Turk J Phy
24 (2000) , 607 – 615.

Molecular Dynamics Simulations of Super Heated Ni_4 Cluster

M. Halûk GÜVEN
Department of Physics, Zonguldak Karaelmas University,
67100 Zonguldak-TURKEY

Received 04.05.2000

Abstract

The fragmentation mechanism of the super heated Ni4 cluster is studied by employing the microcanonical molecular dynamics simulations and an empirical model potential. Ni_4 cluster is heated up above the bulk Ni evaporation point temperature and then classical trajectory analysis as well as RRK theory are used to calculate survival probability, evaporation rate, average kinetic energy release and dissociation energy.

Key Words: microcanonical molecular dynamics, cluster fragmentation.

1. Introduction

The collision induced dissociation and photodissociation experiments have been performed on the fragmentation of energized metallic ion clusters to study the dissociation energies, the relative stability of clusters, the binding energies, and the flow and redistribution of the energy in a cluster [1,2]. The interpretation of the experimental results requires understanding of the fragmentation and, in particular the ejection of a single atom from the cluster, i.e., evaporation mechanism. The fragmentation mechanism has been studied by limited number of molecular dynamics (MD) simulations and by statistical theories which do not give the dynamical description of the phenomenon [3,4,5,6]. When a cluster is heated up above the melting temperature, the cluster does not disintegrates simultaneously, i.e., constituent particles stay together for some time. The atoms in the cluster begin to move like free particles and as soon as an amount of energy exceeding the separation energy is accumulated in one degree of freedom, the atoms leave the cluster as monomers or multiples manner. The monomer ejection, i.e., evaporation is observed for Ni_4 clusters in our simulations. This result is in agreement with the collision induced dissociation experiments done with Ni_4^+ cluster [1]. In this study constant energy molecular dynamics (MD) simulations of the super heated Ni_4 cluster are carried out to

estimate the survival probabilities, the evaporation rates, and the averaged kinetic energy release using an empirical model potential. The dissociation energies are calculated using the results of the simulations at different temperatures by Rice, Ramsperger and Kassel (RRK) theory [7], which explains the unimolecular processes assuming that all the degrees of freedom of the system are vibrational and all are strongly coupled. It states that the system undergoes a unimolecular process when and if the energy localized in a specified vibrational degree of freedom becomes equal or larger than a certain threshold value [4]. The theoretical background and the computational procedures are explained in the next section. The results and the discussions are presented in section III, and the study is summarized in section IV.

2. Theoretical Background and Computational Procedure

In the simulation, the cluster was prepared initially with zero total linear and angular momenta, and then heated up above 5600 K starting from its T_d minimum energy geometry. We have selected 4 different total energies for the super heated cluster, and this cluster was used to generate an ensemble of 100 different (independent) initial conditions. Their dynamical behaviors were obtained by solving the Hamiltons equations of motions for all atoms in the cluster using Hammings modified fourth order predictor corrector propagator with a step size of 10^{-16} s. The total energy of the system was conserved within 0.003%. Maximum length of the run for each initial condition was 10^6 steps, i.e., evaporation of the clusters were observed within 100 ps runs. The interactions between the atoms of the cluster is modeled by Erkoç potential [8,9]. The geometries of the Ni microclusters and their binding energy values obtained by using this potential and their comparison with those of the given in the literatures are given in our recent publication [10] where the melting of the Ni_4 cluster is discussed in detail. The empirical interaction potential has the following form [8]

$$\Phi = \Phi_2 + B\Phi_3, \tag{1}$$

where Φ_2 is the two-body (pair potential) interaction term, more explicitly, [8],

$$\begin{aligned} \Phi_2 &= U(r_i, r_j) = U(r_{ij}) = U_{ij} \\ &= A\left[\left(\frac{r_0}{r_{ij}}\right)^{2n} e^{-2\alpha(r_{ij}/r_0)^2} - \left(\frac{r_0}{r_{ij}}\right)^{n} e^{-\alpha(r_{ij}/r_0)^2}\right], \end{aligned} \tag{2}$$

with $r_{ij} =\mid r_i - r_j \mid$ and A = -8.28 eV, $\alpha = \ln 2$, k = 15.66eV/Å^2 , $r_0 = 2.20$Å, $U(r_{ij}) \mid_{r_{ij}=0} = \varepsilon_0 = -2.07\text{eV}, n = [r_0^2 k/(2 \mid \varepsilon_0 \mid)]^{1/2} - 2\alpha = 2.892470$ [8]. The Φ_3 is the three-body interaction potential expressed as the linear combination of the pair energies formed by the three particles. It is given by [8]

