

Molecular Dynamics Study of Classical Complex Systems and Quantum Systems in Condensed Phase

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science



OKAZAKI, Susumu
MIURA, Shinichi
YOSHII, Noriyuki
YAMADA, Atsushi
MIKAMI, Taiji
ANDOH, Yoshimichi
KAJIMOTO, Shinji
FUJIMOTO, Kazushi

Professor
Assistant Professor*
Assistant Professor†
Assistant Professor
Post-Doctoral Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow‡
Graduate Student

1. Free Energy of Water Permeation into Hydrophobic Core of Sodium Dodecyl Sulfate Micelle by Molecular Dynamics Calculation¹⁾

In our previous analysis of the structural stability of sodium dodecyl sulfate (SDS) micelle based on molecular dynamics calculation, vacancies were found in the center of the micelles (*Chem. Phys. Lett.* 425, 58 (2006)). It is very interesting to clarify whether a water molecule is expected in the vacancy in thermodynamic equilibrium at room temperature. In order to investigate the stability of water in the core of micelle, free energy of transfer of water from bulk to the core has been calculated for the SDS micelle in water for two micelle sizes, $N = 61$ and 121 , at temperature $T = 300$ K and pressure $P = 1$ atm. The calculated free energy of transfer, $\Delta G_{c \leftarrow b}$, from the bulk to the core is about 28 ± 4 and 26 ± 4 kJ/mol for the micelle of size $N = 61$ and 121 , respectively, where the corresponding Boltzmann factor, $\exp(-\Delta G_{c \leftarrow b}/kT)$, is in the order of one over several ten thousand. Thus, water molecule hardly permeates into the core of the micelle.

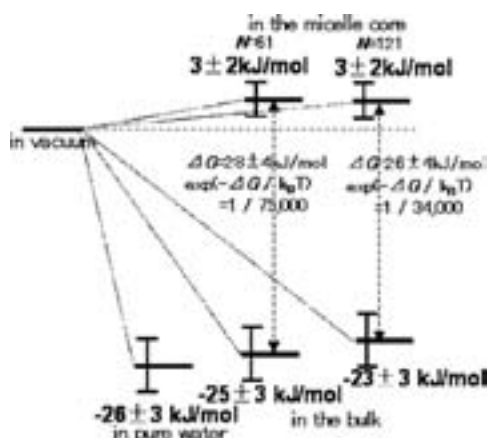


Figure 1. The calculated free energy of transfer of water molecule from vacuum to the core and to the bulk water for the micelle of the size $N = 61$ and 121 . The hydration free energy of water in pure water itself is also presented.

2. A Molecular Analysis of the Vibrational Energy Relaxation Mechanism of the CN^- Ion in Water Based upon Path Integral Influence Functional Theory Combined with a Dipole Expansion of the Solute–Solvent Interaction²⁾

The molecular mechanism of vibrational energy relaxation of the CN^- ion in water has been investigated using path integral influence functional theory combined with a dipole expansion of the solute–solvent interaction. First, in order to find out which solvent water molecules contribute most to the absorption of the solute excess vibrational energy, the normal modes of the solution, adopted for the harmonic oscillators

bath approximation in the influence functional theory, have been back-transferred to the molecular coordinates and a contribution to the relaxation has been assigned to each water molecule according to the transformation matrix. Then, the coupling intensity $C^{(i)2}$ between solute and solvent molecules playing a major role in the relaxation, has been analyzed by dipole expansion of the solute–solvent interaction, where bending, rotational and translational degrees of freedom were all represented by the standard variables μ_1 , μ_2 , R , θ_1 , θ_2 , and ϕ for the dipole expansion. From these analyses, it is clarified that (1) the contribution of the solvent water to the relaxation decreases rapidly in proportion to $1/R^6$, such that only water molecules in the first hydration shell take part in the relaxation, (2) water molecules located in the direction of C–N bond contribute much to the relaxation, and (3) the excess energy is transferred to the bending of the relevant water molecule and its rotational libration represented by the variable θ_2 .

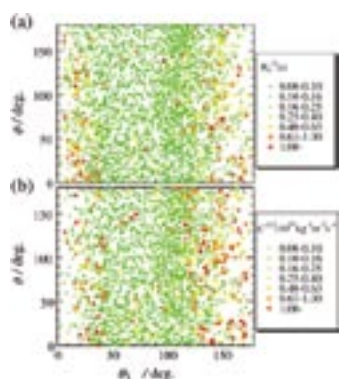


Figure 2. Actual (a) molecular relaxation $R^{(1)}$ and (b) molecular coupling intensity $C^{(1)2}$ for the water molecules in the first hydration shell.

