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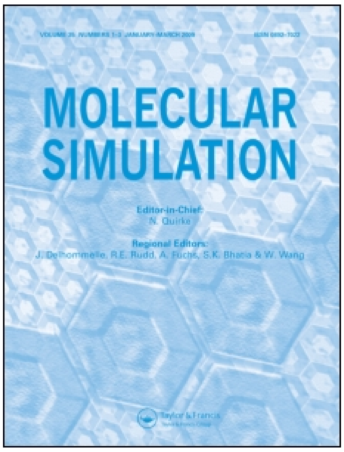

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MOLECULAR DYNAMICS OF LIQUID SURFACES

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The long-standing problem of how the evaporation-condensation rate differs with each materials was solved with molecular dynamics computer simulations and recent experiments. The difference among various fluids (argon, methanol, water, and acetic acid) is described in terms of the condensation coefficient. In the case of associating fluids, a very low condensation rate is caused by frequent molecular exchanges, which have been neglected in the conventional theoretical treatments. A qualitative explanation is given and an attempt to develop a new evaporation-condensation model is described from the view point of microscopic heat transfer near the liquid surface.

KEY WORDS: Liquid surface, molecular dynamics, evaporation, condensation, simple fluid, associating fluid.

1 INTRODUCTION

For decades, various experimental techniques have been applied to measure the absolute rates of the evaporation or condensation, but there remain many problems [1]. The principle of measurement is very similar to the measurement of chemical reaction rates, in which a small perturbation is given to the equilibrium system and the relaxation is observed. The main difficulties in obtaining an accurate evaporation or condensation rate arise from the character of interfacial systems: (i) temperature control, and (ii) surface contamination.

Microscopically, condensation is caused by the flux of vapor molecules hitting on the liquid surface, which is very easily estimated with the kinetic theory of gases. However, all incident molecules are not necessarily caught on the surface, and thus the condensation coefficient α, which is the ratio of the observed condensation rate to the ideal condensation rate, becomes relevant. It is usually assumed that α is very close to unity (complete condensation) for many fluids [1], but there has been long-standing controversy over α of associating fluids (*e.g.*, water and alcohols). Due to the experimental difficulties mentioned above, detailed analyses and accurate experimental data for α have not been accessible until quite recently [2, 3].

There has been little theoretical progress either, mainly due to the lack of information concerning the molecular mechanism of condensation and evaporation. Under the assumption that the condensation is a unimolecular processs, a classical transition state theory (TST) has been applied, and the potential barrier near the surface has been estimated. It predicts that associating fluids such as alcohols and water should have a smaller α than simple fluids due to the molecular orientational order near the liquid surface [4–6]. This prediction seems to have a qualitative agreement with some of the experimental results, but it cannot be conclusive, considering the large discrepancy among experiments.

Figure 1 depicts the evaporation-condensation process under the equilibrium condition from three points of view in order to see the difference between the experimentally observed evaporation-condensation rate and the theoretically derived one. In the Figure 1(a) which is macroscopic, two fluxes of condensation and evaporation balances each other; this picture is correct but hardly useful to predict the evaporation-condensation rate, because estimating these fluxes is difficult. The Figure 1(b) is also a macroscopic view, but the condensation flux is expressed as the difference between the fluxes of collision and reflection. The collision rate is easily evaluated with the kinetic theory of gases if the vapor density is low enough (*i.e.*, the temperature is well below the gas-liquid critical temperature), but the ratio of reflection to collision, or the condensation coefficient α, should be estimated separately. Conventionally, it has been believed that Figure 1(c) is the correct microscopic picture corresponding to Figure 1(b). Thus, the estimation of α was thought to be equivalent to the calculation of the raio of self reflection of vapor molecules at the surface. The above-mentioned prediction with TST is an example of this approach.

Recently, we have carried out molecular dynamics (MD) computer simulations to investigate the microscopic mechanism of evaporation and condensation for argon

