

# Molecular-dynamics study on the equilibrium structure and the stability of a cluster dimer

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The equilibrium structures and the dynamic properties of two interacting clusters (cluster dimer), both of which have 13 atoms with icosahedral symmetry, have been studied by the molecular-dynamics method. A few metastable structures have been observed, but we obtain only one ground-state structure near the zero temperature for the various interaction strengths between two clusters, in which the icosahedral symmetry remains for each cluster. Upon heating, the ground structure for the cluster dimer is destroyed at a certain temperature  $T_c$ , which is strongly dependent on the interaction strength. At a temperature higher than  $T_c$ , one cluster loses the icosahedral symmetry and begins to cap onto the other cluster; and if heating further, both clusters begin to melt. The relationship between  $T_c$  and the interaction strength is also obtained. [S0163-1829(96)03347-4]

## I. INTRODUCTION

Cluster science has been an interesting subject for physicists, chemists, and material scientists. In the last two decades, much effort has been devoted to studies on the structure and stability of isolated cluster, both theoretically and experimentally, and great achievement has been made in understanding their properties. Accordingly, studies on cluster-assembled-material (CAM) have spurred enormous scientific interest in recent years as well. In fact, synthesized with the stable cluster, CAM might have some unusual properties different from the properties of the conventional crystalline solid. Solid  $C_{60}$ , which has many interesting physical properties,<sup>1</sup> can be a well-known example of CAM. By doping some alkaline elements, solid  $C_{60}$  can be a good high-temperature superconductor. Because of this and other potential applications of CAM, researchers are exploring the possibility of the synthesis of CAM. At least a few clusters and also some fullerene-like clusters are proposed to be the candidates for CAM from the theoretical calculations of the isolated cluster.<sup>2,3</sup> But it needs further studies to obtain the conclusion for those clusters to be the structure units of CAM. The interaction between clusters plays a crucial role on the stability of CAM, which may destroy the cluster structure when the clusters approach each other. So it is very important to study the structure and stability of clusters with different cluster-cluster interaction. In fact, some work along this direction has been done; for instance, Saito and Ohnishi<sup>4</sup> have studied the stability of the  $(Na_{19})_2$  dimer on the basis of a jellium model by the local-spin-density-functional method, where the positive charges of nuclei are smeared out as background. More recently, using molecular dynamics (MD) simulation, Rey, Gallego, and Alonso<sup>5</sup> have studied the dynamics properties of the small  $(C_{60})_N$  clusters with  $N$  up to 25, in which the  $C_{60}$  molecule is considered to be rigid and structureless. Since in all these studies the atomic structures of clusters have been neglected, it is impossible to provide

detailed information on how the interaction between clusters affects the structure of each cluster.

In this paper, we try to study the structure and stability of the cluster dimer interaction using a Lennard-Jones (LJ) potential. The atomic structure of clusters has been taken into account explicitly, in order to shed some light on the possibility of the synthesis of CAM.

This paper is organized as follows: In Sec. II, we sketch the main computational method used in the calculations. In Sec. III, we present and discuss the obtained results. In Sec. IV, we summarize the main conclusions of this work.

## II. COMPUTATIONAL DETAILS

To study the equilibrium structure and stability of a cluster dimer, we take two clusters,  $A_{13}$  and  $B_{13}$ , each cluster contains 13 atoms with icosahedral symmetry, which is a stable magic cluster. Atoms of species  $A$  and  $B$  interact pairwise through LJ potential  $\phi$  reads

$$\phi_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6 \right], \quad (1)$$

where  $\varepsilon_{\alpha\beta}$  and  $\sigma_{\alpha\beta}$  ( $\alpha, \beta = A, B$ ) are the depth of the potential well and the collision diameter for atoms of species  $\alpha$  and  $\beta$ , respectively. For simplicity, in this calculation, we assume that  $\sigma_{AA} = \sigma_{BB} = \sigma_{AB} \equiv \sigma$ ,  $\varepsilon_{AA} = \varepsilon_{BB} \equiv \varepsilon$ , which implies that two clusters are mechanically the same, but the interaction between two clusters is different from the interaction within the clusters if  $\varepsilon_{AB} \neq \varepsilon$ . In CAM, the interaction between clusters might be weaker than the interaction within the cluster in the same way, for instance, that the interaction between the  $C_{60}$  molecules in fcc  $C_{60}$  solid is much weaker than that within the  $C_{60}$  molecule.<sup>6</sup> So it is very interesting to see the structure changes of a cluster dimer by changing the interaction strength between clusters; this can be characterized by  $\gamma = \varepsilon_{AB}/\varepsilon$ .

