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Molecular dynamics of fluid phase change

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Abstract

We have applied molecular dynamics simulation for various fluid systems to investigate microscopic mechanisms of phase change. The paper reviews the works recently done in our group. (1) Evaporation–condensation dynamics of pure fluids under equilibrium condition: Besides the difference of condensation coefficient among species, its strong temperature dependence is found, which can be explained from the viewpoint of the structure of liquid surface and the molecular exchange. (2) Evaporation–condensation dynamics of pure fluids under non-equilibrium condition: The condensation behavior seems strongly dependent on the temperature and the density of vapor. This kind of molecular simulation will be useful for longstanding questions such as how fast hot vapor condenses on cool liquid surface, or what the evaporation coefficient means. (3) Gas absorption dynamics: CO_2 gas absorption mechanism on water surface is similarly analyzed, from the view point of adsorption–desorption dynamics. © 1998 Elsevier Science B.V.

Keywords: Liquid evaporation; Vapor condensation; Gas absorption; Computer simulation; Molecular dynamics

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1. Introduction

Investigation of fluid phase change has both fundamental and practical importance in many fields of science and engineering. A number of experimental techniques have been invented to measure the absolute rate of phase change, such as evaporation and condensation rates, but there remain many technical problems [1]. Another problem is our very limited knowledge of molecular dynamic processes during the phase change. For example, the condensation coefficient α, defined as the number ratio of condensation flux to collision flux of vapor, has been calculated with the classical transition state theory. In this treatment, however, the condensation process is assumed to be unimolecular 'chemical reaction', the validity of which assumption was found to be inappropriate only recently by us [2,3].

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Recently, we have applied molecular dynamics (MD) computer simulation technique to these fluid phase change phenomena [2–4] to investigate the dynamic process accompanying the phase change. The MD technique is simple, but applicable to wide range of phase change phenomena, such as evaporation and condensation. In this paper, we describe some of our recent approaches. The topics are: (1) evaporation–condensation of pure fluids under liquid–vapor equilibrium, (2) evaporation–condensation of pure fluids under non-equilibrium condition, and (3) evaporation–condensation of fluid mixtures. Using similar techniques, we also studies other phenomena (homogeneous nucleation in supersaturated vapor and cavitation in negative pressure liquid) closely related to this, the method and part of the results of which are described elsewhere [5,6].

2. Evaporation–condensation under liquid–vapor equilibrium

It is impossible to experimentally measure the evaporation and condensation rates under the complete liquid–vapor equilibrium condition, because both fluxes of evaporation and condensation are balanced. Using an MD simulation method, however, we can investigate the dynamic behavior of molecules under such conditions.

A liquid film of enough thickness is prepared in the simulation box. Both sides of the film are the vapor phase, and after a sufficient equilibrating process, the vapor becomes saturated. Examples of molecular configuration are shown in Fig. 1 for an argon (Lennard–Jones) system. At low temperatures, the liquid surface seems very flat. However, as the temperature rises, the fluctuations of surface position increases, and finally, the surface looks very fuzzy at 140 K. note that the critical and triple point temperatures of this system is ~ 150 K and ~ 80 K, respectively. Also seen in the figure are clusters in the vapor phase at high temperatures. Several theoretical treatments of monomer gas condensation exists [1], but condensation behavior of clusters should be separately considered.

By analyses of molecular trajectories in the MD simulations, dynamic behavior of molecules near the surface is found to be classified into four categories [2–4], as shown in Fig. 2. The first three (evaporation, self-reflection, and condensation) have long been considered in analyzing experimental data. However, for some cases such as associating fluids (water, alcohols, organic acids, etc.) and fluids at high temperatures, the fourth type, i.e., molecular exchange, becomes quite important [2,3].

The condensation coefficient α is defined to be the ratio of condensation flux to vapor collision flux. Since the molecular exchange does not contribute to the condensation flux, the observed α is much less than unity for associating fluids. Moreover, we found that α has a strong temperature dependence even for simple fluids at high temperatures, which is also caused by the molecular exchange. The MD results of α are shown in Fig. 3.