$$\begin{aligned} W(r_i, r_j, r_k) &= W(r_{ij}, r_{ik}, r_{jk}) = W_{ijk} \\ &= B(U_{ij} f_{ijk} + U_{ik} f_{ikj} + U_{jk} f_{jki}) \end{aligned} \tag{3}$$

with

$$f_{ijk} = e^{-(r_{ik}^2 + r_{jk}^2)/r_0^2} \tag{4}$$

$$f_{ikj} = e^{-(r_{ij}^2 + r_{jk}^2)/r_0^2} \tag{5}$$

and

$$f_{jki} = e^{-(r_{ij}^2 + r_{ik}^2)/r_0^2} \tag{6}$$

with B = -1.290433. Since B has a negative value, the three-body potential has a positive contribution to the total interaction energy.

Further, each of the initial conditions previously prepared was first equilibrated and then run 100 ps to record the evaporation time. When the nearest neighbor distance of an atom in the cluster is larger then 5Å, then it is assumed to be evaporated (this assumption was used as an evaporation criterion). These evaporation times were used later to calculate the cluster survival probabilities, P(t),

$$P(t) = \frac{1}{N} \sum_{i=1}^{N} \theta_i(t), \tag{7}$$

with $\theta_i(t) = 1$ when there is no evaporation at time t for the initial condition i, and $\theta_i(t) = 0$ in the case of evaporation. Here N is the total number of the trajectories and it is equal to 100 for each total energy. The survival probabilities, which give the percentage of the clusters which are not disintegrated at time t, obtained by this procedure are fitted to exponential functions $P(t) = Ae^{-Rt}$. Here R is the evaporation rate. The average cluster lifetime is given by R^{-1}.

To characterize the phases and phase changes, i.e., evaporation, we calculated short-time averaged, over 5,000 steps, the kinetic and potential energies of the cluster. The temperatures of the clusters are calculated from the averaged kinetic energies as

$$T(K) = \frac{2 < E_k >}{k_B(3n-6)}, \tag{8}$$

where E_k is the total kinetic energy of the cluster, k_B is the Boltzmann constant, and $<>$ stands for time average, n is the number of particles in the cluster and the factor 3n-6 results from the vibronic degrees of freedom of the system. The dissociation energies are calculated from the RRK theory as [2],

$$R(E) = g\nu_D \left(1 - \frac{D}{E}\right)^{s-1}. \tag{9}$$

Here, the vibrational frequency is approximated by the Debye frequency of Ni, $\nu_D = 0.94 \times 10^{13}$ Hz, s = 3n - 6 is the number of vibronic degrees of freedom and g is the number of the surface atoms of the cluster, which is four in the present case, E is the internal

energy , D is the dissociation energy. The internal energy is determined as the sum of the thermal energy as E = sk$_B$T [2].

3. Results and Discussions

MD simulations show that the fluctuations in the kinetic energy per atom of the super heated Ni_4 cluster is found to be 0.4eV, as a result the constituent particles move almost freely but the cluster does not immediately decay. Therefore, it makes sense to talk about the survival probability of the super heated clusters. The survival probabilities of the Ni_4 cluster are shown in Figure (1). Figure (1-a) shows P(t) for the two lowest energies, whereas Figure (1-b) presents P(t) for two highest energies considered. All the curves in Figure (1) contains 100 evaporated trajectories of the 100 investigated. The curves follow an exponential decay behavior for P(t) as a function of time. Therefore the curves are fitted to the exponential decay curves. In Figure (2) evaporation rate is plotted as a function of temperature from which the average lifetime can be obtained. In Figure (3) ln(R) versus total energy of the cluster is plotted, in which, as energy increases the logarithm of the reaction rate increases linearly. From the graph one can deduce that after a certain energy value the cluster disintegrates and as the energy increases the reaction rate increases exponentially, this behavior belongs to a system obeying the Arrhenius equation and is expected. In this sense, this graph shows the stability of the clusters in the range of the energies considered. The average release kinetic energies of the departing atom from the cluster are calculated from the simulations. The total energies and the averaged release kinetic energies are tabulated in Table 1.

