Formation of ice nanotube with hydrophobic guests inside carbon nanotube

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[ABSTRACT]

A composite ice nanotube inside a carbon nanotube has been explored by molecular dynamics and grandcanonical Monte Carlo simulations. It is made from an octagonal ice nanotube whose hollow space contains hydrophobic guest molecules such as neon, argon, and methane. It is shown that the attractive interaction of the guest molecules stabilizes the ice nanotube. The guest occupancy of the hollow space is calculated by the same method as applied to clathrate hydrates.

I. INTRODUCTION

The carbon nanotube provides a well-defined nanoscale cylindrical pore which serves to prepare quasi-one-dimensional materials. Water is known to be confined in the carbon nanotube, but its properties in the quasi-one-dimensional space have been as little studied as or even less studied than those of other substances in spite of the fact that water itself has been more studied than the others. However, recent theoretical studies on water confined in the carbon nanotube and the experimental studies followed have demonstrated that the confined water freezes into crystalline structures that have never been found in the bulk counterpart and exhibits continuous and discontinuous freezing transitions.[1,2]

Computer simulation studies revealed that the structure of solid water in the zigzag $(\ell, 0)$ single-walled carbon nanotube (SWCN) (with ℓ =13, 14, ..., or 17) is quite different from the bulk ice structure; it is a one-dimensional array of n-gonal "rings", called an ice nanotube.[1,2] As in the ordinary ice, every water molecule in the carbon nanotube is hydrogen-bonded to its four neighbors in the solid state. Thus far, the simulations[1,2] with the TIP4P potential[3] have shown that liquid water confined in carbon nanotubes freezes into square, pentagonal, hexagonal, and heptagonal forms of the ice nanotube, each corresponding to n =4, 5, 6, and 7, respectively.[1] The ring type upon freezing depends on the diameter of the carbon nanotube, the pressure, and the temperature. It is also found from the simulations and free energy calculations that the phase behavior of confined water is qualitatively different from the bulk phase.

In 2002 appeared a report[4] that the structure of water inside the carbon nanotube at low temperatures determined by X-ray diffraction is consistent with that of the ice nanotube. Another experimental study by neutron scattering was published recently which confirmed formation of ice nanotubes and gave some insight into structure and dynamics of extra water molecules other than those constituting the ice nanotube.[5] Other simulation studies on water in carbon nanotubes have also been reported.[6-10]

Since the strain of an ice nanotube increases with increasing the interior angle of each ring from the ideal hydrogen-bond angle, the n-gonal form of ice nanotube with $n > 6$ becomes increasingly unstable with n. In fact, no octagonal ice nanotube is found at temperatures

above 200 K by simulation study with the TIP4P model. Hydrophobic molecules can be, however, incorporated into the octagonal ice nanotube to stabilize the otherwise unstable host lattice, provided that they are small enough not to distort the original ice tube structure. This is somewhat different from the incorporation of water molecules inside an ice nanotube, which interact strongly with the host water molecules. Mechanism to stabilize an ice tube with hydrophobic molecules is expected to be similar to that of clathrate hydrates, which are composed of host water and small guest molecules.

The interaction energy between a guest and the surrounding water molecules is around 10 kJ mol^{-1}, which is sufficient to compensate the energy raised by the strain of an octagonal ring.[11] Thus, we investigate formation of the (composite) ice nanotube by molecular dynamics (MD) simulations and equilibrium conditions are examined by grandcanonical Monte Carlo (GCMC) simulations. Then, we propose a "mean-field" type approximation which reduces the quasi-one-dimensional system into a true one-dimensional system and thereby enables us to calculate, without simulations, the occupancy of the hollow space by guests as a function of equilibrium pressure.

II. MODEL AND METHOD

The interaction of a pair of water molecules is described by the TIP4P potential.[3] We examine accommodation of three kinds of guest molecules: argon, neon, and methane. Those interactions between guest molecules are represented by Lennard-Jones (LJ) potentials, whose parameters are listed in Table I.[12,13] The methane molecule here is also treated as a spherical one. The interactions between water and guest are also described by LJ potentials assuming the Lorentz-Berthelot rule. All the pair interactions are truncated smoothly at 0.8655 nm and the long-range interaction for guests is taken into account by assuming the uniform distribution of guests in the carbon nanotube. The force field of the model SWCN is taken to be an LJ potential integrated over the cylindrical area of the SWCN using the area density of the carbon atoms and the potential parameters for graphite[14] as in the previous study. The diameter of

the SWCN d is set to 1.419 nm corresponding to (18 ,0) nanotube. We hereafter refer to the direction along the carbon nanotube as z-axis.

GCMC simulations are carried out at temperatures, 200 K and 250 K and at various chemical potentials of the guest gas in bulk phase in order to examine the equilibrium condition on the number of guest molecules to be encapsulated. The guest species at a given chemical potential is in equilibrium with that inside the composite nanotube in GCMC simulation. Since the equation of state for LJ fluid is well established[15], it is straightforward to express the chemical potential as a function of pressure. The periodic boundary condition is applied in the axial direction of the tubule length L, which is fixed to 11.16 nm containing 320 water molecules with the neighboring distance of 0.279 nm.

III. RESULTS AND ANALYSES

A. MD and GCMC simulations

An MD simulation is performed at temperature 200 K to show that the ice nanotube is spontaneously formed with the guests sitting in the interior of the ice tube.[16] The numbers of water molecules and guest argon atoms are fixed to 160 and 10, respectively. The periodic boundary condition is applied in the axial direction and the tubule length, L, which fluctuates around the average (5.9 nm) subject to the constant axial pressure of 50 MPa. The MD simulation starts with random positions and orientations of all the molecules and the whole simulation time is 250 ns. Molecular arrangements are drawn in Fig. 1 after the elapse of 40 ps, 28 ns, 100 ns, and 172 ns. The angular order parameter for $k-$fold symmetry defined by

$$\eta = \left\langle |\sum_{j}^{N_w} \exp(ik\theta_j)|^2 / N_w^2 \right\rangle, \tag{1}$$

is tabulated in Table II, where θ_j is the angle of j-th molecule in the cylindrical coordinate system, N_w is the number of water molecules, and $\langle \cdots \rangle$ denotes the average. It is zero at the initial stage and later grows rapidly. Then, it fluctuates around 0.3 for a long time in inherent structure[17,18], and occasionally becomes small.[19] Finally, it exceeds 0.9 and the structure of

water inside is almost perfect after time 172 ns. The potential energy also decreases with elapsing time as given in Table II. Thus, the octagonal ice nanotube forms spontaneously at the given condition, although its formation takes much longer time than that of a pure ice nanotube in a carbon nanotube with a smaller diameter.