Now the relevant question is: why the molecular exchange occurs so often on associating fluid surface? Analysis of the MD data in more detail from the view point of microscale energy transfer provide several hints concerning the question. The difference of α is now explained as follows [4]: (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

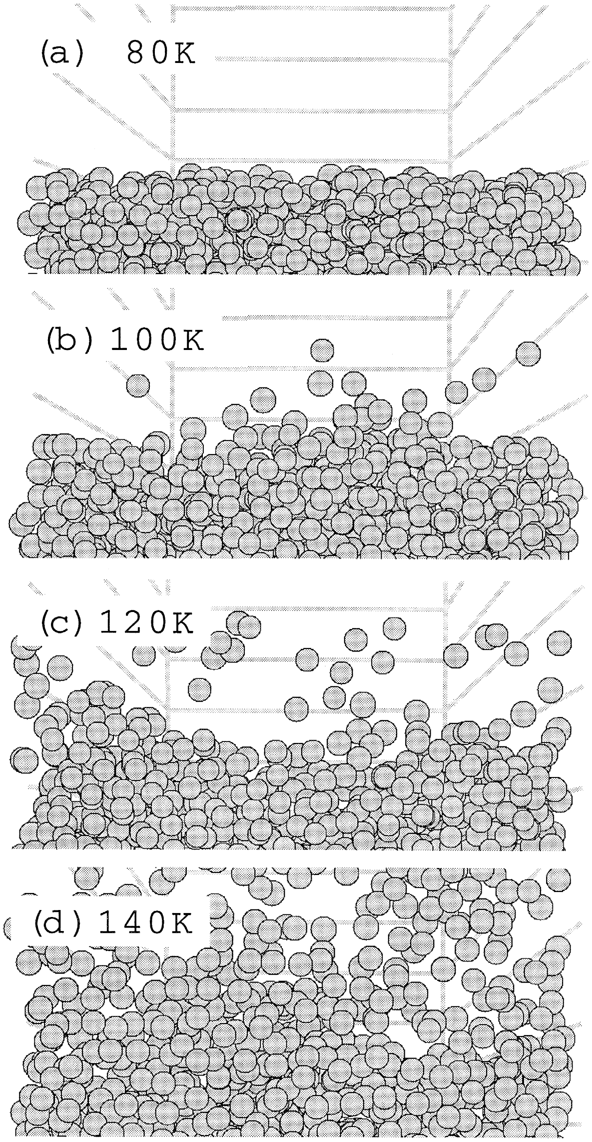

Fig. 1. Snapshots of argon liquid surface under the liquid–vapor equilibrium.

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.

The small α at high temperatures can be understood in a similar sway: The surface is not sufficiently stable, and the density near the surface is much smaller than that at low temperatures. Thus, the released heat cannot be effectively dissipated, but easily causes the molecular exchange.

Finally, let us consider the ‘evaporation coefficient’ α_{evap}. The definition of α_{evap} has not been unique in past studies [1]. In the case of liquid–vapor equilibrium, we can give a consistent definition

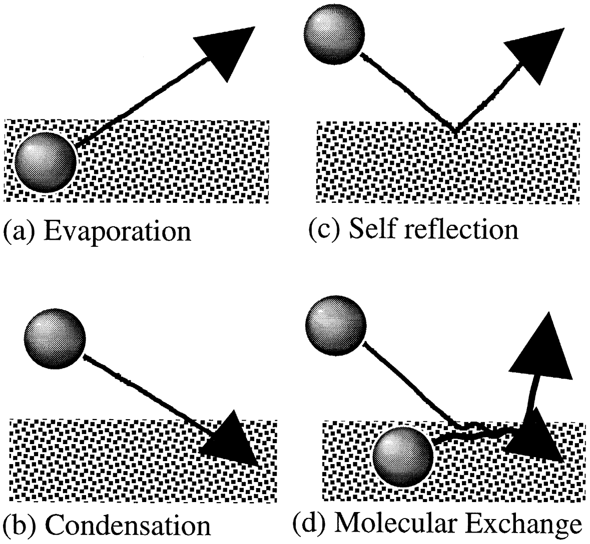

Fig. 2. Typical dynamic behavior of molecules near liquid surface.

with the fluxes shown in Fig. 4. The evaporation flux can be divided into two components; one is the ‘true’ evaporation which is inherent to the liquid, i.e., uncorrelated with the collision flux. Another is the ‘reflection’ which includes both self reflection and molecular exchange. In other words, the apparent evaporation flux can be classified into spontaneous and stimulated evaporation fluxes; the definition is unique when we use the memory function method developed in [1].

