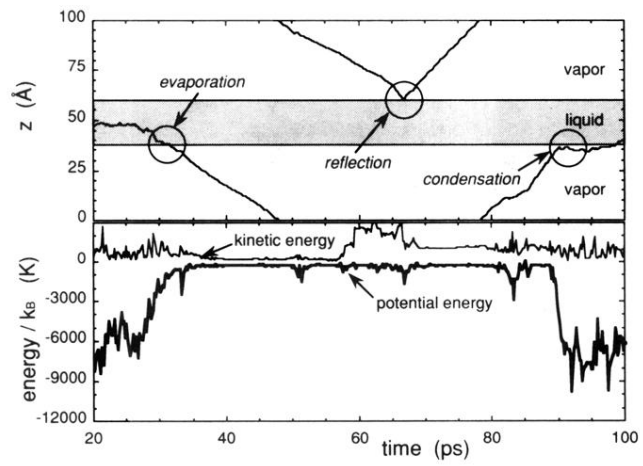


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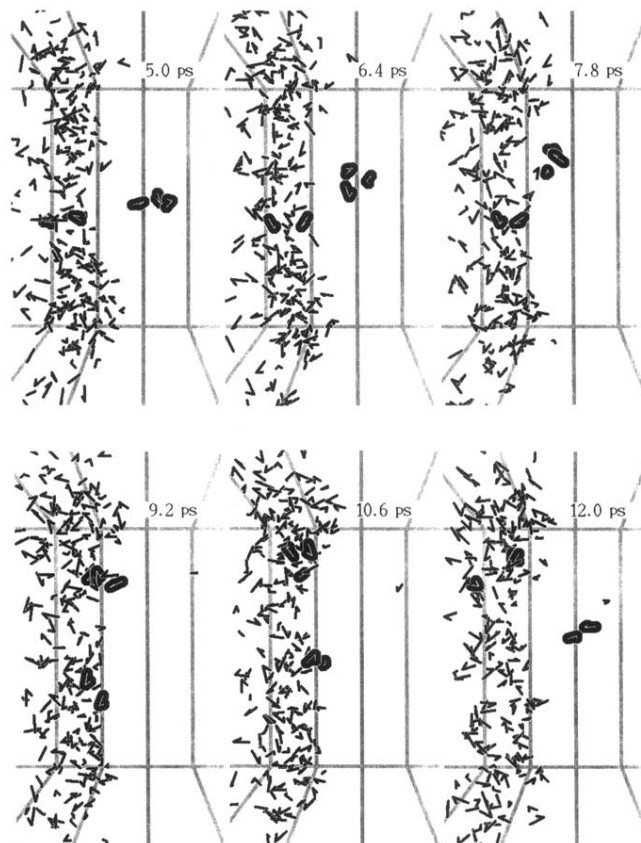


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