MOLECULAR DYNAMICS METHOD OF THE NUCLEATION OF WATER ON IONS (1)

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Abstract. The molecular dynamics (MD) method is shown to be applicable to the study of the nucleation of water on ions. The method of study is described toward development of the heterogeneous nucleation theory.

1. Introduction

An experiment of the nucleation of water on ions in Wilson's cloud chamber is famous and this phenomenon may be a continual attractive theme in the field of atmospheric electricity. We have often applied the classical Thomson theory to this problem of nucleation but many shortcomings of macroscopic liquid model in the theory have been pointed out. The present purpose of this study is to consider this problem by microscopic molecular model.

The molecular dynamics (MD) method is very successful in understanding the molecular structures. We should import fruits of the MD method (Rahman and Stillinger, 1971; Perera and Berkowitz, 1991) to the nucleation theory. On the other hand, the molecular theory of nucleation was presented by Lee et al. (1973), Reiss et al. (1990), and Ellerby et al. (1991). We should extend their nucleation theory to include effects of polyatomic molecules. While an interesting molecular model for the nucleation of water on ions was presented by Briant and Burton (1976), the method of calculation of the internal Helmholtz free energy was oversimplified and should be improved.

2. Method and discussion

We apply their nucleation theory referred above to our case but make a part of the theory somewhat simple, in order to consider a rather complicated system of polyatomic molecules.

Firstly we consider the homogeneous nucleation of water vapor and secondly extend it for the heterogeneous nucleation of water on ions. The nucleation rate of homogeneous nucleation is expressible as,

$$J = \left(\sum_i \frac{1}{\beta(i) N_i} \right)^{-1}, \quad (1)$$

where N_i is the equilibrium distribution of the cluster with i water molecules (we call it the i -cluster), $\beta(i)$ represents the averaged rate that an i -cluster captures new water molecules and

$$N_i = \int_0^{V_c^*(i)} n_i(V_c) dV_c, \quad (2)$$

$$n_i(V_c) dV_c = \left(\frac{dV_c}{\Delta V_c} \right) \exp \left[-\frac{W_i(V_c, T)}{kT} \right], \quad (3)$$

where $V_c^*(i)$ is the maximum of volume V_c of i -clusters which are physically significant and ΔV_c in the prefactor of the exponential function represents the range where V_c changes. In Ellerby et al. (1991), this prefactor was (NdV_c/V) , where $N \equiv N_1$ is the total number of molecules and V is the volume of system. This prefactor is to yield $N_i \propto N_1^{i+1}$, which is a violation of the law of mass action because for a reaction of the

association of i molecules one must have $N_i \propto N_1^i$.

In case of the heterogeneous nucleation under this study, the ions are sufficiently fewer than water molecules and the clusters include only one ion. For the case of heterogeneous nucleation, we can write the similar expressions to Eqs. (1), (2), and (3). The function of $W_i(V_c, T)$ in Eq. (3) is the Gibbs free energy involved in the formation of the cluster, which depends on i , V_c , and T .

We consider the Gibbs free energy $W_i(V_c, T)$ and also that for the heterogeneous nucleation; we call the latter $W_i^{(hetero)}(V_c, T)$. The partition functions for the whole system Q and an i -cluster q_i are given by

$$Q = \sum_{\{n_i\}} \frac{(\gamma V \eta 4\pi^3)^{N_1}}{N_1!} \prod_i \frac{q_i^{n_i}}{n_i!}, \quad (4)$$

$$q_i = \frac{1}{i! h^{6i}} \iiint \exp[-\beta \{ \frac{1}{2} \sum_{k=1}^i (\frac{|\bar{p}_k|^2}{m} + \bar{\omega}_k \cdot \bar{I}_k \cdot \bar{\omega}_k) + u_i \}] d\bar{r}_1 \dots d\bar{r}_i d\bar{o}_1 \dots d\bar{o}_i d\bar{p}_1 \dots d\bar{p}_i d\bar{\omega}_1 \dots d\bar{\omega}_i, \quad (5)$$