The reduced units are used in the calculations, namely,  $\sigma$  for length,  $\varepsilon$  for energy,  $\tau=(m\sigma^2/\varepsilon)^{1/2}$  for time, and  $T^*=KT/\varepsilon$  for temperature, where  $K$  is the Boltzmann constant and  $m$  is the mass of the particles. Since the momentum of the center of mass and the total angular momentum of the system are carefully eliminated from the calculations, the temperature refers only to the vibrational modes, and is given by<sup>7</sup>

$$T = \frac{2\langle E_{\text{kin}} \rangle}{K(3N-6)},$$

where  $\langle E_{\text{kin}} \rangle$  is the time average of kinetic energy.

To characterize structure changes with temperature, we calculate the average principal radii of gyration ( $\langle R_1 \rangle$ ,  $\langle R_2 \rangle$ ,  $\langle R_3 \rangle$ ) of individual clusters ( $A_{13}$  and  $B_{13}$ ) and the cluster dimer, and the average separation  $d$  between the centers of mass of two clusters. The principal radii of gyration  $R_i$  are given by

$$R_i = \sqrt{I_i/N}$$

and the separation  $d$  by

$$d = \left| \left( \frac{\sum_{i=1}^{N_A} \mathbf{r}_i^{(A)}}{N_A} - \frac{\sum_{i=1}^{N_B} \mathbf{r}_i^{(B)}}{N_B} \right) \right|,$$

where  $I_i$  are the principal moments of inertia of clusters, and the vectors  $\mathbf{r}_i^{(A)}$  and  $\mathbf{r}_i^{(B)}$  are the positions of the atoms for species  $A$  and  $B$ , respectively. The interaction energy between two clusters  $E_i$  is also calculated by

$$E_i = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \phi_{AB}(r_{ij}).$$

To obtain the equilibrium structure of two clusters at low temperature, we have performed the steepest-descent calculations by placing two clusters separated at a distance about  $3.5\sigma$  with various initial orientations. Constant energy MD simulations are carried out to study the thermal stability of the cluster dimer with a time step of  $5 \times 10^{-3}\tau$ . At low temperature, the state is allowed to propagate over  $3 \times 10^4$  steps in each run,  $1 \times 10^4$  steps for slowly increasing temperature,  $1 \times 10^4$  steps for equilibrium, and the rest of the time steps for obtaining the corresponding average. At high temperature, some expected reactions may occur as each state runs longer up to  $20 \times 10^4$  steps.

### III. RESULTS AND DISCUSSIONS

#### A. Static structure and properties near zero temperature

In contrast to the atomic dimer, which has only two atoms and a structure determined only by the distance between two atoms, a cluster dimer may have a complicated structure, since the orientation dependence can play an important role as two clusters approach each other in forming as cluster dimer.<sup>2</sup> In the present calculation, the equilibrium structures of cluster dimers with four interaction strengths  $\gamma=0.5, 0.8, 1.0,$  and  $1.2$  are investigated by using the steepest-descent method. The initial structures are constructed by placing two clusters at a separation distance about  $3.5\sigma$  with a few different orientations. Because it is impossible to try all orien-

