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# The Fragmentation Simulations of $Ni_6$ Cluster

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**Abstract :** The fragmentation mechanism of the super heated $Ni_6$ cluster is studied by employing the microcanonical molecular dynamics simulations and an empirical model potential. $Ni_6$ 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. It is found that the super heated clusters does not immediately disintegrate but survive for some time and then it fragments as monomers.

The objectives of the experimental studies on the cluster fragmentation are to estimate cluster lifetimes, to find kinetic energy distribution after fragmentation and to determine the binding energies of the clusters which lead to the estimation of their minimum energy geometries[1,2]. The complexity of clusters and their properties require theoretical modeling. Performing ab initio calculations for transition metal clusters, even for their structure determination, is limited to structures of high symmetry. Therefore, model potentials are used in dynamical simulations to mimic interatomic interactions. In this study microcanonical molecular dynamics simulations are performed by employing an empirical model potential, i.e., the Erkoç potential [3] to simulate the super heated $Ni_6$ cluster fragmentation. The super heated clusters may be useful in the fabrication and annealing of nanoscale particles. The Erkoç potential gives the correct minimum energy geometries and comparable binding energy and bond length values of small Ni clusters with those of given in the literature as recently reported in Ref.[4].
The empirical interaction potential has the following form [3]

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

where $\Phi_2$ is the two-body (pair potential) interaction term, more explicitly,

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

with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $A = -8.28$ eV, $\alpha = \ln 2$, $k = 15.66\,\text{eV/Å}^2$, $r_o = 2.20$ Å, $U(r_{ij})\big|_{r_{ij}=0} = \varepsilon_0 = -2.07\,\text{eV}$, $n = \left[r_0^2 k / (2|\varepsilon_0|)\right]^{1/2} - 2\alpha = 2.892470$. The $\Phi_3$ is the three-body interaction potential expressed as the linear combination of the pair energies formed by the three particles. It is given by

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

with

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

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

and

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

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

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 $O_h$ minimum energy geometry. We have selected five different total energies for the super heated cluster, and this cluster was used to generate an ensemble of 100 different (independent) initial conditions. The fluctuation in the kinetic energy per atom of the super heated clusters at these energies is found to approximately 0.4 eV. Their dynamical behaviors were obtained by solving the Hamilton's equations of motions for all atoms in the cluster using Hamming's 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., fragmentation of the clusters were observed within 100ps runs. In our simulations monomer ejection, i.e. evaporation , is observed for this cluster. 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) [5],

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

$\theta_i(t) = 1$ 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 probability of the super heated $Ni_6$ cluster is calculated as a function of time is calculated for five total energies. They are showed in Fig. 1. From the figure we observe that they follow an exponential decay behavior for P(t) as a function of time. Therefore the functions are fitted to exponential functions $P(t) = Ae^{-kt}$. Here k is the evaporation rate. The average cluster lifetime is given by $k^{-1}$.

The lifetimes are between 26ps –30ps depending on the temperature for the energies considered in the simulations. The temperature dependence of the cluster shown in Fig.2 in which lnk versus T is plotted. Fig. 3 shows the evaporation rate as a function of the cluster total energy per atom. The behavior of the curve points out that the system obeys Arrhenius equation. Drawing the Arrhenius curve the activation energy is obtained which is approximately equal to –2.67 eV, which is equal to the binding energy per atom for this cluster [4]. The average lifetime as a function of its total energy per atom can be obtained directly from Fig. 3.

At moments of evaporation the kinetic energy of the ejected atom is calculated and then these values are averaged. The average kinetic energy release of the evaporated atoms are changing between 0.26 eV – 0.34 eV. During the evaporation, it is observed that the departing atom of the cluster may have the smallest or has one of the largest kinetic energies, see Fig.4 and Fig.5. One may conclude that in order to leave the system kinetic energy is necessary but not the sufficient parameter, direction of the motion is also important. The evaporation causes to drop off the cluster's temperature about 57% of its initial value.