3-1. Rotational Fluctuation of Molecules in Quantum Clusters. I. Path Integral Hybrid Monte Carlo Algorithm³⁾

We present a path integral hybrid Monte Carlo (PIHMC) method for rotating molecules in quantum fluids. This is an extension of our PIHMC for correlated Bose fluids [S. Miura and J. Tanaka, *J. Chem. Phys.* **120**, 2160 (2004)] to handle the molecular rotation quantum mechanically. A novel technique referred to be an effective potential of quantum rotation is introduced to incorporate the rotational degree of freedom in the path integral molecular dynamics or hybrid Monte Carlo algorithm. For a permutation move to satisfy Bose statistics, we devise a multilevel Metropolis method combined with a configurational-bias technique for efficiently sampling the permutation and the associated atomic coordinates. Then, we have applied the PIHMC to a helium-4 cluster doped with a carbonyl sulfide molecule. The effects of the quantum rotation on the salvation structure and energetics were examined. Translational and rotational fluctuations of the dopant in the superfluid cluster were also analyzed.

3-2. Rotational Fluctuation of Molecules in Quantum Clusters. II. Molecular Rotation and Superfluidity in OCS-Doped Helium-4 Clusters⁴⁾

Helium-4 clusters are studied as a function of cluster size N in a small-to-large size regime ($2 \leq N \leq 64$). The molecular rotation of the dopant shows nonmonotonic size dependence in the range of $10 \leq N \leq 20$, reflecting the density distribution of

the helium atoms around the molecule. The size dependence on the rotational constant shows a plateau for $N \geq 20$, which is larger than the experimental nanodroplet value. Superfluid response of the doped cluster is found to show remarkable anisotropy especially for $N \leq 20$. The superfluid fraction regarding the axis perpendicular to the molecular axis shows a steep increase at $N = 10$, giving the significant enhancement of the rotational fluctuation of the molecule. On the other hand, the superfluid fraction regarding the axis parallel to the molecular axis reaches 0.9 at $N = 5$, arising from the bosonic exchange cycles of the helium atoms around the molecule. The anisotropy in the superfluid response is found to be the direct consequence of the configurations of the bosonic exchange cycles.

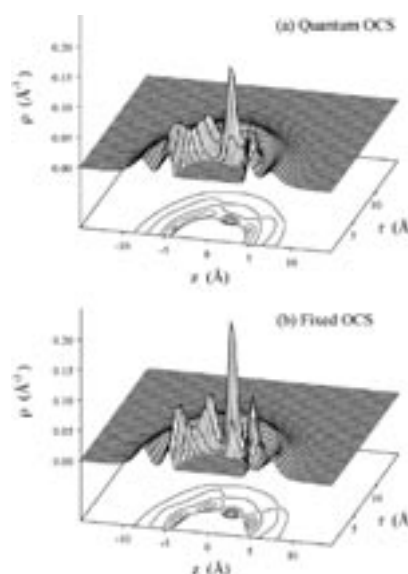


Figure 3. The total helium density distribution around the OCS molecule $\rho(z,r)$ in the $\text{OCS}({}^4\text{He})_{64}$ cluster [top: $\rho(z,r)$ for the quantum OCS case; bottom: $\rho(z,r)$ for the fixed OCS case]. z is the molecular axis and r the radial distance from the z axis. The OCS center of mass is located at the origin and the molecule is oriented as O–C–S from $+z$ to $-z$. All distances are in units of angstrom.

References

- 1) N. Yoshii and S. Okazaki, *J. Chem. Phys.* **126**, 096101(3 pages) (2007).
- 2) Y. Okamoto, T. Mikami, N. Yoshii and S. Okazaki, *J. Mol. Liq.* **134**, 34–39 (2007).
- 3) S. Miura, *J. Chem. Phys.* **126**, 114308 (10 pages) (2007).
- 4) S. Miura, *J. Chem. Phys.* **126**, 114309 (7 pages) (2007).

* Present Address; Kanazawa University, Kanazawa 920-1192

† Present Address; Himeji Dokkyo University, Himeji 670-8524

‡ Present Address; Tohoku University, Sendai 980-8577