In Table 2 the internal energies and the dissociation energies calculated as explained in the text are presented.

Table 1. Total energies and the calculated average release kinetic energies from MD simulations.

Total Energy (eV)	Average release energy(eV)
-4.370	0.112
-4.232	0.152
-3.880	0.196
-3.750	0.187

Table 2. The internal energies and the dissociation energies calculated from RRK theory.

Internal energy (eV)	Dissociation energy(eV)	Temperature(K)
3.42	2.59	6620
3.53	2.59	6818
3.64	2.51	7047
3.67	2.49	7094

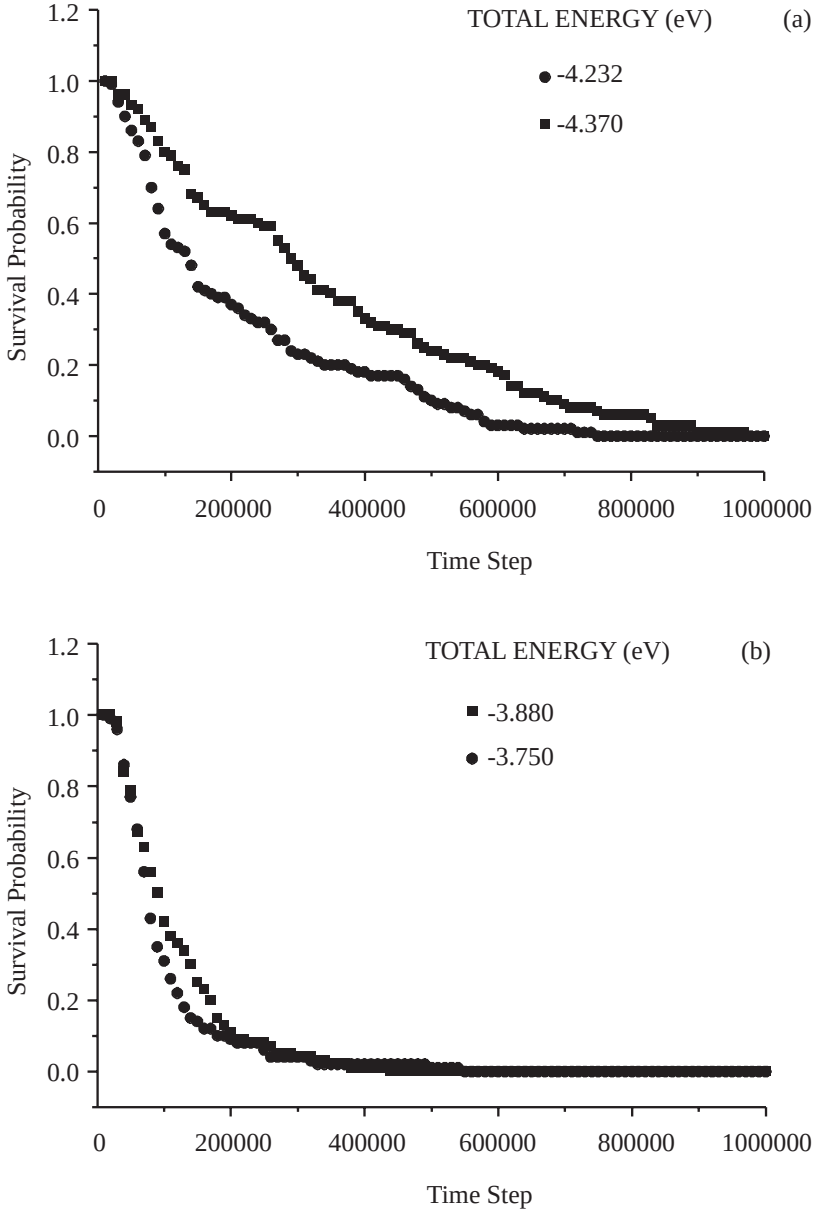

Figure 1. Survival probability as a function of time for different a)lowest, b) highest total energies considered.