The dissociation energies are calculated from RRK theory [6] as

$$k(E) = g\nu_D\left(1 - \frac{D}{E}\right)^{s-1} \tag{8}$$

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, E is the internal energy , D is the dissociation energy. The internal energy is determined as the sum of the thermal energy as $E = sk_BT$ where $k_B$ is the Boltzmann constant. The dissociation energies are calculated as about 3.10 eV for the energies considered in the simulations.

## Conclusions

The atoms of the super heated clusters moves almost freely but the cluster does not immediately disintegrates. In our simulations only the monomer ejection, i.e. evaporation, is observed. This result is in agreement with the experiments done with $Ni^+_6$ clusters and with that clusters with even number of atoms evaporate monomers[1,2] . In order to leave the system, kinetic energy is not only the dominant factor the direction of the motion is also important.

## References

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## Figure Captions

**Figure 1.** Survival probability as a function of time for different total energies per atom considered.

**Figure 2.** Logarithm of evaporation rate vs. temperature of the cluster.

**Figure 3.** Energy dependence of the evaporation rate.

**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.

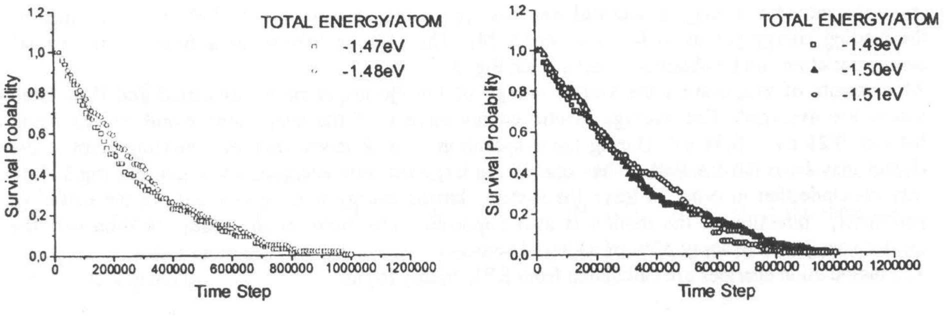

Fig. 1

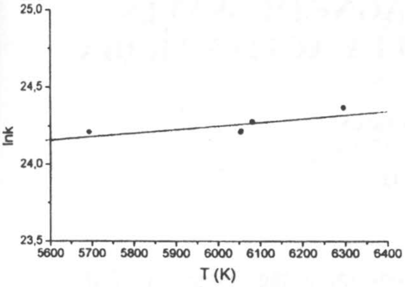

Fig.2

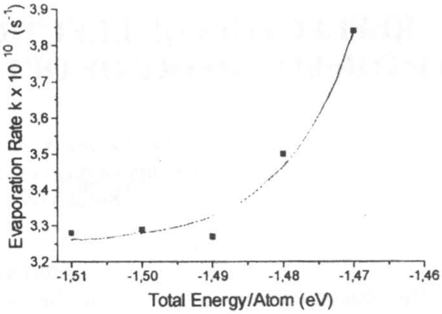

Fig. 3

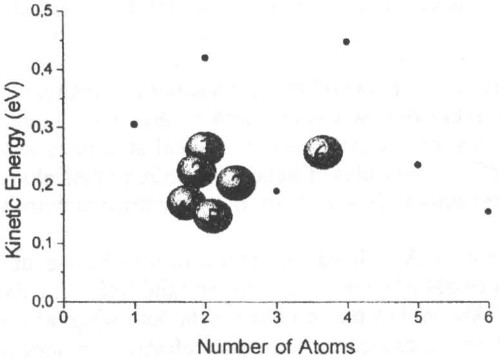

Fig. 4

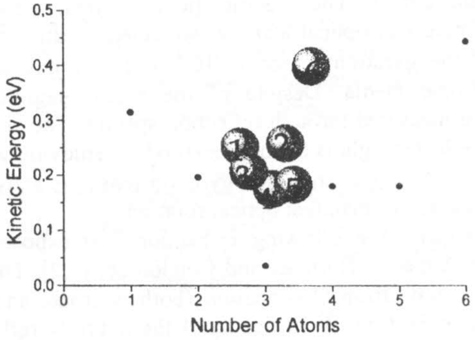

Fig. 5