In one GCMC simulation, the initial positions and the orientations are assigned randomly. At 200 K and at pressure of 10-100 MPa, we observe the composite ice nanotubes containing argon, one of which is drawn in Fig. 2. It seems, however, to take a huge number of MC steps to complete the octagonal ice nanotube structure (A single MC step is composed of one trial creation or annihilation of a guest and 10 trial moves.) In the other simulations, an initial configuration of the octagonal ice nanotube is generated such that it has the lowest free energy (sum of the interaction energy and the vibrational free energy) among all the proton-disordered forms.[11] Then the GCMC simulations start with this configuration at a given chemical potential (pressure) of the guest. Each GCMC simulation consists of more than 10^8 MC steps. Plotted in Fig. 2 are the ice nanotube structures at 200 K containing three kinds of guest species. All the ice nanotube structures containing the each guest species are maintained at the given guest pressure. Both argon and methane form the ice nanotubes with those guest molecules located at the center of the ice tube. The neon atoms drift from the center but they still stay inside the ice nanotube.

Temperature and pressure dependences of guest occupancy are shown in Fig. 3 and are compared with those of the theoretical calculation as discussed later. Except for the case of collapse of the ice nanotube, the angular order parameters defined by Eq. (1) are mostly greater than 0.3, which indicates a rough octagonal structure is maintained.[19] The potential energies both for water and guest argon are given in Table III. The potential energies at 200 K are almost constant in the whole range of the gas pressure examined, which implies that the octagonal tube structure is not destroyed even below the atmospheric pressure. At 250 K, on the other hand, the ice tube structure is broken at pressures below 1 MPa.

B. Approximate evaluation of the occupancy

The number of guest molecules inside the ice nanotube is in principle calculated from the grandcanonical partition function. In cases of bulk water+guest systems, the partition function cannot be obtained in practice (even if guests are LJ particles); an exceptional case is a system that can be divided into small subsystems with a small number of guest molecules. Fortunately, there are two rationales for the division of the whole system into mutually independent subsystems each containing smaller number of water and guest molecules. Firstly, an *intermolecular* interaction potential between guest molecules plays a minor role in the partition function compared with the other interaction which may arise partly from some sort of confinement. Secondary, the interaction between two adjacent subsystems is weak; the quasi-one-dimensional system has a relatively smaller interfacial region compared with a three-dimensional system. Once the division is accepted, it is rather straightforward to calculate the grandcanonical partition function with the smaller subsystems.

The composite tube is treated as an open system with respect to guest molecules while the number of water molecules is fixed. The present system resembles a clathrate hydrate, in which each cage is multiply occupied, and therefore, a statistical mechanical treatment for clathrate hydrates is applicable.[20] Divide the hollow space into n_w subsystems, each of which is multiply occupied by guests, and take into account indistinguishability of the same kind of guest molecules. Then, the relevant grandcanonical partition function is given as

$$\Xi = \exp(-\beta n_w A_w^0)[\sum_{n_g=0}^{n_m} \exp\{\beta(n_g\mu_g - f_{n_g})\}]^{n_w}, \tag{2}$$

where f_{n_g} is the free energy of occupancy by n_g guest molecules of the mass m in a subsystem. The average guest number is calculated as

$$< N_g >= \frac{\partial \ln \Xi}{\partial(\beta\mu_g)} = \frac{n_w[\sum_{n_g=1} n_g \exp\{\beta(n_g\mu_g - f_{n_g})\}]}{[\sum_{n_g=0} \exp\{\beta(n_g\mu_g - f_{n_g})\}]}. \tag{3}$$

The free energy, f_{n_g} is calculated by the integration for n_g (atomic) guest coordinates in a single subsystem as

$$\exp(-\beta f_{n_g}) = \frac{1}{n_g!}(\frac{2\pi m k_B T}{h^2})^{3n_g/2} \int \prod_i^{n_g} d\mathbf{r}_i \exp[-\beta\{\sum_i^{n_g} w(\mathbf{r}_i) + \sum_{i<j}^{n_g} \phi(\mathbf{r}_i, \mathbf{r}_j)\}]. \tag{4}$$

where $w(\mathbf{r})$ is the interaction of a guest with all the water molecules and the carbon nanotube, and $\phi(\mathbf{r}, \mathbf{r}')$ is the guest-guest interaction. This integration becomes extremely difficult to be performed for a subsystem with $n_g > 4$. To examine the occupancy of guest molecules more accurately with a larger subsystem, an approximate treatment is proposed. The free energy of a single molecule occupying a cylindrical space inside the ice nanotube, f_1, is given by

$$\exp(-\beta f_1) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \int_0^l dz \int dx \int dy \exp[-\beta w(\mathbf{r})] \tag{5}$$

where the integration in z-coordinate is performed with the tubule length l of the subsystem. If the integration in x-y coordinates is limited to a narrow cylindrical region along the ice nanotube, the effective interaction, $\psi(z, z')$, is given by averaging over x-y coordinates of a pair of guest molecules which interact directly with each other via the pair potential, $\phi(\mathbf{r}_1, \mathbf{r}_2)$, as

$$\exp[-\beta\psi(z, z')] = \frac{\int d\mathbf{r}_1 \int d\mathbf{r}_2 \delta(z - z_1)\delta(z' - z_2) \exp[-\beta\{w(\mathbf{r}_1) + w(\mathbf{r}_2) + \phi(\mathbf{r}_1, \mathbf{r}_2)\}]}{\int d\mathbf{r}_1 \int d\mathbf{r}_2 \delta(z - z_1)\delta(z' - z_2) \exp[-\beta\{w(\mathbf{r}_1) + w(\mathbf{r}_2)\}]} \tag{6}$$

