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Novel neon-hydrate of cubic ice structure

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ABSTRACT

The stability of ice I cubic (ice I_c) whose voids are occupied by neon particles is investigated using a hybrid type of isobaric grand-canonical Monte Carlo simulation. We show that the resulting neon hydrate is stable under high pressure and temperature where ice I_c alone is unstable, suggesting the existence of a novel neon hydrate of ice I_c. We also show through chemical potential calculation that the neon hydrate of the ice I_c structure is more favorable than the neon hydrate of the ice II structure, whose existence was proven from experiment under high pressure condition.

1. Introduction

Noble gases such as krypton and xenon are encaged in polyhedra made from water molecules to form clathrates of two crystallographic structures, known as type sI and sII [1,2]. Light noble gases such as helium and neon have been generally believed to be unable to form clathrate hydrates although the prospect for light gas to occupy the cavities of ice structure was noted from the solubility of helium and neon inside ice I_h [3]. The inability was deduced solely from the fact that their particle sizes are insufficient to stabilize the cage of clathrate hydrates. However, Londono et al. showed the possibility of helium to be accommodated inside ice II [4]. It was also found that neon can be encaged inside ice II [5].

A novel gas hydrate of hydrogen has been found [6] where water lattice forms a diamond-like structure equal to cubic ice (ice I_c). The hydrate, known as C_2, can then be regarded as ice I_c filled with hydrogen. Despite the fact that ice I_c itself is metastable confirmed from an experiment [7] and simulation study [8], the resultant hydrate is stable. This indicates that inclusion of guest particles stabilizes the ice structures. The source of stability is not the weak attractive forces between host water and guest hydrogen, typically described by a Lennard-Jones (LJ) potential. Rather, as implied by the high pressure required to form a hydrate compound, a key factor to stabilize ice I_c seems to be the size of the guest molecule fit into the interstices in ice I_c. In order to verify this hypothesis on the origin of its stability, it is intriguing to explore for other guest species stabilizing the ice I_c structure. From the viewpoint of guest size, it seems plausible that neon is encaged in ice I_c as hydrogen to form a stable gas hydrate.

Here we examine the stability of ice I_c filled with neon by a hybrid type of grand-canonical (GC) and isothermal–isobaric (NPT) Monte Carlo (MC) simulation in order to explore for a novel compound. It has been demonstrated that the MC simulation is a useful tool to study the occupancy of guest molecule inside clathrate hydrates [9–11]. We also apply the same simulation method to evaluate the structure and the occupancy of neon in ice II. The stability of the neon hydrate compound is then investigated in the terms of the chemical potential of water.

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2. Methods

2.1. Potential model and water configuration

All potential interactions are assumed to be pair-wise additive. The interaction between guest particles (neon) is represented by the LJ potentials [12], and the interaction between water molecules is described by TIP4P model [13]. The potential model has been used because of its reliability to reproduce the phase diagram and many other properties of water in a wide range of the temperature–pressure plane within the framework of pair potential [14,15]. The interaction between water and neon is also described by LJ potentials according to Lorentz–Berthelot rule [16,17]. All pair potentials are truncated smoothly at $(r_c =)$ 8.655 Å [18] and correction to the long range interaction is taken into account by assuming uniform distribution beyond the r_c. The simulation cell for ice I_c is taken to be a cubic box constructed from 216 cubic unit cells $(a = b = c = 6.44 \text{ Å})$ each containing 8 water molecules. The cubic ice configuration is a proton-disordered form, generated according to Bernal–Fowler rule [19] so as to have zero net dipole moment. As for ice II structure, the simulation cell is taken to be a rectangular box $(a = 25.97 \text{ Å}, b = 22.49 \text{ Å}, c = 25.01 \text{ Å})$ containing 576 water molecules.

2.2. Simulation method

In order to establish a relation between the pressure P and the chemical potential μ of neon at a given temperature T, the equation of state of pure neon fluid is obtained from usual canonical (NVT) MC simulation with various number density, ρ. The number of neon particles with mass m is taken to be in a range of 96 to 589, depending on the density, so that the volume of the system falls in a certain range corresponding to the volume of ice I_c. The chemical potential of pure neon fluid at T and P is given by

$$\mu(T, P) = k_B T \ln\{\rho (h^2/2\pi m k_B T)^{3/2} e\} + \int_0^\rho (P - \rho k_B T)\rho^{-2} \mathrm{d}\rho + \rho^{-1} P \tag{1}$$

where h and k_B are Planck and Boltzmann constant, respectively. The integral part is contributed from the non-ideal nature of the neon fluid.

