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Evaporation and Condensation as a Unimolecular Chemical Reaction: Does the Potential Barrier Exist at a Molecular Liquid Surface ?

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Synopsis. A particle insertion method is applied to investigate the local chemical potential near a liquid free surface of argon and methanol. Although methanol has a significant ordering of molecular orientation, the chemical potential is constant for both cases, which is contrary to the prediction of a transition state theory.

It is still a challenging task to estimate experimentally the absolute rates of evaporation and condensation at a free liquid surface under the liquid–vapor equilibrium. In an ideal situation where all vapor molecules become condensed after colliding with the surface, the condensation rate is directly obtained from the Hertz–Knudsen equation. If a part of the colliding molecules are reflected at the surface, the condensation rate becomes smaller and so does the evaporation rate due to the equilibrium condition. The controversy has been continued over whether the condensation coefficient α (number ratio of condensed molecules to colliding ones) is unity or not.[1,2]

As far as we know, our report on a molecular dynamics simulation of a methanol surface[3] is the first attempt to investigate the evaporation–condensation mechanism at the molecular level. We have developed an autocorrelation function method[4] to estimate the condensation coefficient and found that $\alpha = 89\%$ for methanol at the temperature T=300 K and α=94% for argon (with the Lennard–Jones interaction) T=80 K. Thus, we confirmed that α is less than unity (even for simple fluids) and that some of incident vapor molecules are reflected at the liquid surface almost instantly.

A classical transition state theory has been applied to estimate the evaporation–condensation rates.[5—7] It predicts that α of molecular fluids (especially associating fluids) is much smaller than that of simple fluids because of the rotational restriction, or orientational ordering, of molecules at the surface. For example, the prediction of Mortensen and Eyring[7] is $\alpha = 0.034$ for methanol at T=0°C, which they claimed satisfactorily agrees with experimental results. Although the existence of the orientational ordering of methanol was confirmed in our simulation,[8] the calculated α is much larger than these predicted values. The model interactions and other artifacts (such as the finite system size) in our simulation can not be totally responsible for the discrepancy because other surface properties, such as the surface tension and the surface potential, are in reasonable agreement with the experimentally obtained ones.[8] Thus, we raise questions about the conventional explanation of evaporation–condensation dynamics in terms of the transition state theory. In this note, we report the estimation of the potential barrier near the surface.

Calculation

We adopted a particle insertion method[9] to estimate the local chemical potential. Consider a system of volume V, temperature T, and number of particles N. The chemical potential $\mu(V,T,N)$ is calculated as an increase of the Helmholtz free energy F when a test particle is inserted to the system:

$$\begin{aligned}
\mu &= (\partial F/\partial N)_{V,T} \\
&\simeq F(V,T,N+1) - F(V,T,N) \\
&= -k_{\mathrm{B}}T \log \frac{\int_{\{N+1\}} \exp\left[-\beta H_{N+1}\right]}{\int_{\{N\}} \exp\left[-\beta H_N\right]} \\
&= -k_{\mathrm{B}}T \log \\
&\quad \frac{\int_{\{N\}} \exp\left[-\beta H_N\right] \int_{N+1} \exp\left[-\beta(H_{N+1} - H_N)\right]}{\int_{\{N\}} \exp\left[-\beta H_N\right]} \\
&= -k_{\mathrm{B}}T \log \left\langle \int_{N+1} \exp\left[-\beta(H_{N+1} - H_N)\right] \right\rangle_{\{N\}} \\
&= \text{Kinetic Term} \\
&\quad -k_{\mathrm{B}}T \log \left\langle \int_{N+1} 1 \times \frac{\int_{N+1} \exp(-\beta\phi)}{\int_{N+1} 1} \right\rangle_{\{N\}} \\
&= \left[\text{Kinetic Term} - k_{\mathrm{B}}T \log \int_{N+1} 1\right] \\
&\quad + \left[-k_{\mathrm{B}}T \log \langle \exp(-\beta\phi) \rangle_{\{N+1\}}\right] \\
&\equiv \mu^{\mathrm{id}} + \mu^{\mathrm{ex}}, \qquad (1)
\end{aligned}$$