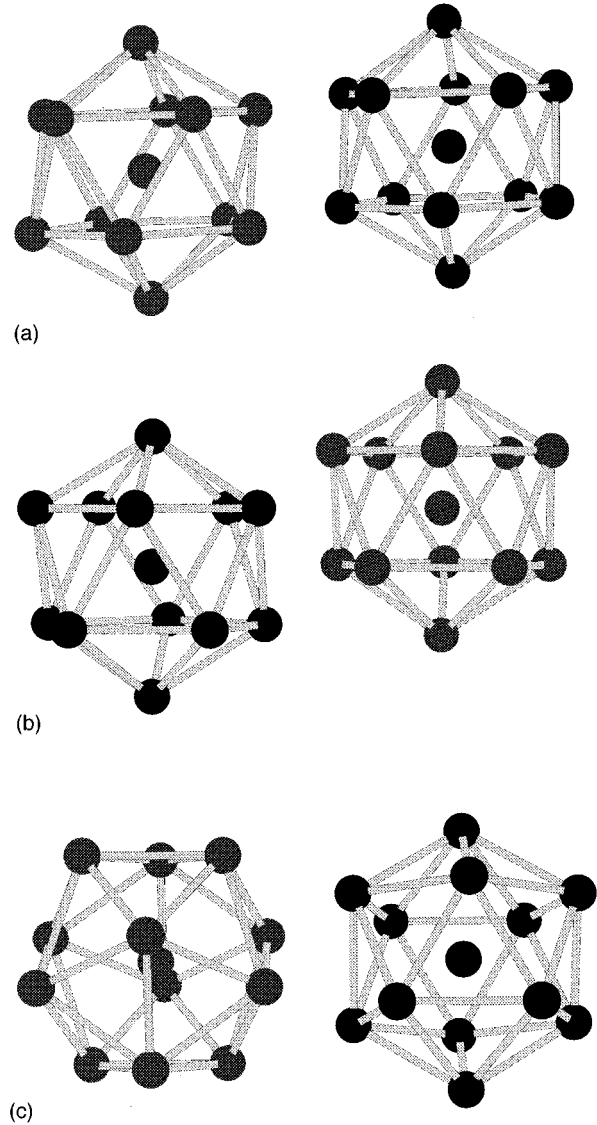


FIG. 1. Equilibrium structures of cluster dimer at 0 K. (a) Structure A, (b) structure B, (c) structure C.

tations, we select four initial configurations. The first one is two clusters with vertex to vertex, in which the four vertical atoms and two central atoms are along the same line. In the second initial configuration, two clusters are placed edge to edge, where the two edges and two central atoms of two clusters are in the same plane. The third one is structured by separating two clusters face to face and rotating one cluster about the axis joining the centers of mass by  $\pi/3$ , where the line that connects the two central atoms goes through the centers of two interfaces. One can obtain the last one by rotating one cluster  $\pi/2$  about the axis joining two central atoms from the second one. Starting from these four initial configurations, we find three different structures by performing the steepest-descent calculation, which are quite different from the initial structures. The obtained structures are shown in Figs. 1(a), 1(b), and 1(c) which are labeled as  $A$ ,  $B$ , and  $C$ , respectively. It is worth pointing out that structures  $A$ ,  $B$ , and  $C$  maintain the icosahedral structure for each cluster, which can be considered as the cluster dimer. Structure  $A$  is obtained only for  $\gamma=0.5$ , which can be obtained from the third initial configuration by moving two clusters more closely

TABLE I. The obtained properties of static structures. The total energy  $E$ , the distance between the centers of mass  $R$ , the cohesive energy  $E_b$ , the deformation energy  $E_d$ , the number of bond  $N_b$  connecting two clusters, and the reduced interaction energy  $\Delta_\varepsilon$ , in units of  $\varepsilon_{AB}$ .

	$\gamma=0.50$	$\gamma=0.80$	$\gamma=1.0$	$\gamma=1.2$
A	$E = -93.043$ $R = 2.649$ $N_b = 5$ $E_b = -4.389$ $E_d = 0.049$ $\Delta_\varepsilon = 8.876$			
B	$E = -93.822$ $R = 2.570$ $N_b = 6$ $E_b = -5.168$ $E_d = 0.040$ $\Delta_\varepsilon = 10.416$	$E = -96.963$ $R = 2.556$ $N_b = 6$ $E_b = -8.309$ $E_d = 0.111$ $\Delta_\varepsilon = 10.526$	$E = -99.077$ $R = 2.545$ $N_b = 6$ $E_b = -10.423$ $E_d = 0.191$ $\Delta_\varepsilon = 10.614$	$E = -101.210$ $R = 2.532$ $N_b = 6$ $E_b = -12.5564$ $E_d = 0.310$ $\Delta_\varepsilon = 10.722$
C	$E = -94.355$ $R = 2.543$ $N_b = 8$ $E_b = -5.7014$ $E_d = 0.042$ $\Delta_\varepsilon = 11.493$	$E = -97.812$ $R = 2.537$ $N_b = 8$ $E_b = -9.1584$ $E_d = 0.076$ $\Delta_\varepsilon = 11.543$	$E = -100.123$ $R = 2.533$ $N_b = 8$ $E_b = -11.469$ $E_d = 0.099$ $\Delta_\varepsilon = 11.568$	$E = -102.438$ $R = 2.530$ $N_b = 8$ $E_b = -13.7844$ $E_d = 0.122$ $\Delta_\varepsilon = 11.589$