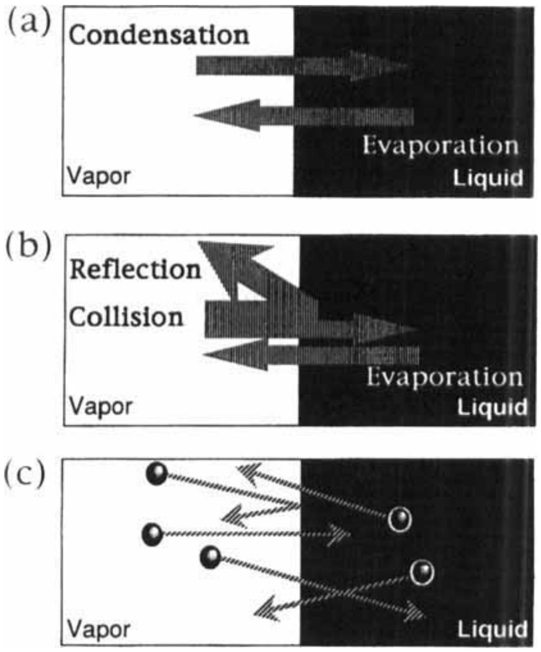

Figure 1 Schematic view of evaporation and condensation: (a) and (b) are from the macroscopic point of view, and (c) is from the microscopic (molecular) one.

and methanol under the vapor-liquid equilibrium [7, 8], and have found that the picture 1(c) is not always correct; there is a missing process which is relevant especially for associating fluids. In this paper, the simulational results for four substances (argon, methanol, water, and acetic acid) are briefly described, and the differences are discussed at a molecular level.

2 COMPUTER SIMULATIONS

A microcanonical ensemble MD method was adopted. We used a rectangular unit cell with periodic boundary conditions. Molecules (methanol, water, acetic acid) are modeled as a rigid body with partial charges and Lennard-Jones interaction sites, and Jorgensen's OPLS potential parameters are adopted [9–11]. For the argon system, we used the 12–6 Lennard-Jones interaction potential. A liquid slab with thickness of several molecules is initially formed. Both sides of the slab are free liquid surfaces, on which molecules can evaporate and condense. The surface area is typically $50 \times 50\,\text{Å}^2$ and the number of molecules is an order of 1000. Conventional techniques such as the Ewald sum and the quaternions were also adopted. Detailed conditions are described elsewhere [7, 8].

Since the temperature dependence of the condensation coefficient is not strong in the temperature range which we investigated here, the comparison is made at one temperature: argon at 80 K, methanol at 300 K, water at 400 K, and acetic acid at 525 K. In either case, the molecular trajectories were accumulated for more than 300 ps after the liquid-vapor equilibrium was achieved.

3 SELF REFLECTION AT THE SURFACE

From the molecular trajectories, we can evaluate the condensation coefficient α_{self} (the number ratio of condensed molecules to colliding ones) by counting the condensation and reflection events; for a more elaborated method using number autocorrelation functions, see ref. [12]. The resulting α_{self} is 5–16% for all substances studied here, contrary to the experimental studies and theoretical predictions with TST. These results suggest that condensation is a barrierless process, which is supported by our calculation of the local chemical potential [13].

4 MOLECULAR EXCHANGE

However, we have sometimes observed that vapor molecules colliding with the liquid surface drive other molecules out of the liquid. The significance of this molecular exchange can be estimated through the correlation of two fluxes on the vapor side of the interfacial region, J_{coll} for the flux of vapor molecular collision, and J_{ent} for the flux entering the vapor region [14]. With a memory function $\kappa(t)$, the relation is expressed as

$$J_{\text{ent}}(t) = J_{\text{evap}}(t) + \int_0^\infty \kappa(t') J_{\text{coll}}(t - t')\,dt', \tag{1}$$

where J_{evap} is the entering flux which is independent of J_{coll}. Taking the ensemble average for each term in eq. (1), we obtain the following expression for the total condensation coefficient α:

$$\alpha = \frac{\langle J_{\mathrm{cnds}} \rangle}{\langle J_{\mathrm{coll}} \rangle} = \frac{\langle J_{\mathrm{evap}} \rangle}{\langle J_{\mathrm{coll}} \rangle} = 1 - \int_0^{\infty} \kappa(t')\,dt'. \tag{2}$$

The kernel $\kappa(t)$ is evaluated from the simulation data [7] as

$$\langle \Delta J_{\mathrm{coll}}(t_1) \Delta J_{\mathrm{ent}}(t_2) \rangle = \begin{cases} 0 & t_1 > t_2 \\ C_{\kappa}(t_2 - t_1) & t_1 \leqslant t_2 \end{cases} \tag{3}$$

where Δ represents the deviation from its average, and C is a constant representing the mean square variation of ΔJ_{coll}.

As a typical result, an example of the memory function and its time integral is shown in Figure 2 for the acetic acid system. The memory function is rather noisy, but we can estimate α from the plateau value of its time integral.