This approximation works if the ice nanotube is narrow enough to constitute a small hollow space along which guest molecules line up, that is, the guest molecules are too large to change the order in $z-$coordinate at a give temperature. The approximate free energy for n_g guest molecules is calculated under this condition as

$$\exp(-\beta f_{n_g}) = l^{-n_g} \exp(-\beta n_g f_1) \int_0^l dz_1 \int_{z_1}^l dz_2 ... \int_{z_{(n_g-1)}}^l dz_{n_g} \exp[-\beta \sum_{i<j} \psi(z_i, z_j)] \tag{7}$$

Plotted in insets of Fig. 3 are the potential energy curves, $w(|\mathbf{r}|)$, against radial distance from the center of the axis, both the averaged and the minimum ones. The potential energy for argon increases significantly for $r > 0.1$ nm. Two argon atoms cannot overlap with each other along the z-coordinates with a thermal energy in the ambient condition. Thus, the assembly of argon atoms (methane molecules as well) can be regarded as a one-dimensional array in the ice nanotube. However, the potential curves of neon are flat near the center and they increase gradually beyond $r = 0.14$ nm, half the size-parameter for neon. Thus, the above approximation is not good for neon but is effective for argon and methane. In actual calculation, the tubule length l is set to 8 times the O-O distance, and maximally ($n_m =$) 8 guest

molecules are encapsulated. Therefore, the approximation is rather poor in the low pressure region where the large l is required to handle the small density ($\rho \leq n_m/l$). Plotted in Fig. 3 are occupancies by guest molecules against guest pressure, which are calculated according to the above approximation together with those by GCMC simulations. Smaller occupancy observed in GCMC simulations at 250 K and at low pressures is due to collapse of the octagonal ice tube. Agreement with GCMC simulations is excellent for methane and argon. However, occupancy of neon is not described by the approximate method.

An alternative way is to follow the standard method to calculate exact partition functions for one-dimensional models with nearest neighbor interactions.[21] Since $\psi(z)$ is short ranged, we may assume that each guest molecule interact with its nearest neighbors alone, which is the only prerequisite for the calculation. Then the isobaric partition function, i.e., the Laplace transform of Eq. (7), is given by

$$Y(P,T) = e^{-N\beta\mu} = y^{N+1}a^N \tag{8}$$

with

$$y = \int_0^\infty e^{-\beta P z} e^{-\beta \psi(z)} dz \quad \text{and} \quad a = e^{-\beta f_1}/l. \tag{9}$$

In the thermodynamic limit $N \to \infty$,

$$\mu = -kT \ln(ya) \tag{10}$$

and

$$\rho = -\left(\frac{\partial \ln y}{\partial \beta P}\right)_T^{-1}. \tag{11}$$

Note that P is not the pressure of the bulk gas but the "pressure" of the one-dimensional gas and just serves as a dummy parameter for relating μ with the number density ρ (number per unit length). The occupancy of argon at 200 K is also plotted in Fig. 3 (a). The second method is not so good compared with the first method at higher pressures because that considers only the nearest neighbor interaction. It becomes, however, better below 0.03 MPa since the thermodynamic limit is taken.

IV. CONCLUSIONS

We have found that the octagonal ice tube is formed with coexistence of hydrophobic molecules in its interior by MD simulation. The occupancy by guest molecules is calculated from the approximate theory, which we found agrees well with the GCMC simulations for guest argon and methane but does not for neon. Stability of the ice nanotube relies on the attractive interaction with the guest molecules.

Some small *hydrophilic* molecules may be accommodated in the ice nanotube if the attractive interaction (including weak hydrogen bonds) between water and the hydrophilic guest molecules is not so strong considering the recent experimental observation that even extra water molecules may exist inside the ice nanotubes.[5]

It is interesting to examine whether an octagonal ice nanotubes is formed inside the carbon nanotube with larger or smaller diameter than the present size. Even if the diameter difference from $\ell = 18$ is small, say, with index $\ell = 17$ ($d = 1.341$ nm) or $\ell = 19$ ($d=1.497$ nm), the most stable structure may be different depending sensitively on the guest species and the axial pressure, the latter of which is known to be important in the phase behavior of water inside a carbon nanotube.[1]

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TABLE I: Lennard Jones size (σ) and energy (ϵ) parameters for guest species.

guest	σ (nm)	ϵ (kJ mol^{-1})
argon	0.3405	0.9960
neon	0.2820	0.3017
methane	0.3758	1.2355

TABLE II: Angular order parameter of 8-fold symmetry η after the elapse of time t(ns), and potential energy of system E (kJ mol^{-1}) in inherent structure.

t	η	E
0.04	0.005	-49.43
1.6	0.15	-51.46
8	0.39	-52.25
28	0.15	-51.17
100	0.26	-52.42
172	0.93	-53.37
250	0.90	-53.56

TABLE III: Potential energies of water, E_w and guest argon, E_g (kJ mol^{-1}) at pressure p(MPa) by GCMC simulation.

	$T =$ 200 K		$T =$ 250 K	
p	E_w	E_g	E_w	E_g
0.01	-49.28	-16.94	-45.08	-22.13
0.03	-49.29	-16.94	-45.22	-21.12
0.1	-49.29	-16.91	-45.10	-21.83
0.3	-49.31	-16.88	-45.16	-21.82
1	-49.31	-16.87	-45.12	-21.78
3	-49.31	-16.80	-47.89	-16.36
10	-49.32	-16.74	-47.74	-16.29
30	-49.31	-16.70	-47.78	-16.22
100	-49.31	-16.65	-47.79	-16.12

Figure captions

Fig. 1 Side views of molecular coordinates in MD simulations at $t = 0.04$, 28, 100, and 172 ns.