( $d=2.649 \sigma$ ) and shifting one cluster upward a little (about  $0.02 \sigma$ ) along the interface. One can get structure *B* from structure *A* by shifting one cluster upward to about  $0.51\sigma$  along the interface. The most stable structure (*C*, see below) is the same for the various  $\gamma$  values. Structure *C* is similar to the last initial structure, and its separation between the centers of mass of the two small clusters are dependent on  $\gamma$ ; we have obtained  $2.543 \sigma$ ,  $2.537 \sigma$ ,  $2.533 \sigma$ , and  $2.530 \sigma$  for  $\gamma=0.5, 0.8, 1.0$ , and  $1.2$ , respectively. To quantitatively characterize each structure and see the difference between these structures more clearly, we have calculated the cohesive energy  $E_b$ , reduced interaction energy  $\Delta_i$ , and deformation energy  $E_d$  which are given by

$$E_b = (E_t - 2E_{13}^0),$$

$$\Delta_i = E_i / \varepsilon_{AB},$$

$$E_d = 2E_{13}^0 - E_{13}^A - E_{13}^B,$$

where  $E_t$  is the total energies of a cluster dimer,  $E_{13}^0$  is the total energy of an isolated icosahedral 13-atom cluster, and  $E_{13}^A$  and  $E_{13}^B$  are the total energy for an isolated cluster *A* and an isolated cluster *B* with the length of bonds equal to that in the cluster dimer. Table I presents some results for the structures (*A*, *B*, *C*) with various  $\gamma$  values. It can be seen that the number of bonds  $N_b$  connecting the two clusters together with a cutoff of  $1.2 \sigma$ , is eight for structure *C*, while structure *B* and structure *A* have only six and five, respectively. Clearly, the larger the number of bonds  $N_b$ , the more stable the structure. From an energy point of view, it is also true that structure *C* is more stable than *B* and *A*. The distance between the mass centers of  $A_{13}$  and  $B_{13}$  is smallest for structure *C*, indicating that structure *C* is most compact. For each

structure, as shown in Table I, the distance between the mass centers of  $A_{13}$  and  $B_{13}$  decreases a little bit with the increase of  $\gamma$ . The reduced interaction energy increases significantly from structure *A* to *C* with the same  $\gamma$ , and also increases a little in the same structure with the increase of  $\gamma$ . It is interesting to note that the deformation energy  $E_d$ , which reflects the energy changes due to the distortion of the atomic structure, is small in structure *C* and increases very slowly with increase of  $\gamma$ . For all the results presented above, we can see that, although structures *A*, *B*, and *C* each have the character of isolated icosahedral clusters, structure *C* is most stable, as it is the most compact and has the lowest total energy, the largest number of bonds, and very small distortion. We can expect that structure *C* would remain in the solid assembled from stable clusters. In fact, a similar structure has been observed in experiments: for example, the  $AB_{13}$  phase,<sup>8</sup> where  $B_{13}$  locally forms an icosahedron and the neighboring icosahedron rotated  $\pi/2$ . The material  $\text{LaCo}_{13}$  with similar structure has been widely studied due to its interesting magnetic properties. The first-principle calculation<sup>9</sup> shows that in  $\text{LaCo}_{13}$  solid the electronic shell of  $\text{Co}_{13}$  with three electrons provided by La is closed, and consequently the interaction between neighboring  $\text{Co}_{13}$  is weakly van der Waals-like, similar to the case of the present simulations. So, the present simulations can qualitatively explain why  $\text{LaCo}_{13}$  forms this kind of structure with neighboring icosahedra rotation  $\pi/2$ .