We consider that the neon particles inside the ice voids are in equilibrium with surrounding neon fluid. This condition corresponds to grand-canonical ensemble where the number of neon particle is variable under constant chemical potential at given pressure and temperature. The accommodation of neon inside the voids space of ice I_c is then investigated by a hybrid type of GC/NPT MC simulations. The insertion and deletion scheme is applied to neon particle. A trial insertion is made at an arbitrary position in (instantaneous) volume V and the trial is accepted with a probability

$$p_{insert} = \frac{\exp[\beta(\mu - w)](2\pi m k_B T/h^2)^{3/2} V}{(N_g + 1)} \tag{2}$$

where w is the interaction energy of the trial inserted particle with all water molecules including N_g neon particles and β stands for $1/k_B T$. Trial deletion of a randomly chosen neon particle out of N_g is attempted with a probability

$$p_{delete} = \frac{\exp[\beta(-\mu + w')]N_g}{(2\pi m k_B T/h^2)^{3/2} V} \tag{3}$$

where w' is the interaction energy of the chosen hydrogen molecule with all other molecules. Each MC step consists of one trial insertion or deletion of guest particle with the same probability, followed by five trial movements of water or guest particle and a trial volume change according to the common NPT MC procedure. Each MC simulation at a given thermodynamic state consists of at least 10^8 steps.

3. Result and discussion

The pressure dependencies of neon occupancy in ice II at various temperatures are shown in Fig. 1. The number of neon particle encaged in ice II increases gradually as the compression proceeds. Ice II does not share in the pressure dependence of accommodation with common clathrate hydrates where high occupancy of guest molecule is a necessary condition for their stability. However, this can be accounted for by the fact that ice II is one of the most stable ices in a certain region of temperature–pressure plane even without guest particles while usual clathrate hydrates cannot maintain its structure without guest particles. Furthermore, the existence of neon as guest particle enhances the stability of ice II; thus it pushes the envelope of the phase boundary of ice II to higher temperature and pressure. At maximum occupancy, the ratio of neon-to-water is found to be 1:6. This ratio is equal to the ratio of hydrogen-to-water in the case of ice II filled with hydrogen as observed from experimental work [6].

The behavior of neon occupancy in ice I_c is, however, different from the case of neon occupancy in ice II. Fig. 2 shows that the number of neon particles in ice I_c changes abruptly at a certain pressure that depends on the fixed temperature. This is mainly caused by the instability of ice I_c under high pressure and high temperature [20,21]. In the absence of neon
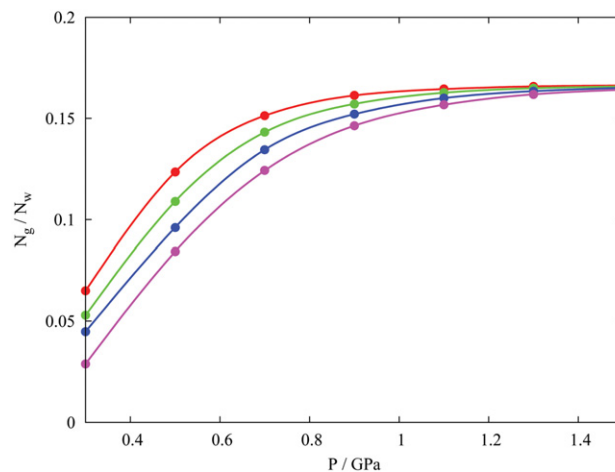
Fig. 1. Pressure dependence of ratio of neon-to-water number in ice II at (from left to right) $T = 273$, 300, 325, and 350 K.
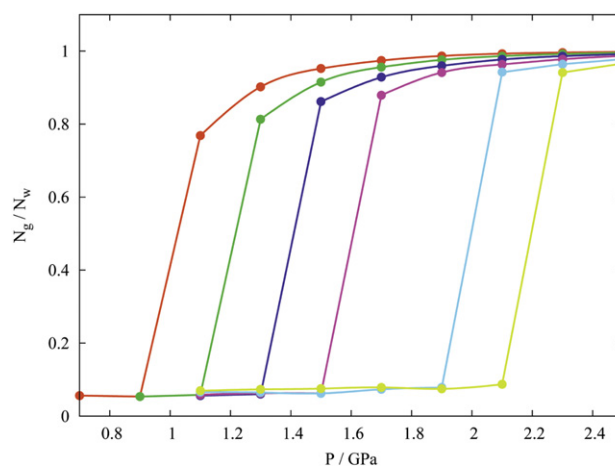