Fig. 2 Top and side views of molecular coordinates of the octagonal ice tubes obtained by GCMC simulations with guest species at 200 K: (a) argon with random initial configurations at 50 MPa, (b) argon at 30 MPa, (c) neon at 100 MPa, (d) methane at 10 MPa,

Fig. 3 Occupancy calculated by GCMC simulations (symbols, filled circle; $T = 200$ K, open circle; $T = 250$ K) together with those calculated by the approximate method (lines, solid; $T = 200$ K, dashed; $T = 250$ K) of guest species; (a) argon, (b) neon, (c) methane. Occupancy by the alternative way with the short-ranged argon-argon interaction at $T = 200$ K is also given (dash-dot line). In insets, potential energy curves are shown (thick line; average over all orientations, thin line; the minimum at the given r).
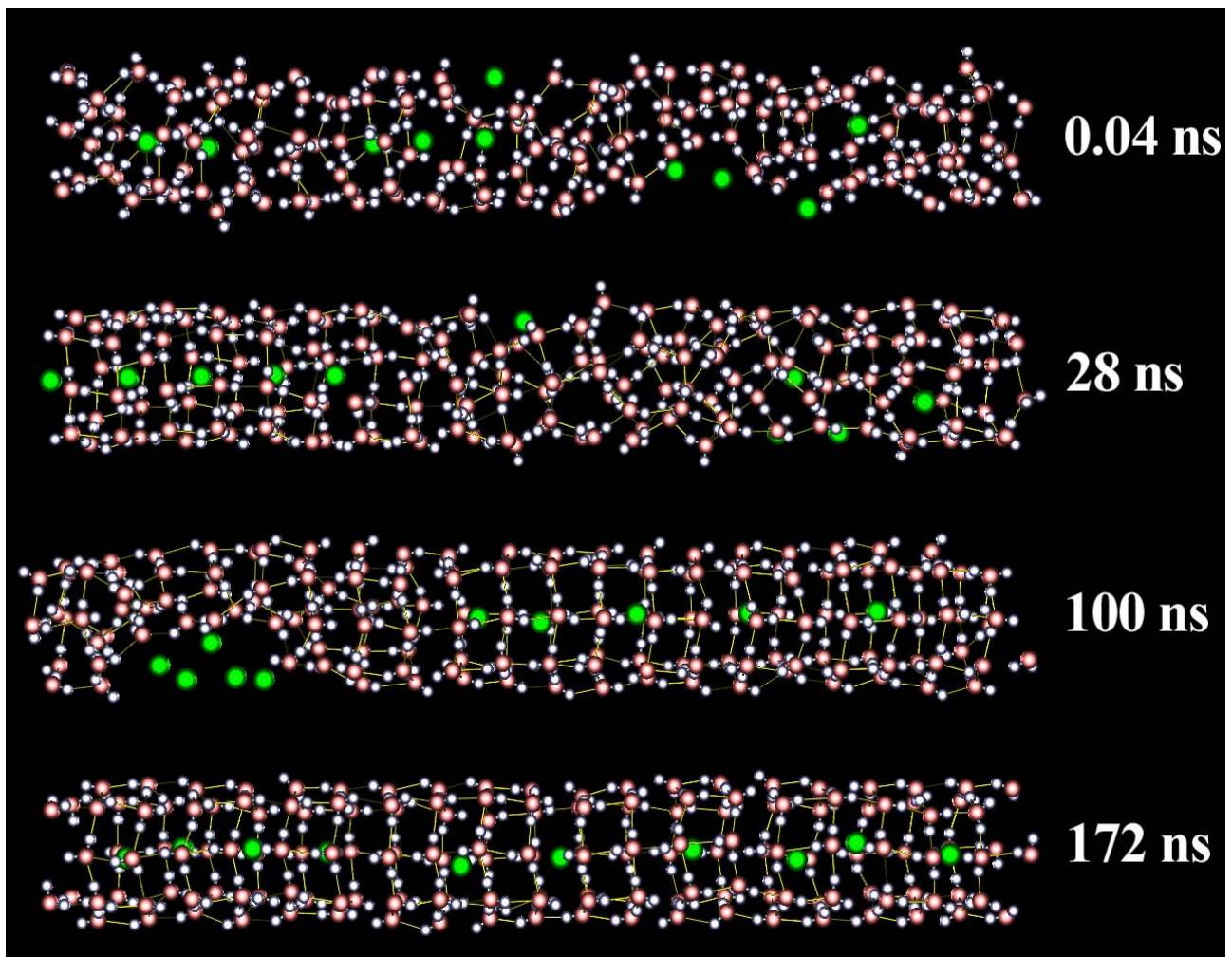
Fig.1 Tanaka & Koga