## B. Thermal stability

In the last section, we obtained the most stable structure for the cluster dimer by the steepest-descent method. How stable will the structure be at finite temperature? We have tried to heat the cluster dimer slowly from zero temperature at the equilibrium structure, and study the thermal stability of the cluster dimer. In this section, we are going to present some results of the cluster dimer at finite temperatures. Since structure *C* is the most stable for all studied values of  $\gamma$ , the calculations presented in this section begin from structure *C*. We have slowly heated the cluster dimer from zero temperature to a very high temperature where the cluster is liquefied, and some physical properties are calculated at various temperatures. In the lower panels of Figs. 2, 3, and 4, we show the average potential energy of the cluster dimer and the interaction energy as the function of temperature with  $\gamma=0.5, 0.8$ , and  $1.2$ , respectively. It can be seen that at low temperatures, the energy changes smoothly with temperature, but up to a certain temperature  $T_c$ , the energy suddenly increases as an indication of a change in structure. In the upper panels of Figs. 2, 3, and 4, we can see that at the temperature  $T_c$ , the distance between the centers of mass of clusters drops significantly, and the number of bonds, which can serve as a measure of the contact area between two clusters, increases substantially. The principal radii of gyration can be used to describe the average shape of the clusters. The calculated principal radii of gyration for the cluster dimer and for clusters  $A_{13}$  and  $B_{13}$  are also shown in Figs. 5, 6, and 7, for  $\gamma=0.5, 0.8$ , and  $1.2$ , respectively. For the cluster dimer, since it is enlarged in one direction, principal radii are almost identical in two directions, and about twice in the third direction. For  $A_{13}$  and  $B_{13}$ , the principal radii are almost equal in three directions, which indicates that  $A_{13}$  and

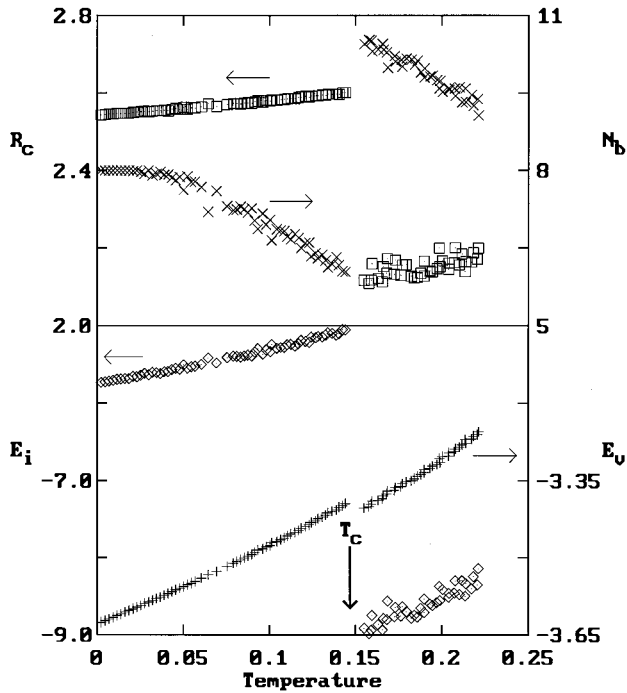


FIG. 2. The interaction energy  $E_i$ , average potential energy  $E_v$ , the bond number  $N_b$ , and the distance between the centers of mass of clusters as a function of temperature for  $\gamma=0.5$ .

$B_{13}$  are spherelike. In fact, we have looked into several snapshots of the structures below  $T_c$ , and it is clearly seen that the icosahedral character of  $A_{13}$  and  $B_{13}$  remains for  $\gamma=0.5$ , 0.8, and 1.2, respectively, as given by the principal radii