where k_{B} is the Boltzmann constant, $\beta \equiv (k_{\mathrm{B}}T)^{-1}$, and H_N is the Hamiltonian of the N-particle system. The symbol $\int_{\{N\}}$ represents a configurational space integral with respect to all degrees of freedom of the N-particle system, $\int_{N+1}$ is a similar integral with respect to the degrees of freedom of the $(N+1)$-th (i.e., inserted) particle, and $\langle \cdots \rangle_{\{N\}}$ is the statistical ensemble average of the N-particle system. In the final form, the chemical potential is expressed as a sum of the excess potential μ^{ex}, which is essentially the averaged Boltzmann factor of the test particle potential energy ϕ, and the chemical potential of the ideal gas μ^{id}, which is either

$$\mu^{\mathrm{id}} = -k_{\mathrm{B}}T \log \left[\left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{3/2} \frac{V}{N}\right] \qquad (2)$$

for monatomic molecules (e.g., Ar), or

$$\mu^{\mathrm{id}} = -k_{\mathrm{B}}T \log \left[\left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{3/2} \frac{V}{N} \left(\frac{8\pi^2 k_{\mathrm{B}}T}{h^2}\right)^{3/2} \frac{\sqrt{\pi I_1 I_2 I_3}}{\sigma} \right] \tag{3}$$

for nonlinear polyatomic molecules (e.g., methanol).[10] Here h is the Planck constant, m is the molecular mass, I_1, I_2, and I_3 are the principal moments of inertia, and σ is the symmetry number, which is equal to unity in the case of methanol. Equation 3 is for a rigid rotor, which we used in our MD simulation of methanol.

From the data of our MD simulations, we picked up 500 configurations which had been stored every 3 ps (for Ar) or 0.2 ps (for methanol). We generated a series of random coordinates (and random molecular orientations for methanol) of the test particle, and took the statistical average of $\exp[-\beta\phi]$ to calculate μ^{ex}. The quantity V/N in μ^{id} was evaluated from the time-averaged density profile. To estimate the positional dependence of μ near the surface, we fixed z (the coordinate along the surface normal) of the test particles and calculated the local chemical potential as a function of z. The number of insertion is 1200 (Ar) or 4000 (methanol) for each configuration, and thus the total number of samplings to obtain $\langle \exp[-\beta\phi] \rangle$ is either 600000 for Ar or 2000000 for methanol. We repeated the calculations several times using different sequences of random numbers to estimate the statistical errors.

Results

The results for Ar are shown in Fig. 1, where we also show the contribution of two terms μ^{id} and μ^{ex} separately. The obtained μ is fairly constant. Figure 2 shows the chemical potentials of methanol. The statistical variations are large in the calculation of μ^{ex} as shown by the crosses, but the results allow us to conclude that μ is constant also for methanol.

In general, the spatially-constant chemical potential merely indicates that the system is in equilibrium; otherwise, molecular flow would arise. In a non-uniform system with interfaces, however, such a molecular flow changes the position and shape of the interfaces. Thus, the above naive argument concerning the chemical potential constancy and the system equilibrium fails for interfacial systems. The constancy is usually assumed implicitly in the statistical physics of liquid surfaces,[11,12] but there is no rigorous proof so far. For the Lennard–Jones system, Rowlinson reported the constancy[13] by a similar particle insertion method. Here, we confirm the constancy for methanol, the system which has strong orientational ordering at the surface. Therefore, we can conclude that the constancy holds for any substances, including polar and associating fluids.

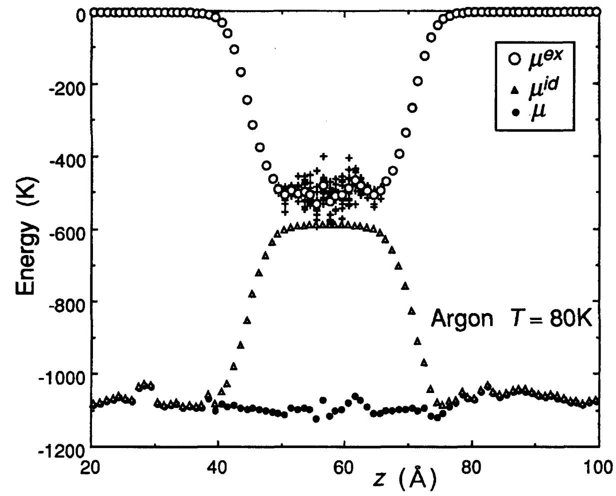

Fig. 1. Local chemical potentials for argon at T=80 K (filled circles). The liquid region is approximately between z=50 and 65 Å. The contributions of the ideal gas term (triangles) and the excess energy term (open circles) are also shown; see Eq. 1. The latter is the average of several trials which are shown as crosses; each trial consists of 600000 particle insertions.