The results are summarized in Table 1. Recently, Fujikawa *et al.* have reported α with high precision using a shock tube technique for several substances [2,3]. Our results for α satisfactorily agrees with their experimental ones, and thus we conclude that the evaporation-condensation rate of associating fluids is much lower than that of simple fluids, mainly due to the molecular exchange phenomena. Thus, Figure 1(c) is an unsatisfactory picture, and the predictions based on it is incorrect, especially for associating fluids.

In particular, α of acetic acid is extremely small. The reason is not fully understood, but vapor dimers stabilized by the double hydrogen bond seem to play some

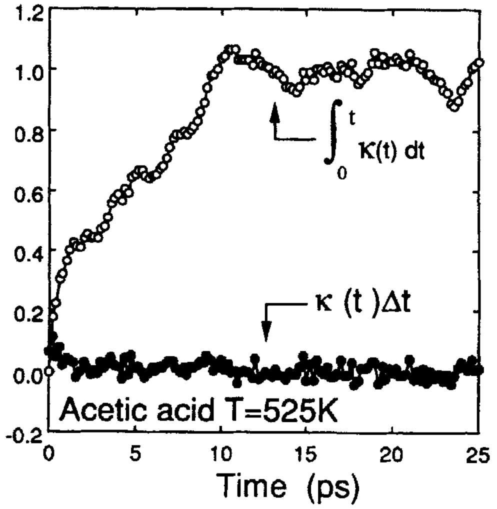

Figure 2 Memory function $\kappa(t)$ and its time integral for acetic acid. Δt is the data storage time step.

Table 1 Ratio of reflection and condensation estimated from out MD simulations.

Substance *Temperature*		*Argon* *80 K*	*Methanol* *300 K*	*Water* *400 K*	*Acetic acid* *525 K*
Ratio	Self	0.06	0.11	0.05	0.16
of	Exchange	0.14–0.24	0.59–0.69	0.5–0.6	> 0.8
reflection	Total	0.2–0.3	0.7–0.8	0.55–0.65	> 0.95
Condensation coefficient α		0.7–0.8	0.2–0.3	0.35–0.45	< 0.05

role. At the temperature of 525 K, nearly half of the vapor molecules form such stable dimers.

5 TOWARD A NEW EVAPORATION-CONDENSATION MODEL

One of the goals for theoretical studies of condensation-evaporation dynamics is certainly to develop a model suitable for calculating the condensation-evaporation rate using observable (preferably macroscopic) material properties, under various inequilibrium conditions as well as under the equilibrium one.

Let us concentrate on the equilibrium case. Since the rates of condensation and evaporation are equal, there are two approaches: modeling the evaporation process to estimate the evaporation rate, and modeling the condensation process to evaluate the condensation rate.

5.1 Modeling the Evaporation Process

The evaporation can be considered as the process in which a liquid molecule escapes from a potential well. A rough estimation of the evaporation rate $\langle J_{\mathrm{evap}} \rangle$ is thus

$$\langle J_{\mathrm{evap}} \rangle \simeq \kappa \tau^{-1} \exp\left(-\frac{\Delta\phi}{\mathrm{k_B} T} \right) C, \tag{4}$$

where $\kappa \simeq 1$ is the transmission coefficient, τ^{-1} is the characteristic frequency of the surface molecule motion, $\Delta\phi$ is the depth of the potential well, $\mathrm{k_B}$ is the Boltzmann constant, T is the temperature, and C is the surface number density which is easily evaluated from the bulk liquid density.

The key point is thus the estimation of τ^{-1} and $\Delta\phi$. We roughly evaluated them by minimizing the potential energy of a surface molecule in fixed surrounding neighbors; spatial freedoms (translations and, if exist, rotations) of a chosen molecule are varied so that the molecule has a minimum potential energy in the fixed surroundings. $\Delta\phi$ is estimated from the depth of the minimum energy, and the period τ is obtained from the quadratic expansion of the energy around the minimum point. An example is shown in Figure 3 where the distribution of the minimized energy and the period of the lowest frequency normal mode are calculated for the argon system. The minimized energy of the surface region is only half that of the bulk liquid, but