Fig.2(a) Tanaka & Koga

(b) argon
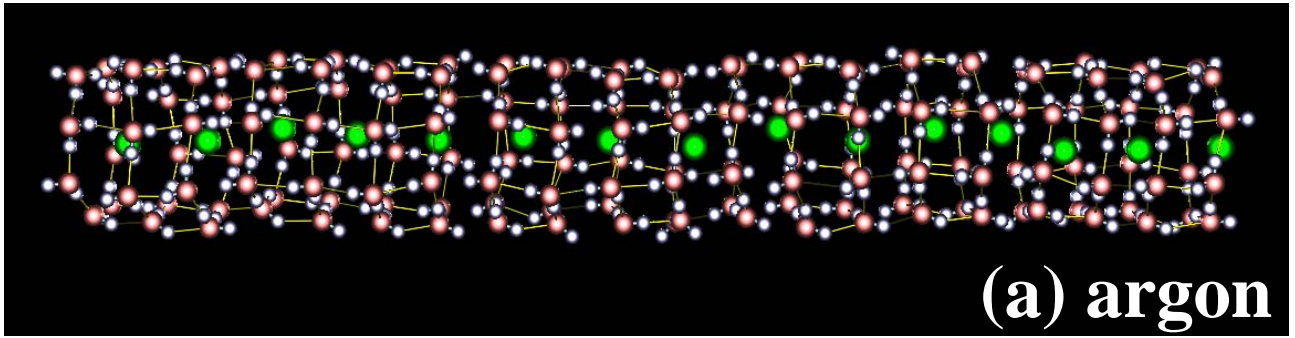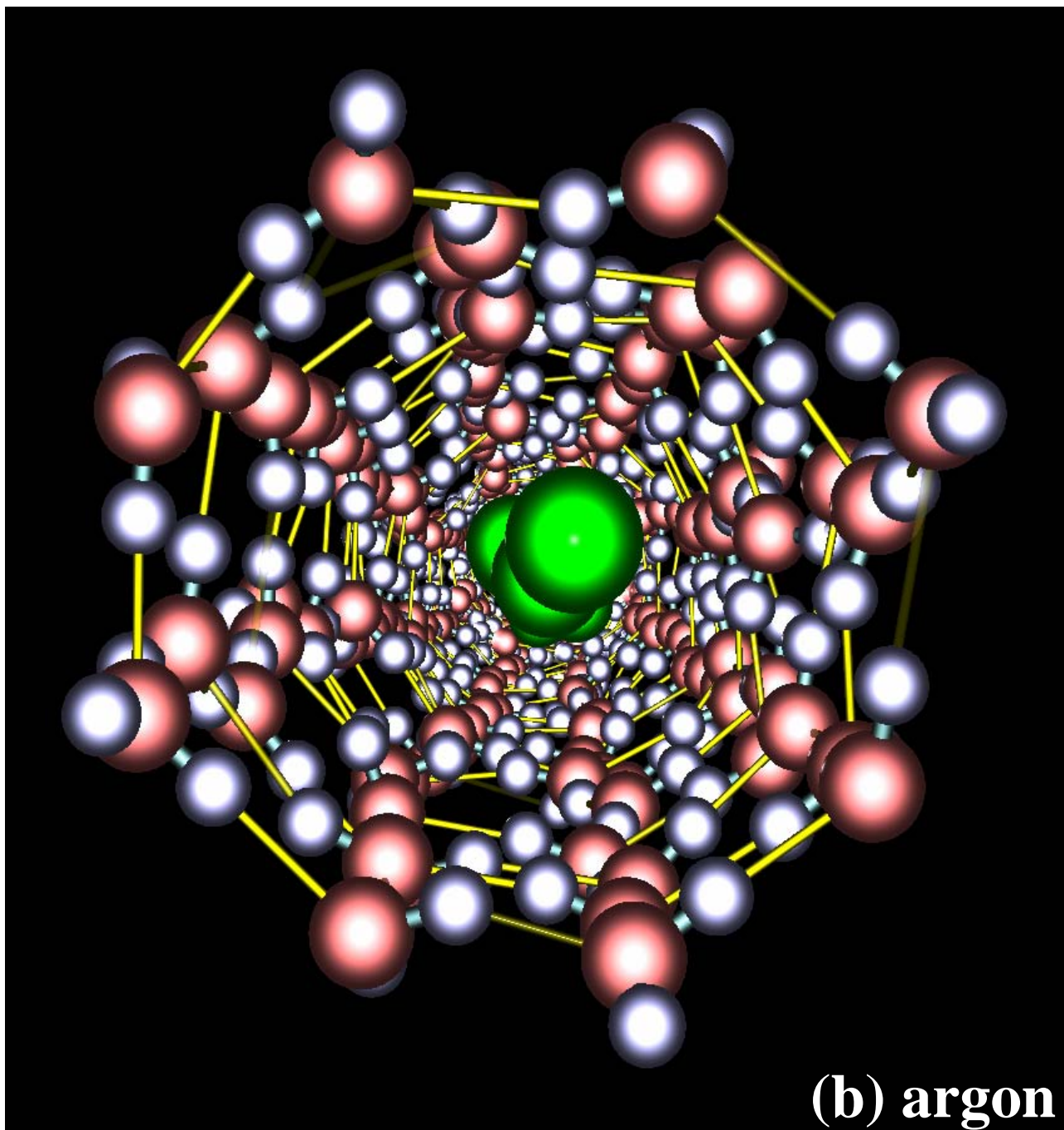