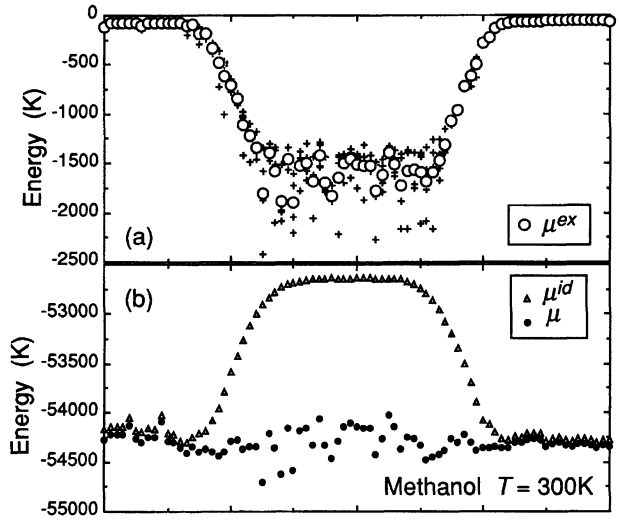

Fig. 2. Local chemical potentials for methanol at T=300 K, similar to Fig. 1 except that each trial consists of 2000000 insertions. The liquid region is approximately between z=40 and 60 Å.

Discussion

Before investigating the implication of the chemical potential constancy, let us summarize the classical transition state theory.[14] Here, we concentrate on a unimolecular reaction, which has always been assumed in the case of evaporation and condensation:[5—7]

$$\mathrm{A} \rightleftharpoons \mathrm{A}^{\ddagger} \rightarrow \mathrm{B} \tag{4}$$

In a condensation process, for example, A and B represent a vapor and a liquid molecule, respectively. The transition state $\mathrm{A}^{\ddagger}$ has been considered as a molecule on (but almost separated from) the liquid surface.[7] The theory assumes a chemical equilibrium between A and

$\mathrm{A}^{\ddagger}$. By defining the degree of reaction advancement λ as

$$\begin{cases} N_{\mathrm{A}} = N_{\mathrm{A}}^{0} - \lambda \\ N_{\mathrm{A}^{\ddagger}} = N_{\mathrm{A}^{\ddagger}}^{0} + \lambda \end{cases} \tag{5}$$

(N_{A}^{0} and $N_{\mathrm{A}^{\ddagger}}^{0}$ are initial numbers of molecules), the equilibrium condition is expressed as

$$0 = \frac{\partial F}{\partial \lambda} = \frac{\partial F}{\partial N_{\mathrm{A}}}\frac{\mathrm{d}N_{\mathrm{A}}}{\mathrm{d}\lambda} + \frac{\partial F}{\partial N_{\mathrm{A}^{\ddagger}}}\frac{\mathrm{d}N_{\mathrm{A}^{\ddagger}}}{\mathrm{d}\lambda} = -\mu_{\mathrm{A}} + \mu_{\mathrm{A}^{\ddagger}}. \tag{6}$$

A basic assumption of the transition state theory is that the reaction rate is proportional to the concentration of the transition state molecules:

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \kappa\frac{k_{\mathrm{B}}T}{h} \times [\mathrm{A}^{\ddagger}], \tag{7}$$

where [ ] represents the concentration (density) of the species, κ is the transmission coefficient, and $k_{\mathrm{B}}T/h$ is the "speed" of barrier crossing along the reaction coordinate. In the case of condensation and evaporation as a unimolecular reaction, the reaction coordinate is equivalent to the coordinate along the surface normal in the real space. Thus, all we need is $[\mathrm{A}^{\ddagger}]$(except for κ, which includes quantum effects and nonequilibrium effects), and Eq. 6 is utilized to estimate $[\mathrm{A}^{\ddagger}]$. Since it is impossible to generally solve Eq. 6 to obtain $[\mathrm{A}^{\ddagger}]$, another assumption is often made that both [A] and $[\mathrm{A}^{\ddagger}]$ are so small that the chemical potentials are expressed as

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{0} + k_{\mathrm{B}}T\log([\mathrm{A}]k_{\mathrm{B}}T), \tag{8}$$

$$\mu_{\mathrm{A}^{\ddagger}} = \mu_{\mathrm{A}^{\ddagger}}^{0} + k_{\mathrm{B}}T\log([\mathrm{A}^{\ddagger}]k_{\mathrm{B}}T), \tag{9}$$

where μ^{0} represents the chemical potential in some standard state, which is usually chosen as 0 °C and 1 atm. Substituting Eqs. 8 and 9 in Eq. 6 to express $[\mathrm{A}^{\ddagger}]$ in terms of [A], we obtain from Eq. 7