where $\gamma = (2\pi m k T)^{3/2} / h^3$, $\eta = (1/\sigma)(\pi I_1 I_2 I_3)^{1/2} (8\pi^2 k T)^{3/2} / h^3$, $\sigma = 2$ (symmetry number) for water molecule, we have $4\pi^3$ in Eq. (4) by the integration with respect to Euler angles specifying the orientation of water molecules, $\beta = 1/kT$, m , $\bar{r}_k$, $\bar{o}_k$, $\bar{p}_k$, $\bar{\omega}_k$, and $\bar{I}_k$ are mass, center-of-mass position, orientation, momentum, angular velocity, and inertial moment tensor of the k -th ($k=1, \dots, i$) water molecule in the i -cluster, respectively, and u_i is the potential energy. $\bar{I}_k$ can be diagonal (I_1, I_2, I_3).

The ion is considered to be a point charge and the expressions for the heterogeneous nucleation of the cluster including i water molecules and an ion are similar to Eqs. (4) and (5). The cluster partition function

$q_i^{(hetero)}$ becomes

$$q_i^{(hetero)} = \frac{1}{i! h^{6i+3}} \iiint \exp[-\beta \{ \frac{1}{2} \sum_{k=1}^i (\frac{|\bar{p}_k|^2}{m} + \bar{\omega}_k \cdot \bar{I}_k \cdot \bar{\omega}_k) + \frac{|\bar{p}_{ion}|^2}{m_{ion}} + u_i^{(hetero)} \}] d\bar{r}_1 \dots d\bar{r}_i d\bar{r}_{ion} d\bar{o}_1 \dots d\bar{o}_i d\bar{o}_{ion} d\bar{p}_1 \dots d\bar{p}_i d\bar{p}_{ion} d\bar{\omega}_1 \dots d\bar{\omega}_i \quad (6)$$

Equations (5) and (6) are reduced to

$$q_i = \frac{\gamma^i \eta^i}{i!} \iiint \exp[-\beta u_i] d\bar{r}_1 \dots d\bar{r}_i d\bar{o}_1 \dots d\bar{o}_i, \quad (7)$$

$$q_i^{(hetero)} = \frac{\gamma^i \gamma_{ion} \eta^i}{i!} \iiint \exp[-\beta u_i^{(hetero)}] d\bar{r}_1 \dots d\bar{r}_i d\bar{r}_{ion} d\bar{o}_1 \dots d\bar{o}_i, \quad (8)$$

where $\gamma_{ion} = (2\pi m_{ion} k T)^{3/2} / h^3$, and m_{ion} and $\bar{r}_{ion}$ are mass and position of the ion. Transformed coordinates and the Jacobians of the integration variables in q_i and $q_i^{(hetero)}$ to separate the cluster's translational motion are:

$$(\bar{R}, \bar{r}'_1, \dots, \bar{r}'_{i-1}), \quad \bar{R} = \sum_{k=1}^i \bar{r}_k / i, \quad \bar{r}'_k = \bar{r}_k - \bar{R}, \quad \bar{r}'_i = -\sum_{k=1}^{i-1} \bar{r}'_k, \quad \text{and} \quad i^3, \quad (9)$$

$$(\bar{R}^{(hetero)}, \bar{r}'_1, \dots, \bar{r}'_i), \quad \bar{R}^{(hetero)} = \{m \sum_{k=1}^i \bar{r}_k + m_{ion} \bar{r}_{ion}\} / (im + m_{ion}), \quad \bar{r}'_k = \bar{r}_k - \bar{R}^{(hetero)},$$

$$\bar{r}'_{ion} = -(m / m_{ion}) \sum_{k=1}^i \bar{r}'_k, \quad \text{and} \quad \{(im + m_{ion}) / m\}^3. \quad (10)$$