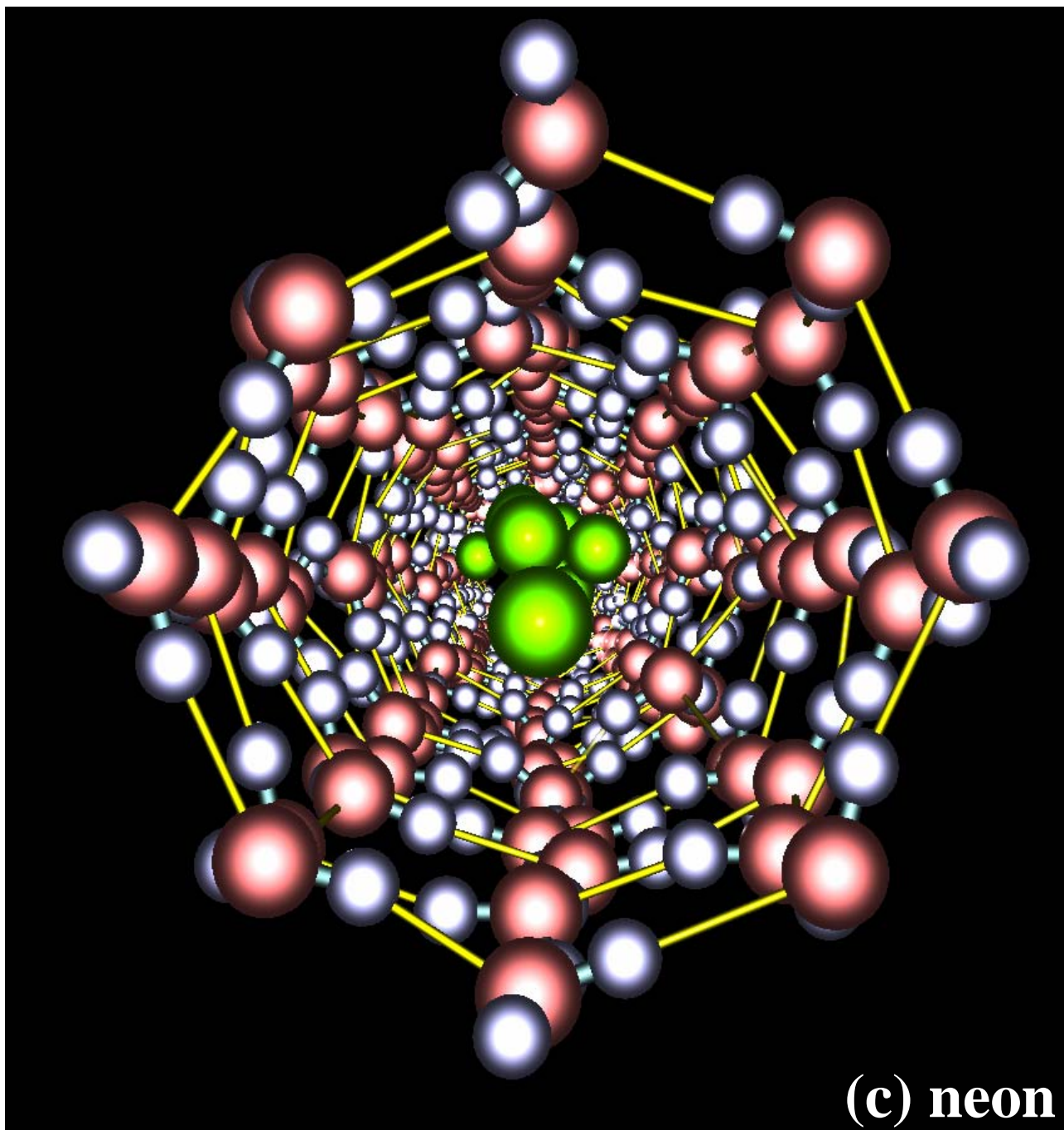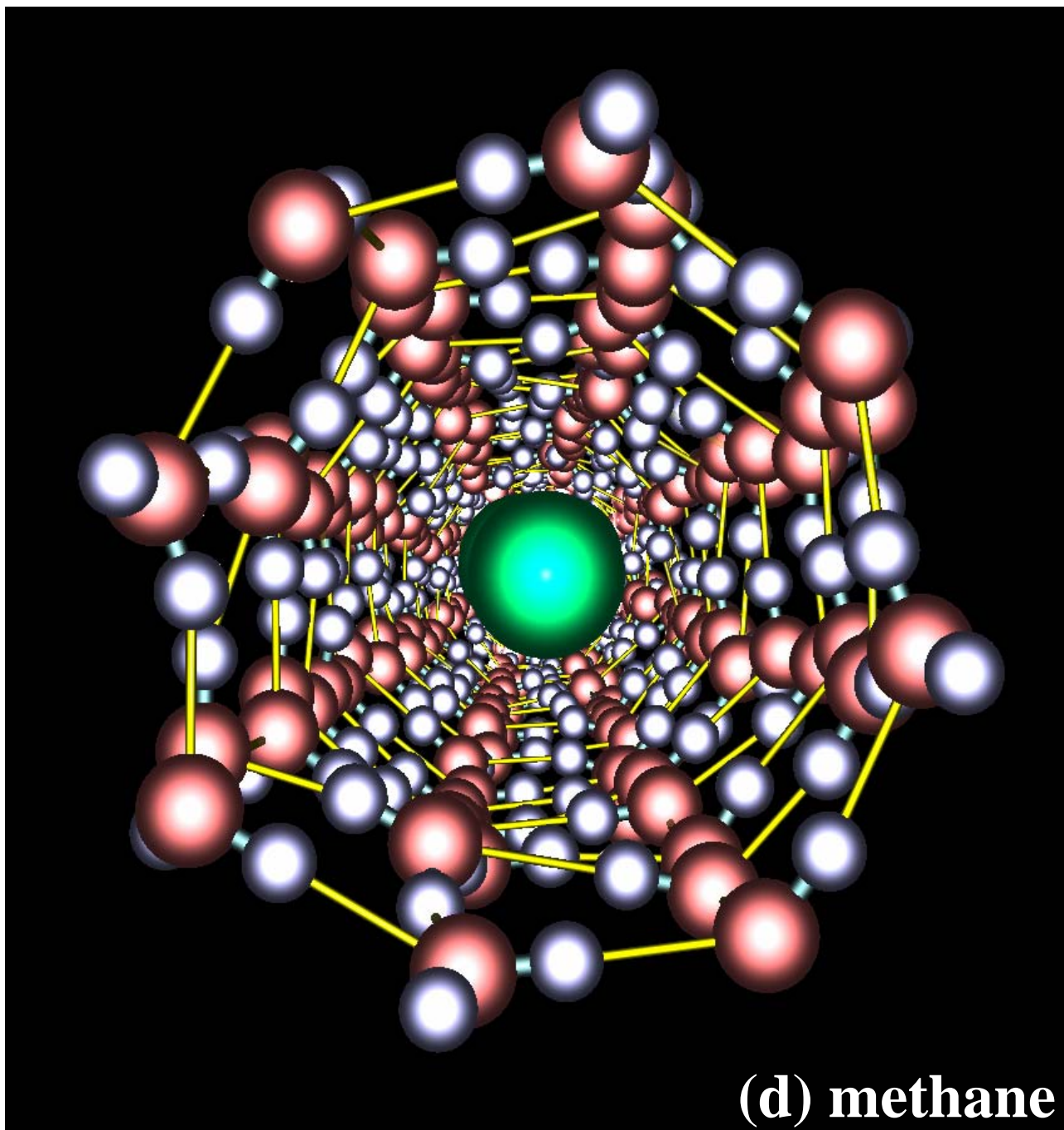Fig. 2(b) Tanaka & Koga