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \kappa\frac{k_{\mathrm{B}}T}{h}\exp\left(-\frac{\mu_{\mathrm{A}^{\ddagger}}^{0} - \mu_{\mathrm{A}}^{0}}{k_{\mathrm{B}}T}\right) \times [\mathrm{A}]. \tag{10}$$

As usually employed,[14] Eqs. 8 and 9 are good approximations for many cases of gas phase reaction. For reaction in condensed phases, however, we need an appropriate model about molecular surroundings to estimate the chemical potential because information about the transition state is often experimentally inaccessible. Various concepts (regular solution, activity, free volume, etc.) have been introduced to justify or modify Eqs. 8 and 9, the validity of which should be confirmed by comparison with experiments. The evaporation–condensation processes have been even more difficult targets because of discrepancy among experiments. Thus, the calculations with the concept of free angles,[5—7] which predict very small condensation coefficient due to the rotational restriction, still need to be examined from various points of view.

The chemical potential constancy that we found above directly confirms the equilibrium condition, Eq. 6. To discuss the potential barrier $\mu_{\mathrm{A}^{\ddagger}}^{0} - \mu_{\mathrm{A}}^{0}$, we have to estimate μ^{0} defined in the standard state. We are not certain whether the "standard state" is a useful concept in treating evaporation–condensation processes, but let us assume the validity of Eqs. 8 and 9; they are expected to hold better for condensation processes than evaporation ones, since both the reaction (vapor molecules) and the transition state molecules have a very low density. Comparing Eqs. 2 and 3 with Eqs. 8 and 9, we notice that the logarithmic term in Eqs. 8 and 9 has the same concentration dependence as μ^{id}. Therefore, μ^{ex} is expected to be a good approximation for μ^{0}, except for a constant which depends only on the temperature. Thus, we can estimate the height of the potential barrier for a condensation process by comparing μ^{ex} of the bulk vapor phase and that of the surface layer. As seen in Figs. 1 and 2, however, μ^{ex} is completely flat from the vapor region to the surface, and we conclude that no potential barrier exists in the condensation process for either methanol or argon. This is a strong support for Cammenga's comment[1)] that the orientational restriction is already taken into account in the vapor pressure.

In the original form of the transition state theory,[7)] the small α of molecular fluids is explained in terms of the transmission coefficient κ. The ideas behind the use of κ are (i) the transition state is a vapor-like molecule without rotational restrictions, (ii) only molecules with special orientation can evaporate or condense, and (iii) activated molecules are not always allowed to pass the barrier because they have finite time of relaxation to reorient themselves.

Our simulation of methanol shows that all molecules near the surface are more or less oriented.[8)] Therefore, there is no need to assume the freely-rotating transition state, and we have to evaluate the barrier as the free energy difference between the reactant and the surface molecule *with* rotational ordering, which we did in the above calculations. This is justified by the fact that Eq. 6 holds between the molecules in the bulk region and the surface molecules with rotational ordering. Thus, our claim of barrier inexistence means that the conventional explanation of the transition state theory for small α in terms of the rotational restriction is inappropriate.

Nonequilibrium effects (or the effects of transmission coefficient κ which is less than unity) may exist, but the theoretical estimation of κ is difficult at this stage. The effects do not seem very large, however, because the simulational results are α=94% for argon and 89% for methanol. It is interesting that even the transmission coefficient of simple fluids is less than unity, which has not been expected. The difference of α between argon and methanol might be attributed to the molecular orientation, but the value in the simulations (5%) is very small.

Now, we are in the following frustrating situation: (i) α is doubtlessly less than unity. (ii) Unexpectedly, even simple fluids are not in the condition of complete capture. (iii) Condensation is a "barrierless" process even for molecular fluids, which agrees with the large α in our simulations but is contrary to the explanation of the transition state theory. (iv) Experimental values of α for methanol are much smaller than our simulational results. Concerning the discrepancy between experiments and our simulation, we have a doubt about another fundamental assumption that the evaporation–condensation is a unimolecular process. In fact, we reported particle exchange phenomena in the previous letter.3) We conjecture that the events of evaporation and condensation are not completely independent, but that there is some mechanism of energy transfer from condensing molecules to evaporating ones. Mechanisms of such energy transfers are being investigated, and will be reported elsewhere.

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