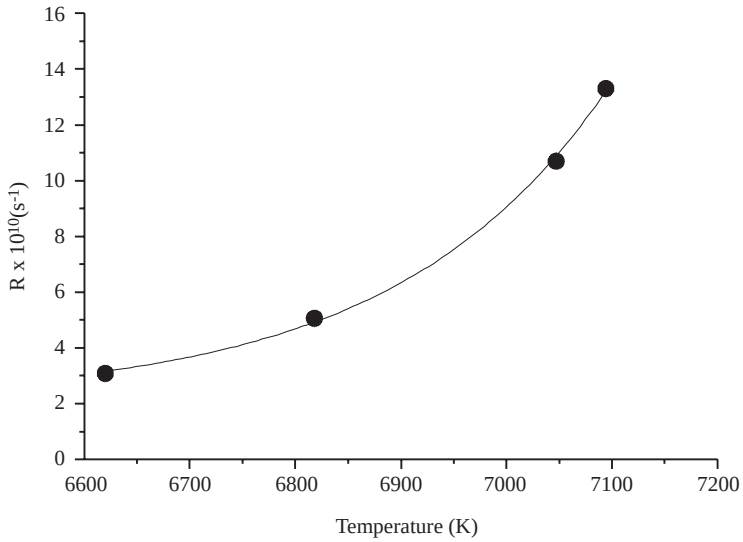

Figure 2. Evaporation rate vs. temperature of the cluster.

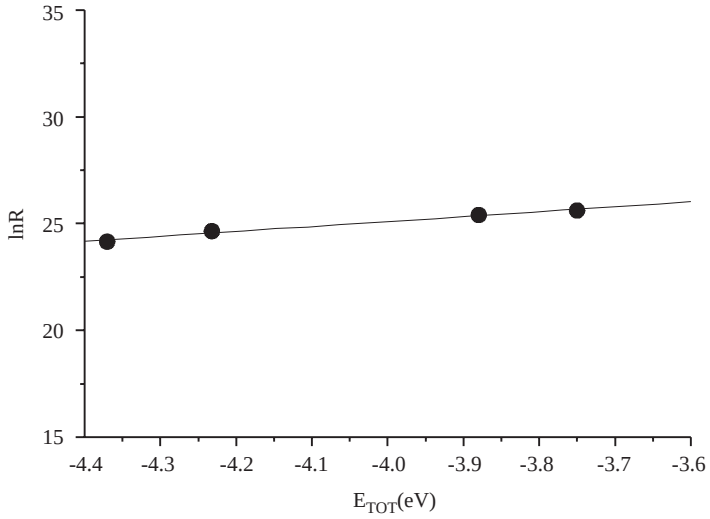

Figure 3. Energy dependence of the evaporation rate.

The dissociation energy decreases as the internal energy increases, but the change is not pronounced. At the moments of the evaporation the coordinates and the momenta of the atoms were recorded to find the kinetic energy distribution among the constituent

atoms. It is observed that the departing atom of the cluster may have the smallest (see Figure 4) or has one of the largest kinetic energies (see Figure 5). In both cases the daughter clusters are Ni_3 and their geometries are triangles. The larger the release kinetic energy, the cooler the daughter cluster. Ni_4 cluster which has the minimum release kinetic energy had the temperature of 6620 K before the evaporation and the cluster was left at a temperature of 2108 K after the evaporation. On the other hand, the Ni_4 cluster with the maximum release kinetic energy had the temperature of 7094 K before evaporation, has only the temperature of 2466 K after evaporation. One may conclude from these kinetic energy distributions that for an atom, in order to leave the system, kinetic energy is necessary but not a sufficient parameter. Direction of the motion of the atom is also important [11]. Disintegrated atom moves away from the system along the normal mode of vibrational motion direction.

According to the chosen total energies the temperatures of the clusters are 6620 K, 6818 K, 7047 K and 7094 K and the lifetimes are 32.5 ps, 19.8 ps, 8.3 ps, and 7.5 ps, respectively. This shows that the lifetime of a cluster strongly depends on its temperature.

Multiple decay is not observed for the total energies used in our simulations.