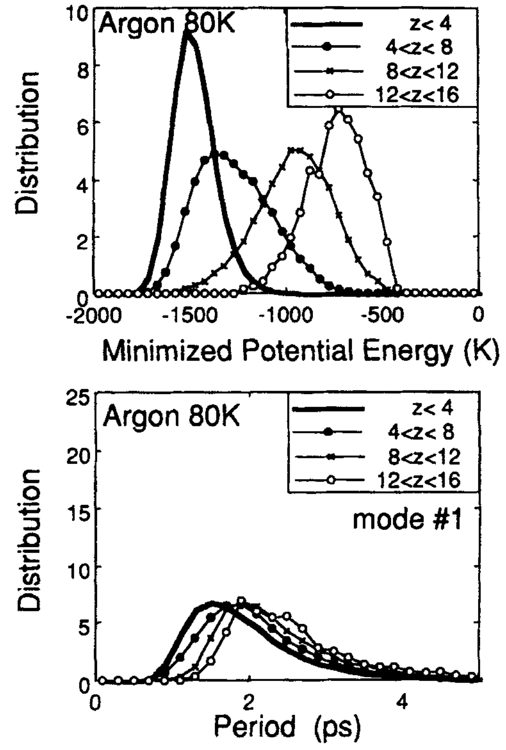

Figure 3 Distribution of the minimized energy (upper) and the period of the slowest normal mode (down). The whole system is sliced into layers of 4 Å in thickness; the region of $z < 4$ Å is the bulk liquid, and the region of $12 < z < 16$ corresponds to the outermost surface layer.

the period is much less sensitive to the environment; similar results are obtained for the case of methanol.

Assuming that $\Delta\phi$ and τ is independent of the temperature, eq. (4) gives $\langle J_{\mathrm{evap}} \rangle$. Combining the collision rate $\langle J_{\mathrm{coll}} \rangle$ which is calculated with the kinetic theory of gases, a monotonous decrease of α is predicted as shown in Figure 4.

This TST-like formulation for the evaporation process is simple, but has a disadvantage that the estimation of $\Delta\phi$ and τ is not easy nor unique.

5.2 Modeling the Condensation Process

Let us imagine what will happen just after a vapor molecule hit the surface. A large amount of energy is released as the form of latent heat, and the hitting point on the surface will be locally heated up. The increase of the local temperature depends both on the amount of the released energy and the local heat capacity in the surface region. Thus, the first question comes up: Can we define (and measure) the local heat capacity, or equivalently molecular specific heat, in the surface region? 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

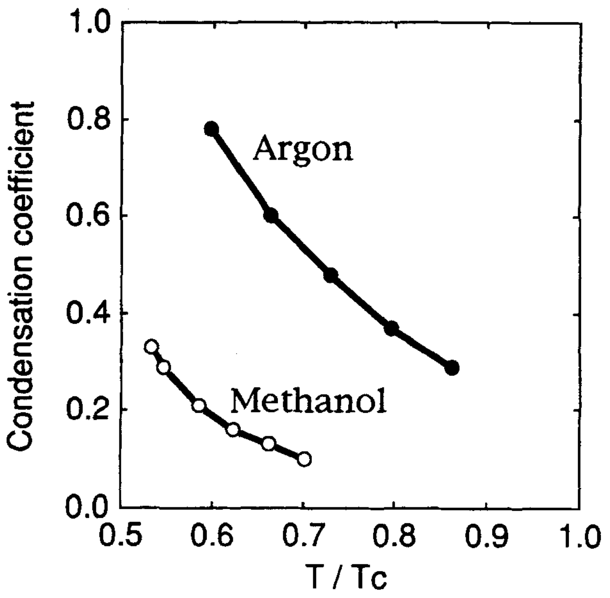

Figure 4 Condensation coefficient obtained from eq. (4) is plotted as a function of temperature. The temperature is normalized by the gas-liquid critical temperature T_c(150.7 K for argon and 512.6 K for methanol).

self-reflection. Now the second question is: How fast is the energy relaxation near the surface? On the other hand, the surface molecules receive the extra energy from the hitting molecule. 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. Thus, the final question is: How does the hitting molecule distribute the extra energy to the neighbors?

We have to answer these questions in order to make a model for the condensation process. The modeling is not completed, though data analyses so far suggest that the above approach is promising [15]. Let us make a rough estimation as follows: (1) the released energy ΔE by the colliding molecule is half the latent heat, which is suggested by the results of the energy minimization mentioned above. (2) the number of molecules N_s surrounding the colliding one is also half the number of nearest neighbors in bulk liquid. (3) the heat conductivity λ_s near the surface is also half that of bulk liquid because the number of "heat conduction channel", roughly corresponding to the number of neighboring molecules, is half of that in bulk liquid.