Then, the evaporation coefficient is defined as

$$\alpha_{\text{evap}} = \frac{\text{Spontaneous evaporation}}{\text{Apparent evaporation}} \tag{1}$$

Under the equilibrium condition, the condensation flux should equal to the spontaneous evapora-

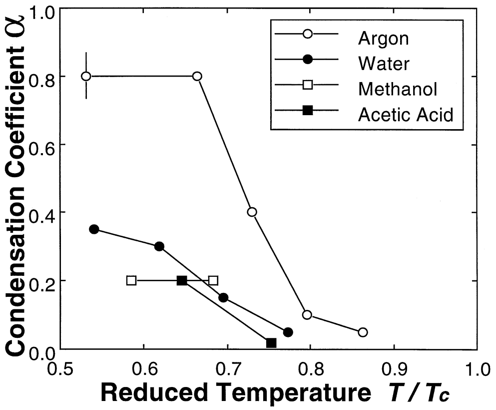

Fig. 3. Temperature dependence of the condensation coefficient: MD results. The temperature is expressed in the unit reduced by the liquid–vapor critical temperature T_c.

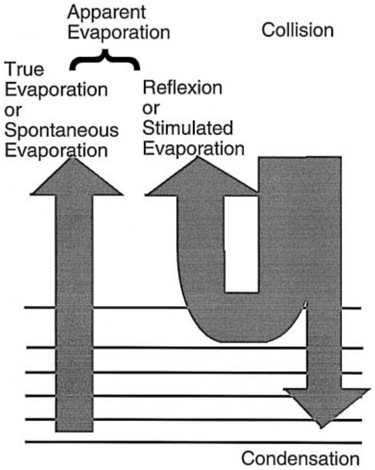

Fig. 4. Schematic figure of fluxes.

tion, and the collision flux should equal to the apparent evaporation. Thus, we conclude that α and $\alpha_{\rm evap}$ are equal.

3. Non-equilibrium condensation / evaporation

The condensation/evaporation behavior is much more complicated in the case of non-equilibrium conditions. Even with the liquid temperature given, there are two more control parameters, i.e., the temperature and the density (or the pressure) of the vapor.

3.1. Hot vapor condensation on cool liquid

To investigate the non-equilibrial phenomena, we have executed similar MD simulations. An example is given in Fig. 5, where hot argon vapor is instantly contacted to cool liquid argon; the initial temperature is 150 K (close to the critical temperature) for the vapor and 80 K (close to the triple point) for the liquid. The vapor density is 1/3 of the critical density.

As the condensation proceeds, the density and the temperature of the vapor decrease (Fig. 6, left). On the other hand, mainly due to the latent heat release, the temperature of the liquid film rises, the rate of which is not large, however. The heat conduction is so rapid that no clear temperature gradient was seen in the temperature profile of the film. Using MD data of initial (time $\leq$ 100 ps) configurations, where the liquid temperature is almost constant, we estimate the condensation coefficient as $\alpha \simeq 0.9$. This value is larger than the equilibrium case $\alpha \simeq 0.7$) at the same liquid temperature.

In the case of water, the difference is much more apparent; while $\alpha \simeq 0.4$ for water at 350 K under the vapor–liquid equilibrium, α becomes as large as 0.9 in the case of hot (650 K) water vapor contacting 350 K liquid water.

So far, we have calculated only several data points, but the general tendency of α is

$$\frac{\partial \alpha}{\partial T_{\rm v}} > 0, \ \frac{\partial \alpha}{\partial \rho_{\rm v}} < 0 \qquad (2)$$

where $T_{\rm v}$ is the vapor temperature and $\rho_{\rm v}$ is the vapor density.