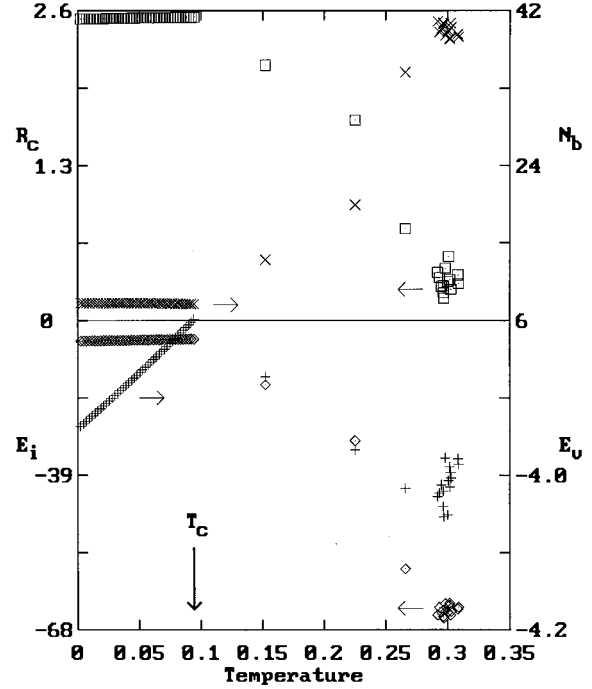


FIG. 4. The interaction energy  $E_i$ , average potential energy  $E_v$ , the bond number  $N_b$ , and the distance between the centers of mass of clusters as a function of temperature for  $\gamma=1.2$ .

result. From Figs. 5–7, we can see that all of them show sharp changes at  $T_c$ . All of these results suggest that the structure of clusters  $A_{13}$  and  $B_{13}$  has been destroyed, and the cluster dimer does not exist any more. To see these structure changes more clearly, several snapshots of the structure with

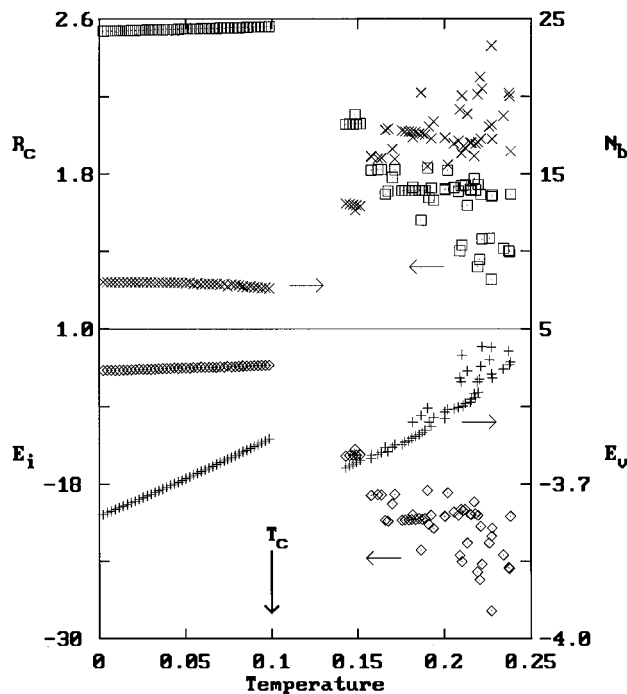


FIG. 3. The interaction energy  $E_i$ , average potential energy  $E_v$ , the bond number  $N_b$ , and the distance between the centers of mass of clusters as a function of temperature for  $\gamma=0.8$ .

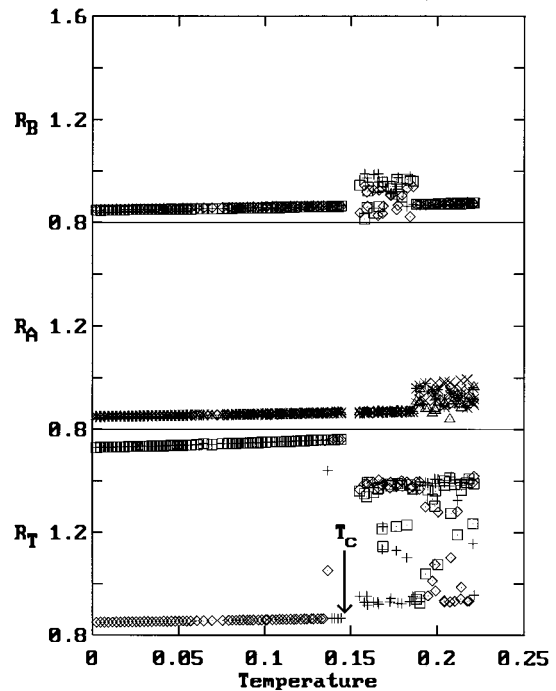


FIG. 5. The principal radii of gyration for the cluster dimer and for clusters  $A_{13}$  and  $B_{13}$  as a function of temperature for  $\gamma=0.5$ .