With these assumptions, we easily estimate the relaxation time τ_E of the released energy as

$$\tau_E \simeq N_s c_p r_s^2 \lambda^{-1}, \tag{5}$$

where c_p is the molecular heat capacity, and r_s is the mean distance between neighboring molecules. Comparing τ_E with the characteristic period τ, the self reflection ratio is roughly evaluated. Moreover, assuming that the ΔE is randomly distributed to N_s neighbors, the molecular exchange ratio can be also estimated.

A test calculation gives $\alpha \sim 0.7$ for argon, 0.1 for methanol, and 0.4 for water, which qualitatively agree with the results in Table 1. Thus, the difference of α among various substances is explained in this model as follows [15]: (1) A surface molecule of simple fluids is weakly interacting with several other molecules. When a vapor molecule collides with the surface, the extra energy (latent heat) diffuses through the interactions. Since the number of "energy receivers" is large and the energy transfer is slow, there is not much molecular exchange, and the condensation coefficient is close to unity. (2) On the other hand, a surface molecule of associating fluids interacts (or forms hydrogen bonds) with much a smaller number of neighbors. The interaction is so strong that the latent heat can be easily and quickly transferred to the neighboring molecules; thus the self condensation is almost complete. However, since the number of the bonding neighbors is small ($1 \sim 2$), the transferred large heat tends to re-evaporate the neighbors, or the molecular exchange takes place. This is only a rough sketch, and quantitative investigations are required to develop a useful condensation model.

6 CONCLUSIONS

Molecular dynamics simulation of liquid surfaces has brought a new insight of "molecular exchange" concerning the evaporation-condensation rate, which has been neglected in the theoretical studies. The obtained condensation coefficient agrees with most recent experiments. By investigating the microscopic mechanism, construction of a new model of evaporation and condensation is promising, especially from the viewpoint of molecular-scale energy transfer.

Acknowledgements

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References

[1] H. K. Cammenga, *Current Topics in Materials Science*, Vol. 5, ed. by E. Kaldis, North-Holland, Amsterdam 335 (1980).

[2] S. Fujikawa and M. Maerefat, "A study of the molecular mechanism of vapour condensation", JSME Int. J. II, **33**, 634 (1990).

[3] S. Fujikawa and M. Maerefat, "A shock-tube method for the study of vapor-liquid interface phenomena", *Therm. Sci. Eng.*, **2**, 60 (1994).

[4] G. Wyllie, "Evaporation and surface structure of liquids", Proc. Royal Soc. London, **197A**, 383 (1949).

[5] S. S. Penner, "On the kinetics of evaporation", *J. Chem. Phys.*, **56**, 475 (1952).

[6] E. M. Mortensen and H. Eyring, "Transmission coefficients for evaporation and condensation", *J. chem. Phys.*, **64**, 846 (1960).

[7] K. Yasuoka, M. Matsumoto and Y. Kataoka, "Evaporation and condensation at a liquid surface I. Argon", *J. Chem. Phys.*, **101**, 7904 (1994).

[8] M. Matsumoto, K. Yasuoka and Y. Kataoka, "Evaporation and condensation at a liquid surface II. Methanol", *J. Chem. Phys.*, **101**, 7912 (1994).

[9] W. L. Jorgensen and M. Ibrahim, "Transferable intermolecular potential functions. Application to liquid methanol including internal rotation", *J. Am. Chem. Soc.*, **103**, 341 (1982).

[10] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey and M. L. Klein, "Comparison of simple potential functions for simulating liquid water", *J. Chem. Phys.*, **79**, 926 (1983).

[11] J. M. Briggs, T. B. Nguyen, and W. L. Jorgensen, "Monte Carlo simulations of liquid acetic acid and methyl acetate with the OPLS potential functions", *J. Phys. Chem.*, **95**, 3315 (1991).

[12] M. Matsumoto and Y. Kataoka, "Evaporation and condensation at a liquid methanol surface", *Mol. Simulation*, **12**, 211 (1994).

[13] K. Yasuoka, M. Matsumoto and Y. Kataoka, "Evaporation and condensation as a unimolecular chemical reaction: does the potential barrier exist at a molecular liquid surface?", *Bull. Chem. Soc. Jpn.*, **67**, 859 (1994).

[14] M. Matsumoto, K. Yasuoka, and Y. Kataoka, "Microscopic features of evaporation and condensation at liquid surfaces: molecular dynamics simulation", *Therm. Sci. Eng.*, **2** 64 (1994).

[15] M. Matsumoto, K. Yasuoka, and Y. Kataoka, "Molecular simulation of evaporation and condensation II. Energy fluctuations and heat transfer", Proc. 4th ASME/JSME Therm. Eng. Joint Conf., **2**, 465 (1995).