Dynamics near a Liquid Surface:
Mechanisms of Evaporation and Condensation

K. Yasuoka, M. Matsumoto, and Y. Kataoka*

Department of Applied Physics, Nagoya University, Furo,
Chikusa-ku, Nagoya 464-01, Japan
*Department of Materials Chemistry, Hosei University,
Kajino 3-7-2, Koganei 184, Japan

Abstract

The rates of evaporation and condensation under the vapor-liquid equilibrium condition are investigated with a molecular dynamics computer simulation for argon at 80 K, methanol at 300 K, and water at 400 K. The molecular reflection at the surface, which is related to the condensation coefficient α, is divided into two parts, self reflection and molecular exchange. There is no significant difference among the three substances concerning the ratio of self reflection to collision. The total ratio of reflection is estimated as $\alpha \simeq 0.8$ for argon, 0.2 for methanol, and 0.4 for water. The ratio of molecular exchange is much larger for methanol and water than for argon, which suggests that the conventional assumption of condensation as a unimolecular process fails for associating fluids.

I. Introduction

Evaporation and condensation are fundamental and important in various fields of science and engineering. Although a number of experimental and theoretical studies have been made on evaporation and condensation rates for decades, there still remain many problems. Although the collision rate is easily estimated with the kinetic theory of gas dynamics, all incident molecules are not necessarily caught on the liquid surface, and thus the condensation coefficient α, which is the ratio of the observed condensation rate to the ideal condensation one, becomes important. It is usually assumed that α is very close to unity (complete condensation) for many fluids,[1] but there has been controversy over α of associating fluids (e.g., water and alcohols). This arises from the experimental difficulty in estimating the absolute rate of condensation or evaporation under the vapor-liquid equilibrium condition. A transition state theory has been applied to calculate α under the assumption that the condensation process is a unimolecular chemical reaction.[2] It predicts $\alpha \simeq 1$ (complete capture) for simple fluids such as argon. In the case of associating fluids, however, much smaller α is expected due to the potential barrier caused by the rotational restriction of liquid molecules. Since the experimental results of α widely scatter,[1] we still have to check with great care the validity of assumptions made in the theoretical treatments.

Computer simulations with molecular dynamics (MD) technique are very suitable to investigate these evaporation condensation phenomena at a molecular level. Thus, we have carried out MD simulations for three systems, argon (a typical simple fluid) at $T = 80$ K and two associating fluids, methanol at $T = 300$ K and water at $T = 400$ K. In this paper, we briefly describe the results of our simulations and data analyses, and discuss the differences among the three from the viewpoint of dynamics at the surface.
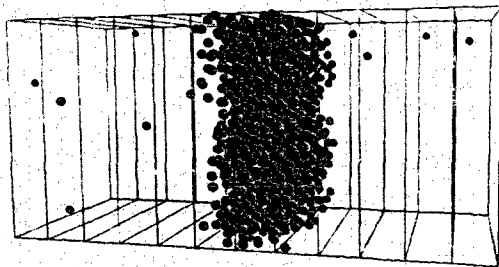
Fig. 1 A snapshot of the simulation (Argon at 80 K).

II. Simulation Technique

We adopted a microcanonical ensemble MD method. The Lennard-Jones potential was used for the molecular interaction in the argon, OPLS potentials for methanol and water. We make a liquid slab with thickness of about 10 molecules at the center of the rectangular unit cell with periodic boundary conditions for all three dimentions. Figure 1 is a snapshot of a typical molecular configuration. Both sides of the slab are free liquid surfaces, on which molecules can evaporate and condense. The cell size along the surface normal is typically 100 Å, and the surface area is 50 Å×50 Å. The number of molecules is 1200 for argon, 864 for methanol, and 1024 for water. Other technical details are described elsewhere.[3,4]

III. Results and Discussion

After equilibrating the system, we accumulated the configurations for 997 ps (argon), 300 ps (methanol) or 375 ps (water), from which we study dynamic properties concerning evaporation-condensation processes.

Self condensation

In most of studies so far (experimental as well as theoretical) on the condensation coefficient α, the condensation process has been considered as a unimolecular chemical reaction, which means that the evaluation of α is equivalent to estimating how many vapor molecules are reflected after colliding with the liquid surface. In order to avoid confusion, let α_{self} be the condensation coefficient from this point of view, since we show later that the assumption of the unimolecular reaction is not always correct.

In principle, we can evaluate α_{self} by direct counting of collision and reflection events from the molecular trajectory data; for both cases, we observed sufficient number (about 200) of collision events. To estimate α_{self} quantitatively, we have developed an autocorrelation function method.[5] The result is $\alpha_{self} \simeq 90\%$ and there is no quaiitative difference among various types of fluids, which suggests that the condensation as a unimolecular chemical reaction is a barrierless process. Calculation of the local chemical potential also supports this barrierless picture.[6]

Total condensation

In visualizing the molecular configurations, we sometimes observed that vapor molecules colliding with the liquid surface apparently drove other molecules out of the liquid. This kind of correlation between the condensation flux and the evaporation flux, or "molecular exchange," may have a significant effect on the rate of condensation. Following