Thus, q_i and $q_i^{(hetero)}$ are written in the forms:

$$q_i = \gamma_i V \exp[-\beta A_i^*(V_c, T)], \quad (11)$$

$$q_i^{(hetero)} = \gamma_i^{(hetero)} V \exp[-\beta A_i^{*(hetero)}(V_c, T)], \quad (12)$$

$$\text{where } \gamma_i = (2\pi imkT)^{3/2} / h^3, \text{ and } \gamma_i^{(hetero)} = \{2\pi(im + m_{ion})kT\}^{3/2} / h^3, \quad (13)$$

$$A_i^*(V_c, T) = -kT \ln Q_i^*, \text{ and } Q_i^* = \frac{\gamma_i^{i-1} \eta_i^{3/2}}{i!} \iiint \exp[-\beta u_i] d\vec{r}_1' \dots d\vec{r}_{i-1}' d\vec{o}_1 \dots d\vec{o}_i, \quad (14)$$

$$A_i^{*(hetero)}(V_c, T) = -kT \ln Q_i^{*(hetero)}, \text{ and}$$

$$Q_i^{*(hetero)} = \frac{\gamma_i^i \eta_i^i \{(im + m_{ion}) / m_{ion}\}^{3/2}}{i!} \iiint \exp[-\beta u_i^{(hetero)}] d\vec{r}_1' \dots d\vec{r}_i' d\vec{o}_1 \dots d\vec{o}_i, \quad (15)$$

The Gibbs free energy $W_i(V_c, T)$ and $W_i^{(hetero)}(V_c, T)$ become

$$W_i(V_c, T) = A_i^*(V_c, T) - kT \ln(\gamma_i V) + pV - i\mu_1, \quad (16)$$

$$W_i^{(hetero)}(V_c, T) = A_i^{*(hetero)}(V_c, T) - kT \ln(\gamma_i^{(hetero)} V) + pV - (i\mu_1 + \mu_{ion}), \quad (17)$$

where μ_1 is the chemical potential of a monomer (water molecule):

$$\mu_1 = kT \{\ln(N_1) - \ln(\gamma V) - \ln(\eta 4\pi^3)\} = kT \{\ln(N_0) - \ln(\gamma V) - \ln(\eta 4\pi^3)\} + kT \ln S, \quad (18)$$

$$\mu_{ion} \text{ is that of an ion: } \mu_{ion} = kT \{\ln(N_{ion}) - \ln(\gamma_{ion} V)\}, \quad (19)$$

$S = N_1 / N_0$, and N_0 and N_{ion} are the number of water molecules in equilibrium and ions.

We do not evaluate the internal Helmholtz free energy $A_i^*(V_c, T)$ and $A_i^{*(hetero)}(V_c, T)$ directly from Eqs. (14) and (15) but from the following relations of the derivatives of the free energy with respect to V_c and T :

$$p = kT \left(\frac{\partial \ln Q}{\partial V_c} \right)_{T,i} = - \left(\frac{\partial A}{\partial V_c} \right)_{T,i}, \quad (20)$$

$$\langle E \rangle = kT^2 \left(\frac{\partial Q}{\partial T} \right)_{V_c,i} = -T^2 \left(\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right)_{V_c,i}, \quad (21)$$

$$A_i^*(V_c, T_0) = A_i^*(V_{c0}, T_0) - \int_{V_{c0}}^{V_c} \frac{pV}{V} dV = A_i^*(V_{c0}, T_0) - \int_{V_{c0}}^{V_c} \frac{(i)kT_0 + \langle pV_{int} \rangle_0}{V} dV, \quad (22)$$

$$\frac{A_i^*(V_{c0}, T)}{T} = \frac{A_i^*(V_{c0}, T_0)}{T_0} + \int_{T_0}^T \frac{\langle E \rangle}{(-T^2)} dT = \frac{A_i^*(V_{c0}, T_0)}{T_0} + \int_{T_0}^T \frac{(3kT/2)(2i) + \langle u_i \rangle_0}{(-T^2)} dT, \quad (23)$$

$$\langle pV_{int} \rangle_0 = \langle -(1/3) \sum_i \sum_j r_{ij}' \{ du(r_{ij}') / dr_{ij}' \} \rangle, \quad (24)$$

$$\langle u_i \rangle_0 = \langle \sum_i \sum_j u(r_{ij}') \rangle. \quad (25)$$

The notations $\langle pV_{int} \rangle_0$ and $\langle u_i \rangle_0$ in Eqs. (24) and (25) are ensemble averages, which are to be evaluated later. Similar expressions to Eqs. (22) and (23) are obtained for the heterogeneous nucleation:

$$A_i^{*(hetero)}(V_c, T_0) = A_i^{*(hetero)}(V_{c0}, T_0) - \int_{V_{c0}}^{V_c} \frac{(i+1)kT_0 + \langle pV_{int}^{(hetero)} \rangle_0}{V} dV, \quad (26)$$

$$\frac{A_i^{*(hetero)}(V_{c0}, T)}{T} = \frac{A_i^{*(hetero)}(V_{c0}, T_0)}{T_0} + \int_{T_0}^T \frac{(3kT/2)(2i+1) + \langle u_i^{(hetero)} \rangle_0}{(-T^2)} dT. \quad (27)$$

The integration constants $A_i^*(V_{c0}, T_0)$ and $A_i^{*(hetero)}(V_{c0}, T_0)$ in Eqs. (22), (23), (26), and (27) are calculated at the reference state of ideal gas where u_i and $u_i^{(hetero)}$ are set to zero (Lee et al. 1973):

$$A_i^*(V_{c0}, T_0) = -kT \ln \left\{ \frac{\gamma^{i-1} \eta^i i^{3/2}}{i!} q_{gas} \right\}, \quad (28)$$

$$q_{gas} = \left(\frac{4}{3} \pi R_c^3 \right)^{i-1} \frac{2}{\pi} 3^{i-1} \int_0^\infty \left(\frac{\sin x - x \cos x}{x^3} \right)^i x^2 dx, \quad (29)$$

$$A_i^{*(hetero)}(V_{c0}, T_0) = -kT \ln \left\{ \frac{\gamma^i \eta^i \{(im + m_{ion}) / m_{ion}\}^{3/2}}{i!} q_{gas}^{(hetero)} \right\}, \quad (30)$$

$$q_{gas}^{(hetero)} = \left(\frac{4}{3} \pi R_c^3 \right)^i \frac{2}{\pi} 3^i \int_0^\infty \left(\frac{\sin x - x \cos x}{x^3} \right) \left(\frac{\sin y - y \cos y}{y^3} \right)^i x^2 dx, \text{ and } y = \frac{m}{m_{ion}} x. \quad (31)$$

It is possible to evaluate the internal Helmholtz free energy $A_i^*(V_c, T)$ and $A_i^{*(hetero)}(V_c, T)$ on any (i, V_c, T) from Eqs. (22), (23), (26), and (27) after calculating the ensemble averages $\langle pV_{int} \rangle_0$, $\langle u_i \rangle_0$, $\langle pV_{int}^{(hetero)} \rangle_0$, and $\langle u_i^{(hetero)} \rangle_0$, which represent the contributions of intermolecular forces to the intrinsic pressure and internal energy of the cluster.

A common method to obtain the ensemble averages may be Monte Carlo technique but it may not be feasible to resort this technique in 6i dimensional space for polyatomic molecules system because of so many Monte Carlo steps. Then we attempt to replace the ensemble averages by the time averages and to get the approximate values of them by the MD method. We need $\langle pV_{int} \rangle_0$ and $\langle pV_{int}^{(hetero)} \rangle_0$ for varying V_c and a fixed T in Eqs. (22) and (26) and also $\langle u_i \rangle_0$ and $\langle u_i^{(hetero)} \rangle_0$ for varying T and a fixed V_c in Eqs. (23) and (27). However, neither of these equi-temperature process and equi-volume process is spontaneous; they are realized only under some restraint. Solving the coupled Newton-Euler equations for molecules in a cluster, we find the temporal evolution of the conditions of the cluster. If we choose some appropriate initial conditions and change the system sometimes by heating or cooling, we happen to attain to a solution which yields any set of (V_c, T) for a definite i and then obtain $\langle pV_{int} \rangle_0$, $\langle u_i \rangle_0$, $\langle pV_{int}^{(hetero)} \rangle_0$, and $\langle u_i^{(hetero)} \rangle_0$ by averaging the corresponding values in the neighborhood of the concerned point of (i, V_c, T) .

We report on some results obtained by our method in a following paper.

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