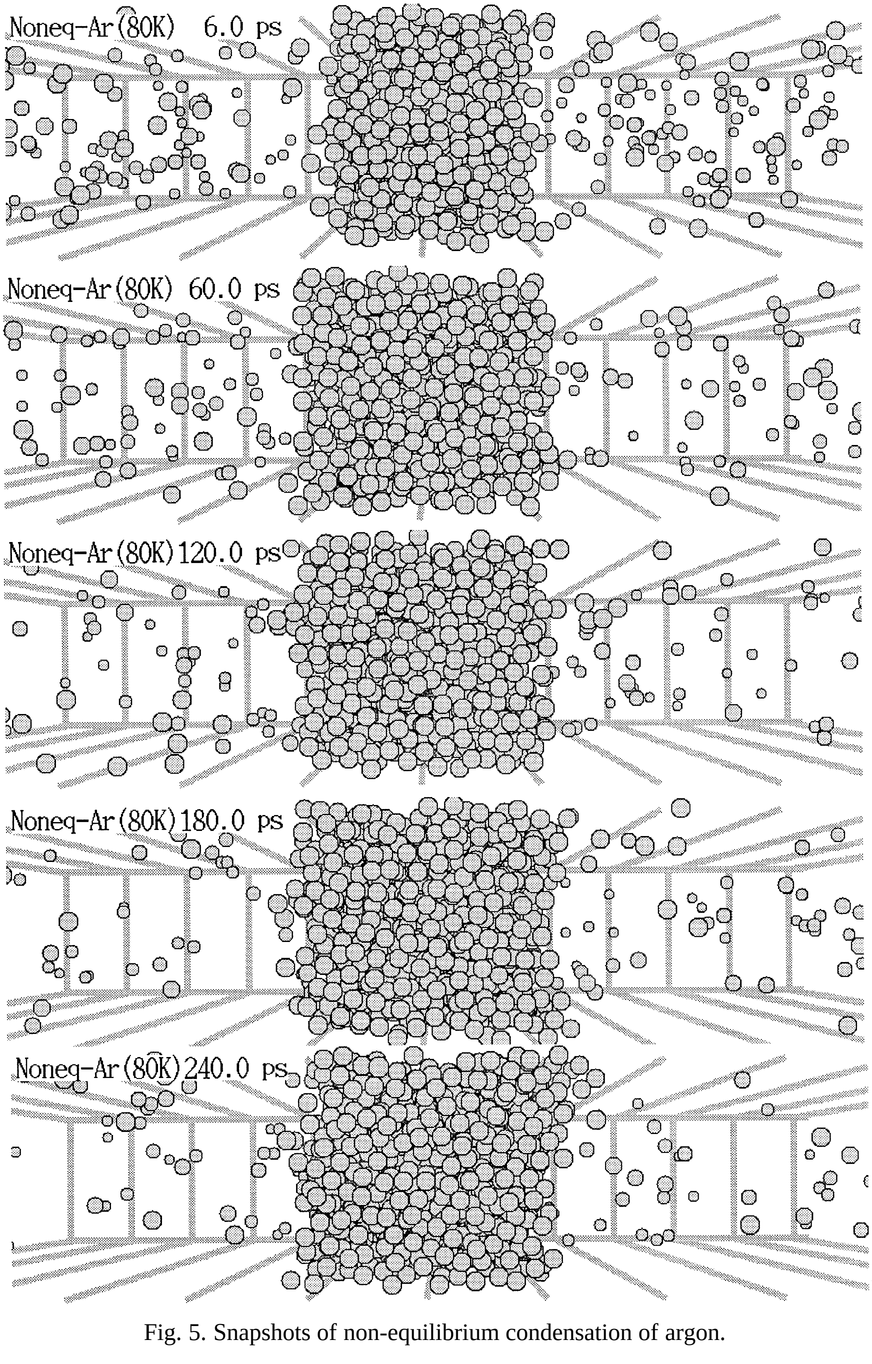

Fig. 5. Snapshots of non-equilibrium condensation of argon.

3.2. Evaporation into vacuum

The other extreme is the evaporation of liquid into the vacuum. The temperature gradually decreases (Fig. 6, right) as expected, but the initial temperature is maintained for ~ 40 ps. From the

