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Symmetry breaking and stability of binary clusters

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Abstract

The minimum energy structures, stability, and symmetry breaking of Lennard-Jones binary clusters have been calculated using the pivot method. We found that the cluster dimer displays distinct symmetry breaking and "phase changes" when the interaction between the clusters is different from that within the clusters. The zero temperature phase diagram shows first-order phase transitions between a phase with symmetry of the cluster dimer to phases with symmetry of the giant cluster. © 1997 Published by Elsevier Science B.V.

1. Introduction

There have been extensive theoretical and experimental efforts recently to unravel the structure, dynamics and phase changes in atomic and molecular clusters [1–4]. One area of special emphasis in theoretical research is the study of structure and dynamics of binary clusters using molecular dynamics (MD) [5], Monte Carlo (MC) [6] and local density functional approximation (LDA) [7].

The interaction between clusters plays a crucial role in the stability of cluster assembled material [8]. Saito and Ohnishi [7] have reported that a dimer of cluster, $(Na_{19})_2$, is energetically stable and explains the abundance of Na_{38} in sodium-cluster mass spectra. More recently, there have been a number of studies of the structure and dynamics of $(C_{60})_N$ clusters [9,10], as well as of pure clusters bound by van der Waals interactions [11,12].

Symmetry breaking and phase transformation processes have been extensively investigated in atomic and molecular clusters [13,14]. Studies of such clusters attempted to establish the connection between phase transitions exhibited by bulk matter and their analogous "phase changes" for finite systems [15]. As discussed by Berry [15], finite systems exhibit some of the same solid-like and liquid-like behavior of bulk solids and liquids but have many phase-like properties that do not extend to bulk matter. These symmetry breaking and phase transitions are different from phase transitions at the absolute zero temperature. In the latter case, we are dealing with symmetry breaking of the ground state energy as some parameter entering the hamiltonian is varied [16,17].

In this letter, we report the structure, stability, and symmetry breaking of the ground state energy of a simple model system consisting of two identical Lennard-Lones (LJ) clusters labeled A and B. The two clusters have the same LJ parameters, $\epsilon_A = \epsilon_B$. The cross interaction, ϵ_{AB}, is varied to explore the "phase changes" and the formation of a stable dimer. All of the studies presented below are restricted to equal number of particles, $N_A = N_B$, where the total number of particles $N = N_A + N_B$ was chosen to be $N = 7 + 7 = 14$ and of a "magic" number

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$N = 13 + 13 = 26$. All the structure calculations carried out by the pivot method for global optimization [18,19].

2. Computational details

We consider a binary cluster of N particles containing equal number of particles of species A and B, with $N_A = N_B = N/2$, interacting pairwise through LJ potential given by

$$V(r) = \epsilon\left(1/r^{12} - 2/r^{6}\right), \tag{1}$$

where the value of the well depth ϵ depends on if both particles belong to cluster A ($\epsilon = \epsilon_A$), cluster B ($\epsilon = \epsilon_B$), or to different clusters ($\epsilon = \epsilon_{AB}$). For simplicity, we assume that the two clusters are equivalent, that is $\epsilon_A = \epsilon_B = 1$, but the interaction between the two clusters is different from the interaction within the clusters $\epsilon_{AB} \neq 1$. In cluster assembled material, the interaction between clusters might be weaker than the interaction within the cluster, for example, the interaction between the C_{60} molecules in fcc C_{60} solid is much weaker than that within the C_{60} molecule [20]. Therefor, it is very important to investigate the structure changes of a cluster dimer by changing the strength of the intra-cluster potential. In order to study the stability of the binary dimer we have calculated the binding energy E which is given by

$$E = \sum_{i<j\in A} V(r_{i,j}) + \sum_{k<l\in B} V(r_{k,l}) + \sum_{i\in A, k\in B} V(r_{i,k}) - E^{\mathrm{hom}}_{N_A} - E^{\mathrm{hom}}_{N_B}, \tag{2}$$

where $E^{\mathrm{hom}}_{N_A}$ and $E^{\mathrm{hom}}_{N_B}$ are the energies of the isolated homogeneous LJ clusters of N_A and N_B particles.