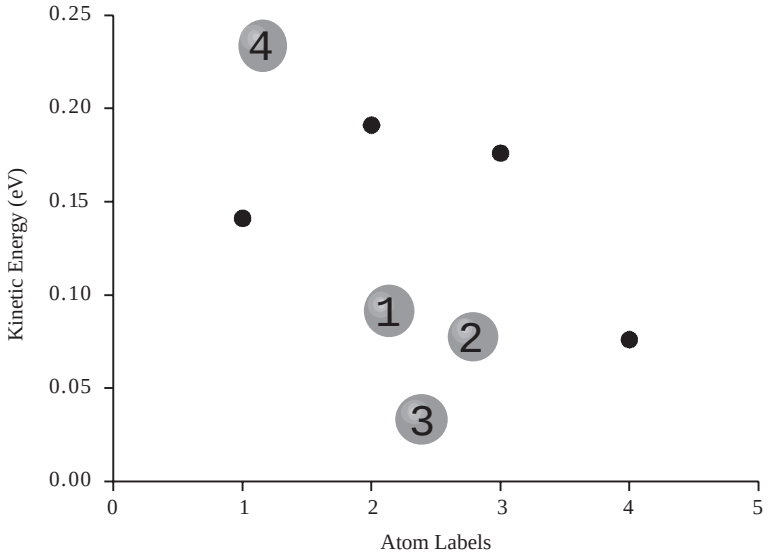

Figure 4. The kinetic energy distribution at the time of evaporation. The departing atom has the smallest kinetic energy.

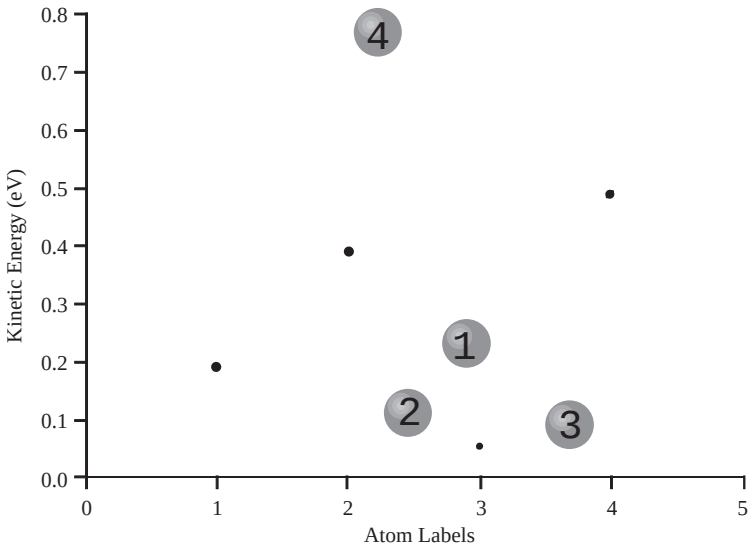

Figure 5. Same as Fig 4. The departing atom has the largest kinetic energy.

4. Summary

Using the Erkoç empirical model potential the fragmentation of the super heated Ni_4 cluster simulated by molecular dynamics techniques. Even though the fluctuations in the short time averaged kinetic and potential energies are large, the cluster doses not immediately disintegrate and survive at the order of picosecond depending upon its temperature. In order to leave the cluster, the direction of the motion of the atom is important. In our simulations multiple decay were not observed. Ni_4 cluster decays as a monomer.

References

[1] L.Lian, C.-X. Su, P.B. Armentrout, *J.Chem.Phys.*, **96** (1992) 7542.

[2] C. Walther, St. Becker, G. Dietrich, H.-J.Kluge, M. Lindinger, K. Lützenkirchen, L. Scheikhard, J. Ziegler *Z.Phys.*, **D 38** (1996) 51.

[3] C.E. Roman, L. Garzon in Physics and Chemistry of Finite Systems:From Clusters to Crystals edited by P. Jena, S.N. Khanna, B.K.Rao, vol.1 (Kluwer Academic, Dortrecht,1992) p.459.

[4] M.J. Lopez, J.Jellinek *Phys.Rev*, **A 50** (1994) 1445.

[5] X. Hu, C. Martens *Z.Phys.*, **D 29** (1994) 139.

[6] Ş. Katırcıoğlu, Ş. Erkoç *Mol. Sim.* **44** (1989) 247.

[7] W. Forst, Theory of Unimolecular Reactions (Academic, New York) 1973.

[8] Ş. Erkoç, *Phys.Stat.Sol.* **(b) 152** (1989) 447.

[9] Ş. Erkoç , *Phys.Rep.* **278** (1997) 79.

[10] M.H. Güven, M. Eryürek, *Phys.Stat.Sol.* **(b) 213** (1999) 283.

[11] R. S. Berry, S. A. Rice , J. Ross, Physical Chemistry (John Wiley and Sons, NewYork) 1980.