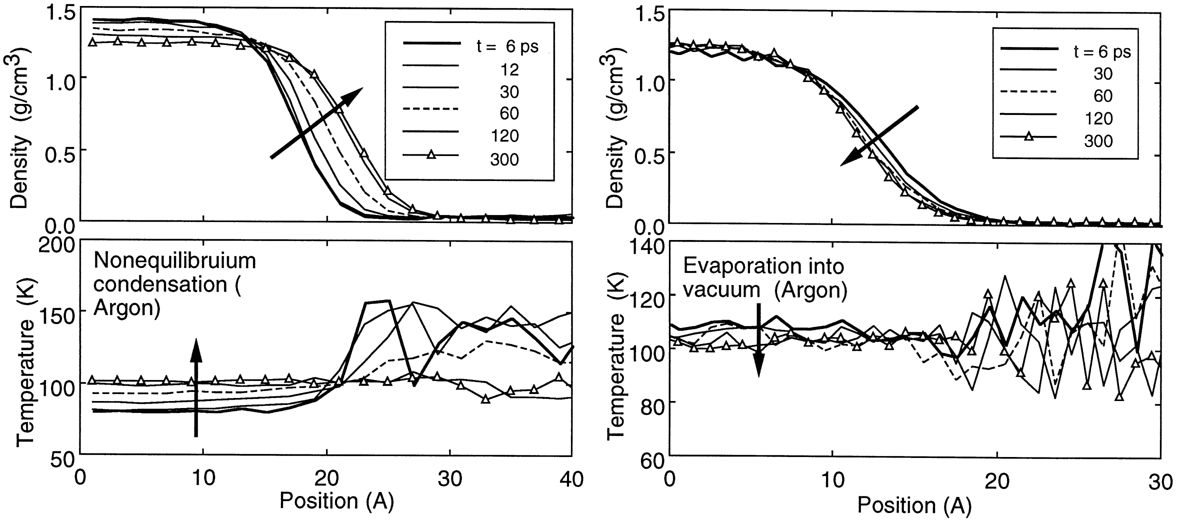

Fig. 6. Change of density and temperature profiles of argon. The arrows indicate the direction of change.

increase of the number of vapor molecules, we can evaluate the evaporation rate; at the same liquid temperature, the rate of evaporation into the vacuum is in general much larger than that under the liquid–vapor equilibrium.

4. Gas absorption

A similar MD method can be applied to investigate gas absorption dynamics on liquid surfaces, which is one of the fundamental processes in chemical engineering. Absorption mechanism of various gases (CO_2, SO_2, NO_x, etc.) on water surface is important also in environmental and earth science. Here, we have studied CO_2 absorption on pure water and salt water with a similar liquid film system to see how absorption rate depends on the solute (NaCl) concentration.

The density profile is shown in Fig. 7. It is known that most of inorganic electrolytes are negatively adsorbed on the water surface (i.e., avoid the surface) mainly due to the Coulombic interactions. We see clearly in Fig. 7 that both ions tend to avoid the surface. On the other hand, CO_2 molecules are

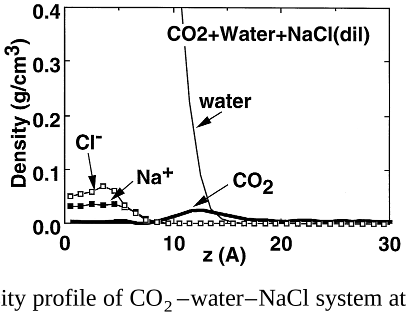

Fig. 7. Density profile of CO_2–water–NaCl system at $T = 300$ K.

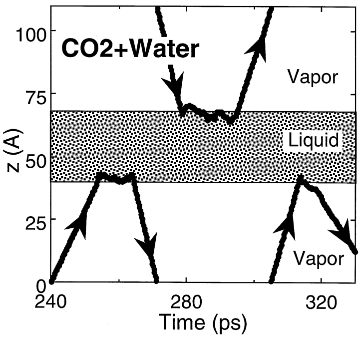

Fig. 8. Trajectory of CO_2 molecules near a water surface at $T = 300$ K.

strongly adsorbed on the surface where little ions exist. Therefore, one can expect that salt concentration has little effect on adsorption of CO_2.

An example of molecular trajectories is plotted in Fig. 8. From this figure, we can clearly define the adsorption time, the average of which is ~ 20 ps and depends only weakly on the salt concentration.

We cannot quantitatively investigate the dynamic process of adsorbed molecules solving into water, because we use here a rigid rotor (without dissociation) for CO_2 molecules. However, this kind of MD simulation is still useful to study the adsorption–desorption dynamics which is certainly one of the determining steps for gas absorption. Detailed analyses are under way.

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