We investigated the minimum energy structures of the cluster dimer as a function of both the interaction parameter ϵ_{AB} and the separation distance between the two center of mass R_{AB},

$$R_{AB} = |\boldsymbol{R}_{AB}|, \quad \boldsymbol{R}_{AB} = \frac{1}{N_A}\sum_{i}^{N_A} \boldsymbol{r}_i^A - \frac{1}{N_B}\sum_{i}^{N_B} \boldsymbol{r}_i^B, \tag{3}$$

where the vectors $\boldsymbol{r}_i^A$ and $\boldsymbol{r}_i^B$ are the positions of the particles for species A and B respectively

In all the calculations, we have used the pivot method [18,19] to obtain the minimum energy structures. The pivot algorithm for the location of a global minimum uses a series of randomly placed probes in phase space, moving the worst probes to the near better probes iteratively until the system converges. The approach chooses as visiting distribution the generalized q-distribution based on the Tsallis entropy [21], which has been recently used with good results in simulated annealing methods [22,23]. In our previous studies of homogeneous LJ clusters, we have found that the optimum value of q is very near $q = 2.5$, so the value of $q = 2.5$ was used in all the calculations. After the convergence criteria was reached, a deterministic gradient algorithm [24] was used to obtain a better accuracy.

3. Results and discussions

We calculated the total binding energy for two different kind of clusters, one with $N_A = N_B = 7$ and another with a "magic" number $N_A = N_B = 13$, corresponding to the completion of a stable icosahedral structure [2]. The binding energy E as a function of the interaction between the clusters, ϵ_{AB}, is shown in Fig. 1. This figure shows clearly a symmetry breaking, where the first derivative of the energy is discontinuous at a critical ϵ_{AB}, which is $\epsilon_c = 0.389$ for $N_A = N_B = 7$ and for $N_A = N_B = 13$ there are two critical ϵ_{AB}, $\epsilon_c^{(1)} = 0.466$ and $\epsilon_c^{(2)} = 0.713$.

In order to understand this symmetry breaking, we show in Fig. 2 the behavior of the separation distance between the two center of mass of clusters, R_{AB}, as a function of the interaction ϵ_{AB}. As shown in this figure, near the critical ϵ_c there is a discontin-

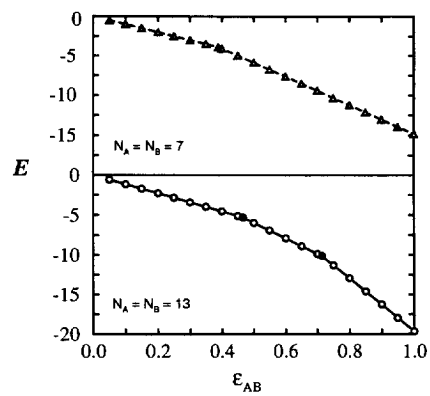

Fig. 1. The binding energy E versus ϵ_{AB} for $N_A = N_B = 7$ and $N_A = N_B = 13$.

uous change in the separation distance between the two clusters. By examining the minimum energy structures as a function of ϵ_{AB}, we found that for $\epsilon_{AB} \leq \epsilon_c = 0.389$ the cluster dimer is the stable structure for $N_A = N_B = 7$ while for $\epsilon_{AB} \geq \epsilon_c = 0.389$ the giant cluster is the stable structure. For $N_A = N_B = 13$ with $\epsilon_{AB} \leq \epsilon_c^{(1)} = 0.466$ we have a stable dimer cluster while for $\epsilon_{AB} \geq \epsilon_c^{(2)} = 0.713$ the giant cluster is the stable structure. For $\epsilon_c^{(1)} = 0.466 \leq \epsilon_{AB} \leq \epsilon_c^{(2)} = 0.713$ a new phase appears which corresponds to a giant cluster but with different configuration than the homogeneous cluster. This behavior, where the first derivative of the energy $dE/d\epsilon_{AB}$ is discontinuous at the critical ϵ_c, is characteristic of a first order phase transition, or more accurately as discussed by Berry [25], for finite systems as "phase changes".