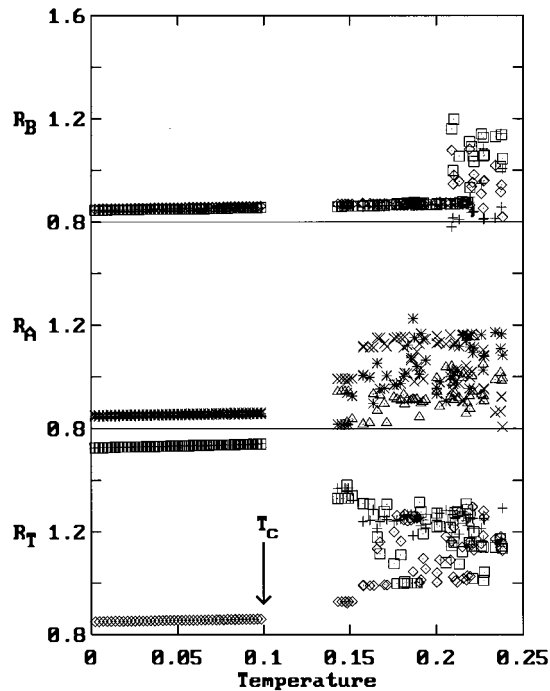


FIG. 6. The principal radii of gyration for the cluster dimer and for clusters  $A_{13}$  and  $B_{13}$  as a function of temperature for  $\gamma=0.8$ .

various values of  $\gamma$  above  $T_c$  are presented in Fig. 8; it is evident that the icosahedral structure has been destroyed. In the case of a smaller  $\gamma$ , one of the two small clusters capped onto the other, which is nearly a perfect icosahedron; but for a larger  $\gamma$ , the icosahedral structure of small clusters are completely changed. The change of clusters structure is in

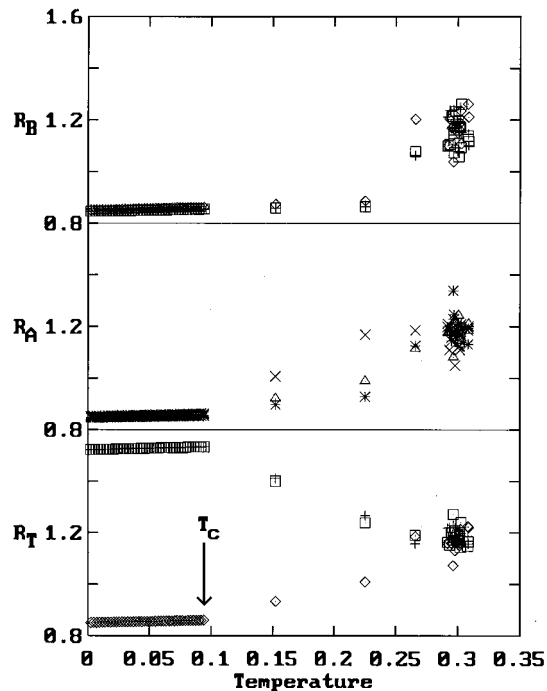
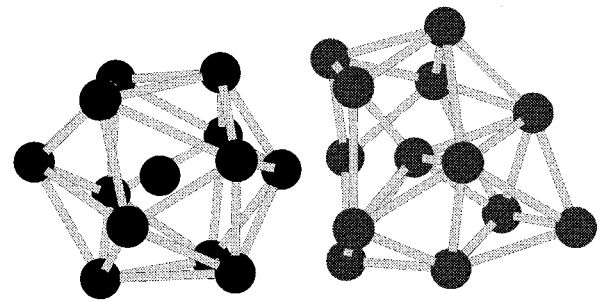
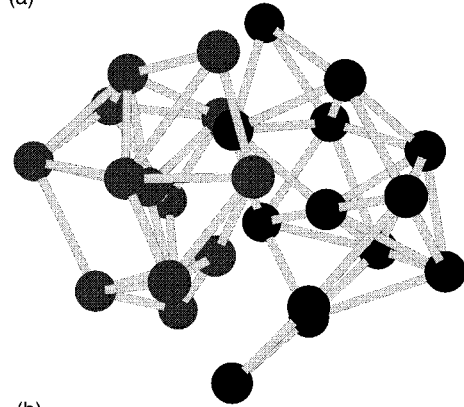