Fig. 2(c) Tanaka & Koga

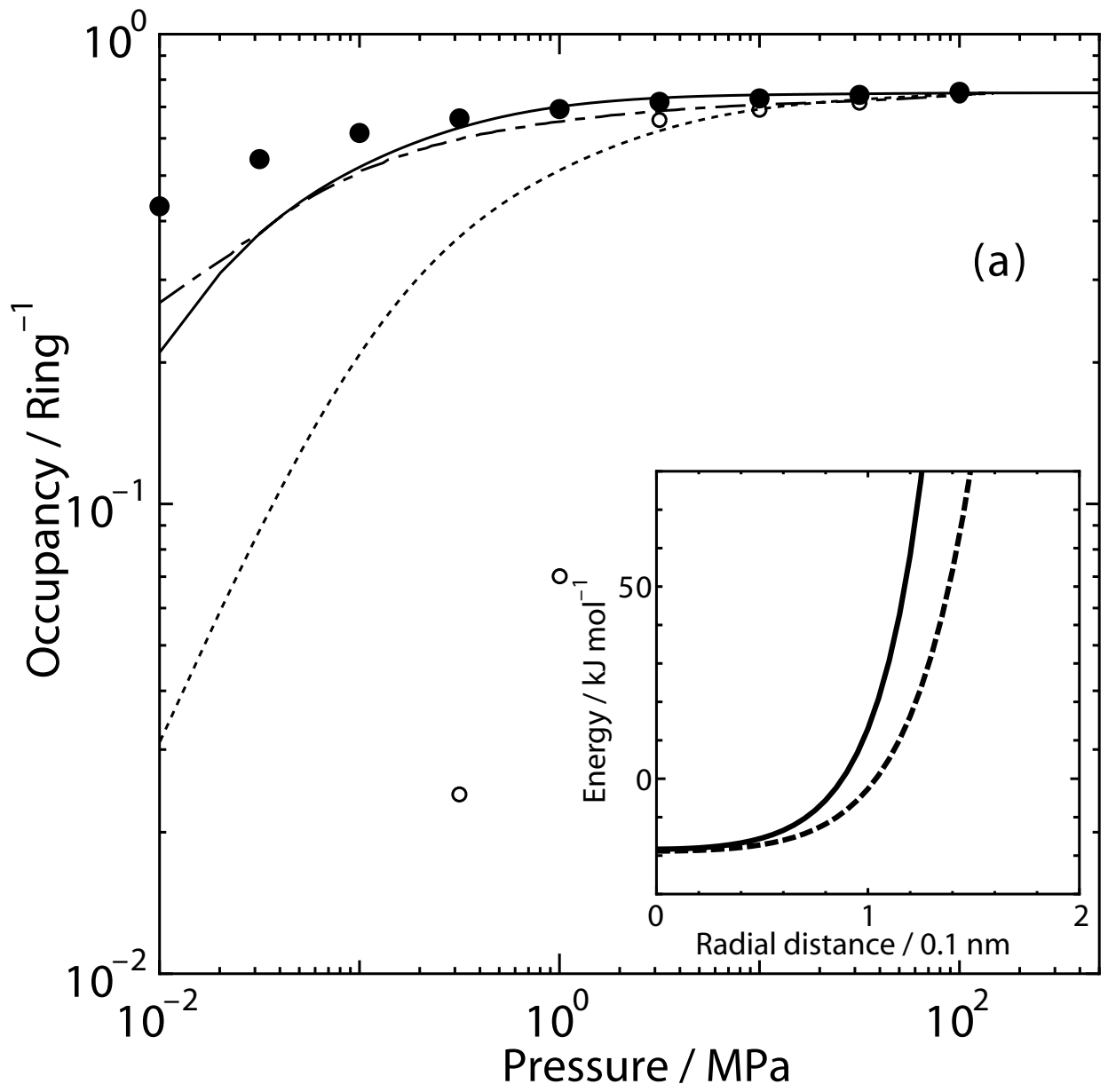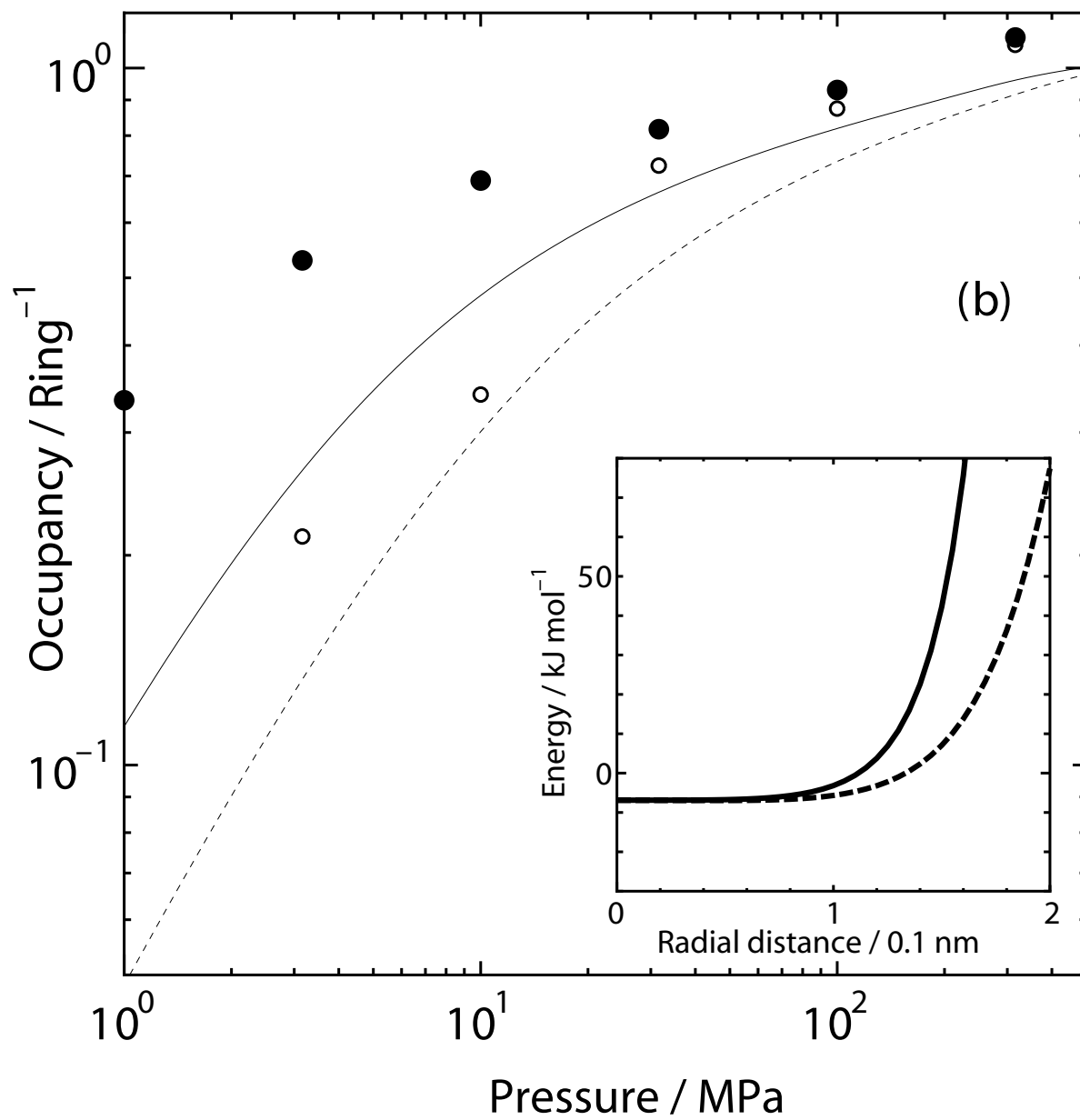(d) methane