To investigate the symmetry properties of the different phases, we plot in Fig. 3 the binding energy of the cluster with $N_A = N_B = 7$ as a function of the separation distance R_{AB} for three values of ϵ_{AB} with $\epsilon_{AB} = 0.5 > \epsilon_c$, $\epsilon_{AB} = \epsilon_c = 0.389$ and $\epsilon_{AB} = 0.3 < \epsilon_c$. In all the cases there exist many local minima, but for $\epsilon > \epsilon_c$ there is no stable dimer in this phase and the global minimum has the symmetry of the giant cluster, the homogeneous phase. On the other hand, for $\epsilon_{AB} < \epsilon_c$ the global minimum corresponds to a stable dimer. For $\epsilon_{AB} = \epsilon_c$, one can see almost three degenerate minima, the one on right corresponds to the cluster dimer while the one on the right to the giant cluster. The minimum in the middle corresponds to a new configuration which is not a global minimum for $N_A = N_B = 7$ but for larger clusters it becomes a global minimum for some values of ϵ_{AB}. This new phase with $\epsilon_c^{(1)} < \epsilon_{AB} < \epsilon_c^{(2)}$ appears as a global minimum for $N_A = N_B = 13$ as shown in Figs. 1 and 2. These different local and global minima could be of important value for molecular dynamics and Monte Carlo studies on the equilibrium structure and stability of the cluster dimer as a function of the temperature.

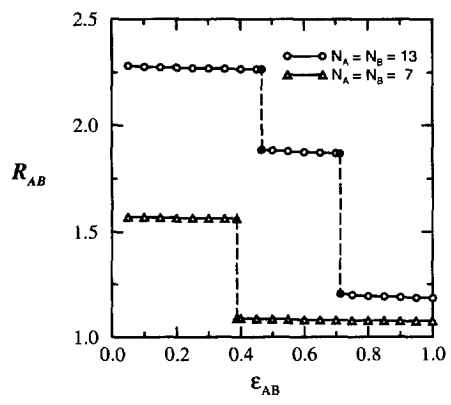

Fig. 2. The separation distance between the two centers of mass R_{AB} as a function of ϵ_{AB} for $N_A = N_B = 7$ and $N_A = N_B = 13$.

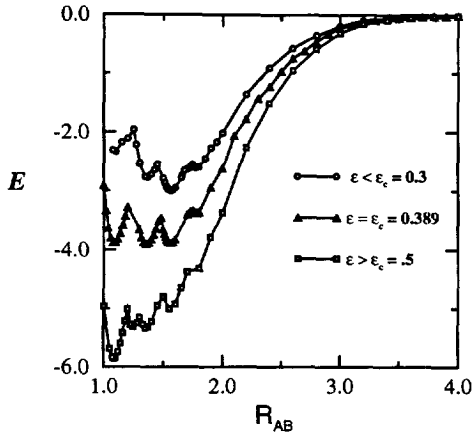

Fig. 3. The binding energy E versus the separation distance between the two centers of mass of clusters R_{AB} for $N_A = N_B = 7$ with $\epsilon_{AB} = 0.3 < \epsilon_c = 0.389$, $\epsilon_{AB} = \epsilon_c$ and $\epsilon_{AB} = 0.5 > \epsilon_c$.

In summary, in this letter we reported a symmetry breaking that is a "phase change" at zero temperature for LJ clusters of different sizes. At $T = 0$, the ground state of a finite system of LJ clusters exhibit a symmetry breaking as a function of ϵ_{AB}. For both clusters of $N_A = N_B = 7$ and $N_A = N_B = 13$, the symmetry breaking is a first-order "$T = 0$ phase transition" since the first derivative of the energy $dE/d\epsilon_{AB}$ is discontinuous at ϵ_c. For both clusters we show that one can form a stable cluster dimer if $\epsilon_{AB} < \epsilon_c$ and the cluster orientation dependence plays an important role as the two clusters approach each other.

Acknowledgements

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