Table 1 Comparison of condensation behaviors estimated from the simulation data

		Argon $(T = 80\,K)$	Methanol $(T = 300\,K)$	Water $(T = 400\,K)$
Ratio of reflection	Self $(1 - \alpha_{self})$	0.12	0.14	0.05
	Exchange	0.08	0.66 ± 0.10	0.55 ± 0.05
	Total $(1 - \alpha)$	0.20	0.80 ± 0.10	0.60 ± 0.05
Condensation coefficient α		0.80	0.20 ± 0.10	0.40 ± 0.05
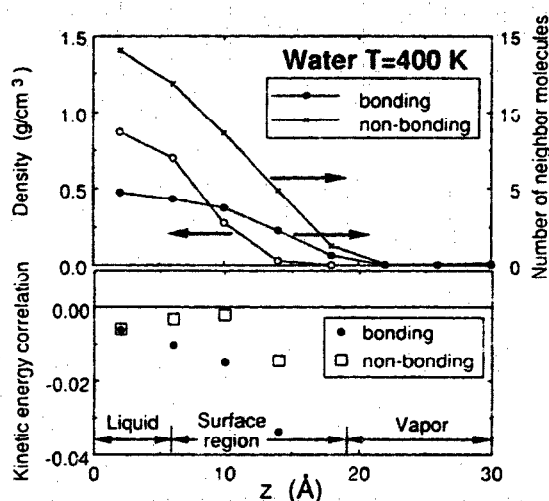
Fig. 2 Surface of liquid water at T=400 K. Density profile and number of neighboring molecules (top) and the kinetic energy correlation (bottom).

a general framework of chemical reaction theory, we have developed a memory function method to estimate the phenomena.[7] The total condensation coefficient α is calculated by using the correlation of colliding and evaporating fluxes with a memory function. The estimated value is $\simeq 0.80$ for argon, $\simeq 0.20 \pm 0.1$ for methanol, and $\simeq 0.40 \pm 0.05$ for water. Comparing α with α_{self}, we can also evaluate the ratio of the molecule exchange.

The results are summarized in Table I. The ratio of self reflection and molecular exchange is very similar for argon. However, in the case of associating fluids, the ratio of the exchange is several times larger than that of the self reflection. This implies that the condensation cannot be regarded as a unimolecular process, especially in the case of associating fluids.

Heat transfer by hydrogen bonds

A key point to understand the above difference between simple fluids and associating fluids is the mechanism of molecular heat transfer accompanying the evaporation and condensation at the surface. If the energy is not transferred (or dissipated) fast enough, the hitting molecule cannot lose the extra energy to condense itself, and will finally re-

evaporate, which is the self-reflection. On the other hand, the surface molecules receive the extra energy from the hitting molecule, and if the amount of the received energy is too much, the surface molecule may get evaporated in exchange of the condensation of the hitting molecule, which is the molecular exchange.

Since it is difficult to evaluate the precise local heat conductivity from the simulation data, we instead calculate the kinetic energy correlation between neighboring pairs; if a large amount of heat is transfered between a pair of neighboring molecules, there should be a strong correlation between the kinetic energy fluctuations of each molecule. A part of the results is shown in Fig. 2, where the kinetic energy correlations are shown for hydrogen-bonding pairs and non-bonding pairs in the case of water. The correlation is several times stronger for bonding pairs than non-bonding ones; a similar result is obtained for methanol. In the case of argon, the correlation is similar to that between non-bonding pairs of associating fluids.

From these evidences, we can easily imagine what happens in the condensation process of associating fluids: The latent heat released in the instance of condensation is rather large, but is transferred efficiently by the strong hydrogen bonds. However, since the number of bonding pairs is only 1 or 2, the neighbor becomes easily evaporated by the transferred heat, and thus the molecular exchange is often observed. Further analyses are now under way.

Summary

Using a molecular dynamics computer simulation, we have investigated the evaporation–condensation dynamics for argon, methanol, and water. The ratio of condensed molecules to surface-colliding ones, α_{self}, is about 90 % for all substances, although surface properties of methanol and water are very different from those of argon. However, the total condensation coefficient α estimated with flux correlation of evaporation and condensation is much smaller for methanol and water than for argon. The difference between α and α_{self} is caused by molecular exchange at the surface. In the case of methanol and water, the molecular exchange is a dominant factor to determine the condensation–evaporation rate. A rough sketch for the difference among the species is given from the viewpoint of heat transfer near the liquid surface.

Acknowledgments

References

1   H.K. Cammenga, *Current Topics in Materials Science*, ed. by E. Kaldis (North-Holland, Amsterdam, 1980), Vol. 5, and references therein.
2   S. Fujikawa and M. Maerefat, JSME II, **33**, 634 (1990).
3   K. Yasuoka, M. Matsumoto, and Y. Kataoka, J. Chem. Phys., **101**, 7904 (1994).
4   M. Matsumoto, K. Yasuoka, and Y. Kataoka, J. Chem. Phys., **101**, 7912 (1994).
5   M. Matsumoto and Y. Kataoka, Mol. Simulation, **12**, 211 (1994).
6   K. Yasuoka, M. Matsumoto, and Y. Kataoka, Bull. Chem. Soc. Jpn., **67**, 859 (1994).
7   M. Matsumoto, K. Yasuoka, and Y. Kataoka, Therm. Sci. Eng., **2**, 64 (1994).