Fig. 2(d) Tanaka & Koga
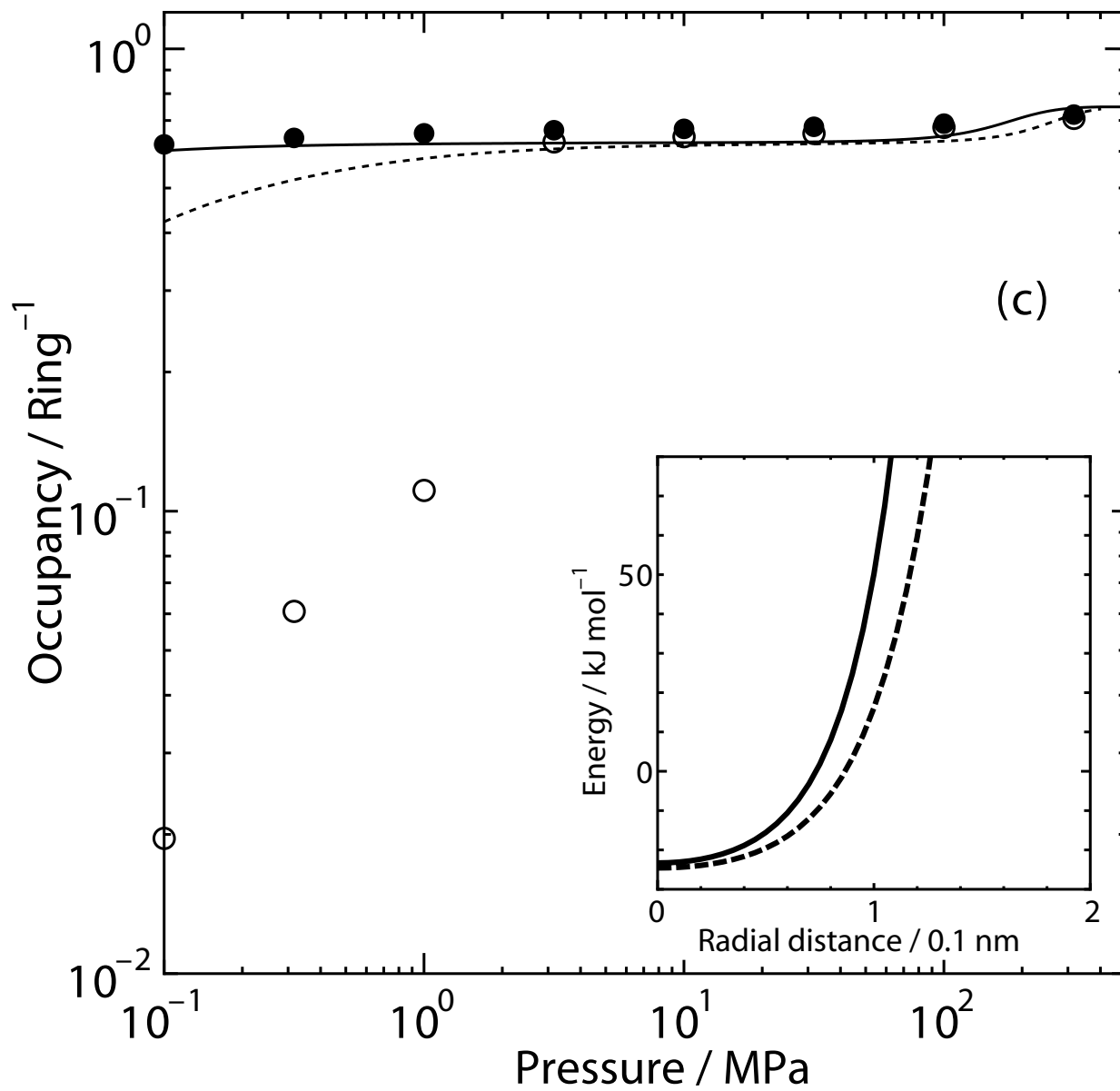
Fig. 3 (a)   Tanaka & Koga

Fig. 3 (b)   Tanaka & Koga

Fig. 3 (c)   Tanaka & Koga