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Title	Evaporation dynamics of clusters(4) Quantum chaos and semiclassical theory in molecular science and nuclear theory, Chaos and Nonlinear Dynamics in Quantum-Mechanical and Macroscopic Systems)
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Citation	(2005), 84(3): 479-480
Issue Date	2005-06-20
URL	http://hdl.handle.net/2433/110209
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

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Evaporation dynamics of clusters

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単分子分解の統計的反応速度定数を求める際、分子を剛体と近似する方法がよく用いられる [1]。しかし、Ar_8 の分子動力学計算からクラスターのように柔らかい分子では解離反応に構造転移反応が伴う事が明らかになり、形を変えながら解離する分子をある特定の剛体として近似する事は望ましくないと考えられる。そこで、我々は構造転移を伴う解離反応を扱い得る統計的速度論を提案する。さらに、Ar_8 の解離反応に於いての検証結果も紹介する。

1 Introduction

In the statistical rate theory for the unimolecular dissociation, molecules are approximated to rigid bodies[1]. However, we have great difficulties to approximate flexible molecules like clusters to rigid bodies, because clusters undergo the evaporation accompanying structural isomerizations. In this report, we present our studies about dynamics and statisctical rate theory for the cluster evaporation.

2 Model

We have carried out constant-energy MD simulations for an Ar_8 cluster where the pairwise Morse potential are employed to describe the atom-atom force field. The Hamiltonian in reduced unit is given by,

$$H = \frac{1}{2} \sum_{i=1}^{8} \left[\left(\frac{dx_i}{ds}\right)^2 + \left(\frac{dy_i}{ds}\right)^2 + \left(\frac{dz_i}{ds}\right)^2 \right] + \sum_{i<j} \left(e^{-2\rho_0(r_{ij}-1)} - 2e^{-\rho_0(r_{ij}-1)} \right), \quad (1)$$

where (x_i, y_i, z_i), r_{ij}, and s represent the position of the ith atom with respect to the Cartesian frame, the reduced interatomic distance between ith and jth atoms, and the reduced time, respectively. ρ_0 is the parameter, which is set to 6.0.

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3 Dynamics

The Ar_8 cluster has eight local minima, which connect with the local minima of Ar_7 or Ar_6 clusters. Figure 1 shows the index of the local mimum in the dissociation process. The index 0 represents the global minimum. In figure 1, t_{in} is the time when the relative translational velocity is equal to zero before the evaporation, and t_{out} is the time when the two fragments are separated. As one can see from figure 1, this dissociation reaction accompanies structural isomerizations. Such a dissociation was frequently observed in MD sumulations.
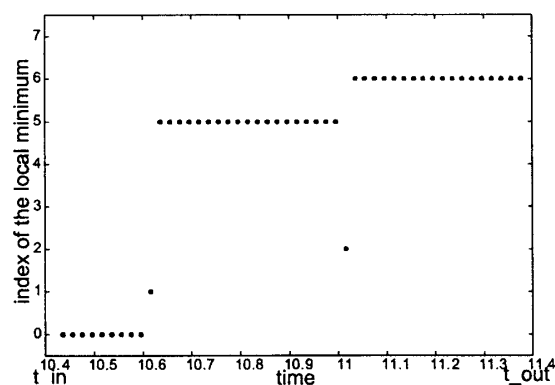

Figure 1: The index of local mimum. The index 0 represents the global minimum. t_{in} is the time when the relative translational velocity is equal to zero before the evaporation, and t_{out} is the time when the two fragments are separated.

4 Statistical rate theory

The statistical expression for the microscopic rate coefficient $k(E)$ for a given energy E is written as,

$$k(E) = \frac{W(E)}{\Omega(E)}, \qquad (2)$$

$$\Omega(E) = \int \prod_{i=1}^{N} dr_i dp_i \delta[H(\{r_i\}, \{p_i\}) - E], \qquad (3)$$

$$W(E) = \int \prod_{i=1}^{N} dr_i dp_i \delta[H(\{r_i\}, \{p_i\}) - E]$$
$$\times \delta[r_{re} - r_{re}^\ddagger]\dot{r}_{re}, \qquad (4)$$

where $\Omega(E)$ and $W(E)$, respectively, represent the phase space volume of the reactant and the flux cossing the dividing surface. In this study, the reaction coordinate r_{re} is chosen as the distance between the centers of mass of the two fragments. By integrating $\Omega(E)$ and $W(E)$ over the momentum space with fixed total momentum and total angular momentum, $\Omega(E)$ becomes,

$$\Omega(E) = \frac{(2\pi)^{\frac{s}{2}}}{\Gamma(\frac{s}{2})8^{3/2}} \int \prod_{i=1}^{7} \frac{d\mathbf{R}_i}{\sqrt{\det I_c}}$$
$$\times (E - V(\{\mathbf{R}_j\}))^{\frac{s-2}{2}}, \qquad (5)$$

and $W(E)$ becomes,

$$W(E) = \frac{(2\pi)^{\frac{s-1}{2}}}{\Gamma(\frac{s+1}{2})8^{3/2}} \int \prod_{i=1}^{7} \frac{d\mathbf{R}_i}{\sqrt{\det I_c}}$$
$$\times (E - V(\{\mathbf{R}_j\}))^{\frac{s-1}{2}} \delta[r_{re} - r_{re}^\ddagger], \qquad (6)$$

where $V(\{\mathbf{R}_j\})$, I_c, and $\Gamma()$ represent the potential energy, the inertia tensor, and gamma function, respectively. Although equation (5) and (6) are formulated under total momentum and total angular momentum equal to zero, it is easy to extend this formula to any total momentum and total angular momentum. Equation (6) is integrated over the dividing surface, which make us be able to count the contributions of any configurations to the flux. Therefore, our formulation is applicable in the evaporation accompanying structural isomerizations.

Figure 2 shows the evaporation rates obtained by MD simulations and those estimated by our method. The both results are found to be in good agreement to within the statistical uncertainties.
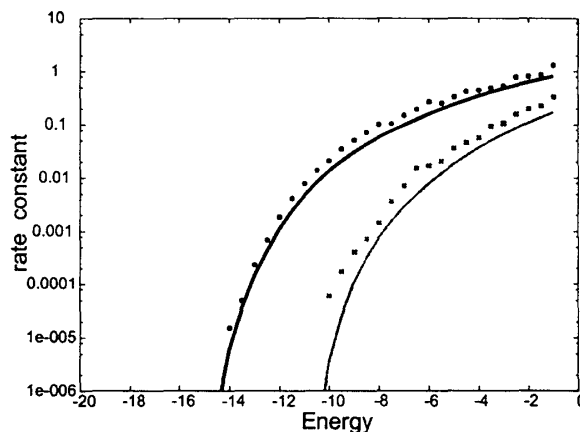

Figure 2: The evaporation rates obtained by MD simulations and those estimated by our method for monomer and dimer evaporation. Simulation data are given by dots, predictions of the statistical theory are given by curve. Black and gray represent monomer and dimer, respectively.

5 Conclusion

The MD simulation indicated that clusters evaporate accompanying structural isomerizations. Although the evaporation accompanying structural isomerizations have not been treated by the past formulation employing rigid bodies approximation, our formulation is applicable in such a evaporation dynamics.

References

[1] X. Yang and K. Liu, *MODERN TRENDS IN CHEMICAL REACTION DYNAMICS*, World Scientific, (2004)