Fig. 2. Pressure dependence of ratio of neon-to-water number in ice I_c at (from left to right) $T = 273$, 300, 325, 350, 375, and 400 K.

particles to fill its vacant spaces, ice I_c structure gradually collapses resulting in a disordered form with less empty spaces for neon particle to occupy. We find that when the pressure is not sufficiently high to keep neon particles inside ice I_c up to certain neon-to-water ratio, ice I_c transforms into another amorphous ice morphology; the number of neon particle shown in lower region of Fig. 2 is attributed to the capability of amorphous ice to trap noble gas as suggested by experimental evidence [22] or due to the solubility of the gas in liquid water. Fig. 3 depicts the difference in the density between two ice morphologies. Outside of pressure region where the structure transformation occurs, the increase in density can be attributed to the hydrostatic pressure. When the neon occupancy is high, ice I_c structure is found to be intact even at 400 K. Fig. 4 shows the structure of ice I_c whose voids are occupied by neon particles at well-defined locations under high pressure. The maximum ratio of neon-to-water is found to be 1:1 at all temperatures studied. Thus ice I_c filled with neon can be seen as ice VII in which half the total water molecules are replaced by neon atoms since ice VII is composed of two interpenetrating ice I_c sublattices.

The same simulation method is also applied to thermodynamic states where ice I_c is metastable in its pure form in order to examine the occupancy (solubility) of neon inside ice I_c at low pressure. It is found that at 210 K and 30 MPa, the solubility of neon in mole fraction is 2.98×10^{-4}, and increase to 3.09×10^{-3} when compressed to 180 MPa in which the ice I_c structure is still preserved. The amount of neon inside ice I_c at low pressure is indeed different from the case of high pressure where the ice I_c structure is stabilized by the existence of neon. It is also different from the case in moderate pressure where the ice I_c structure is unstable and the amount of encaged neon is insufficient to stabilize it. Considering that the occupancy of noble gas inside ice increases with the decrease of temperature, the solubility of neon inside ice I_c at low pressure provided by MC simulation is comparable to the result from earlier prediction [3].

The stability of ice II and ice I_c filled with neon can be evaluated in terms of chemical potential. The free energy of a solid with N_w water molecules is calculated by its individual components: the interaction energy at 0 K, $U_q(V)$, the harmonic free
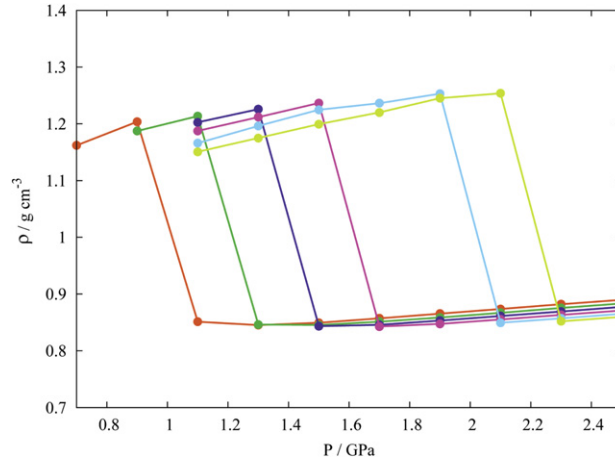
Fig. 3. Pressure dependence of density of water in ice I_c filled with neon at (from left to right) $T = 273, 300, 325, 350, 375,$ and 400 K.
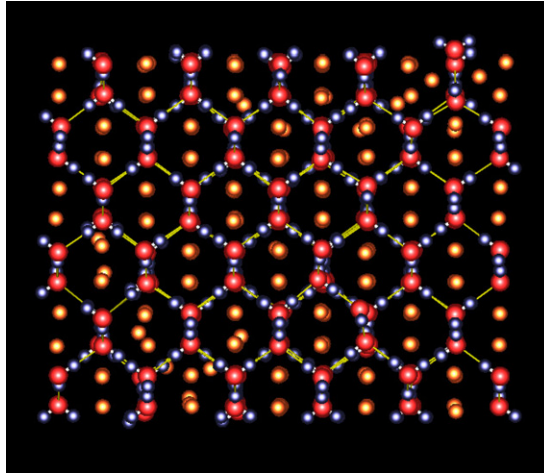

Fig. 4. Orthogonal view of the structure of ice I_c filled with neon at $T = 273$ K, $P = 2.5$ GPa.

energy, $F_h(T, V)$, and the residual entropy term, S_c, as

$$A^0(T, V) = U_q(V) + F_h(T, V) - TS_c \qquad (4)$$

with the harmonic free energy is calculated from a set of normal frequencies, v, obtained from normal mode analysis by diagonalizing the Hessian matrix of water [23]

$$F_h(T, V) = \frac{k_B T}{N_w} \sum_i \ln \left(\frac{h v_i}{k_B T} \right) \qquad (5)$$

and the residual entropy is given by

$$S_c = N_w k_B \ln(3/2), \qquad (6)$$

by neglecting the anharmonic free energy. This is justified when comparison between two ice forms is made. The chemical potential of filled ice is then calculated by

$$\mu = \mu_0 + \alpha k_B T \ln (1 - x) \qquad (7)$$

where μ_0 is the chemical potential of pure ice calculated as $\mu_0 = (A^0 + PV)/N_w$, α is the maximum ratio of guest to host, and x is the occupancy rate [24]. Fig. 5 shows the chemical potential of ices filled with neon, and pure ice VII. It can be seen that at lower pressure region, ice II filled with neon has the lowest chemical potential and thus indicates that ice II filled with neon is the most favorable compounds. This condition is relevant to the neon hydrate structure observed from experimental work [5]. As the pressure increases and a large number of neon particles are kept inside ice I_c voids, the chemical potential of ice I_c filled with neon becomes the lowest among the three structures. This implies that, at higher pressure, ice I_c filled with neon is the most favorable structure and the transformation from ice II to ice I_c filled with neon, can be expected.
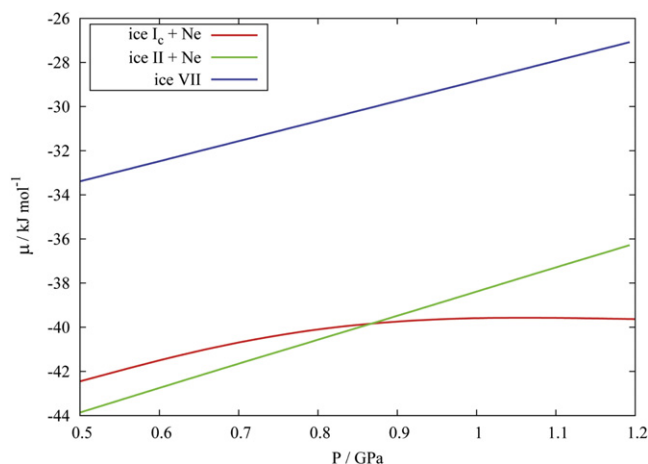
Fig. 5. Pressure dependence of chemical potential of ices (I_c and II) filled with neon and pure ice VII at $T = 273$ K.

4. Concluding remarks

We show that ice I_c filled neon is stable under high pressure of GPa order and high temperature, suggesting the possibility for the existence of a novel neon hydrate compound. The chemical potential of water in the compound is found to be lower than in ice II filled with neon and lower than ice VII. Therefore, the ice I_c structure is favorable under the thermodynamic states studied. The occupancy of neon studied here is almost unity and the pressure is so high that ice I_c structure alone is unstable. Consequently, the present hydrate also denoted as filled ice is fairly different from that predicted previously where the pressure is low enough for the ice structure to be intact and the resultant occupancy is much lower. Through the evaluation on the stability of ice II filled with neon, which is in good agreement with the experimental evidence, we demonstrate that GC/NPT MC simulation is useful to study the accommodation of guest particles inside ice structures.

Acknowledgements

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