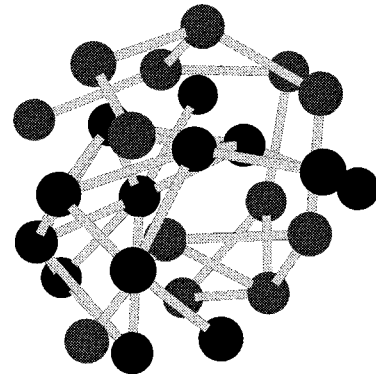
FIG. 7. The principal radii of gyration for the cluster dimer and for clusters  $A_{13}$  and  $B_{13}$  as a function of temperature for  $\gamma=1.2$ .



(a)



(b)



(c)

FIG. 8. The some snapshot structure above  $T_c$ , (a), (b), and (c) for  $\gamma=0.5$ ,  $0.8$ , and  $1.2$ , respectively.

agreement with previous results by Clarke *et al.*<sup>11</sup> and Rey and Gallego,<sup>10</sup> where they found that the two-component liquid favors demixing with  $\gamma$  smaller than one, and favors the formation of an alloy with  $\gamma$  larger than one. According to the results presented above, we note that equilibrium structure  $C$  of a cluster dimer is only stable below the temperature  $T_c$ , and  $T_c$  is lower than the melting temperature of the 13-atom LJ cluster. Obviously, the  $T_c$  is  $\gamma$  dependent: when  $\gamma$  is increased,  $T_c$  is decreased. To obtain a relationship between  $\gamma$  and  $T_c$ ,  $T_c$  has been calculated with more  $\gamma$  values (0.5, 0.65, 0.8, 0.90, 1.0, 1.05, 1.1, and 1.2). The obtained results are shown in Fig. 9. At a smaller value  $\gamma=0.5$ ,  $T_c$  is very high up to 0.15, but drops quickly with increasing  $\gamma$ . It is of interest that  $T_c$  changes slowly with  $\gamma$  near  $\gamma=0.9$ , and drops quickly again with  $\gamma$  larger than 1.0. Although it is not very clear why  $T_c$  changes with  $\gamma$  in this strange way, especially becoming flat near  $\gamma=0.9$ , the interaction between two clusters may play an important role on the structure change

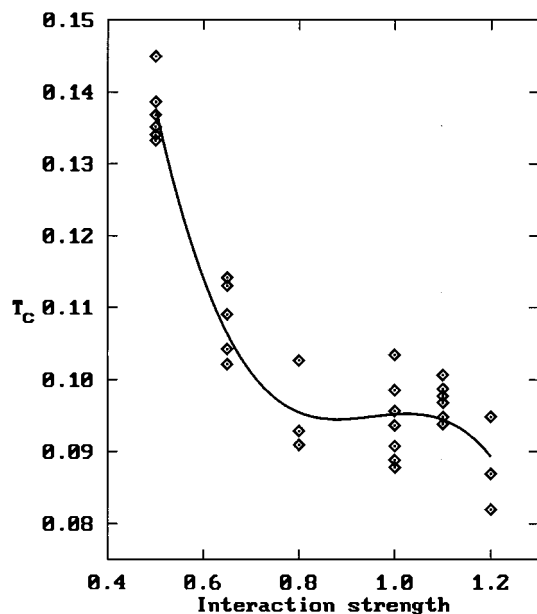


FIG. 9. The  $\gamma$  dependence of  $T_c$ . The solid line is fitted by a polynomial.

of the cluster dimer. The smaller the value of  $\gamma$ , the less the energy accommodation between the two small clusters. Although the present results have been obtained from studies on cluster dimers, these should be able to provide useful guidelines for the synthesis of CAM. From the results shown in Fig. 9, it would be better to select with  $\gamma$  around  $\sim 0.5$  for the synthesis of a stable CAM.

#### IV. SUMMARY

The interaction between the clusters may play a key role in some materials, such as CAM, nanomaterials, or some amorphous materials. In this paper, by using the constant-energy molecular-dynamics method, we have studied the equilibrium structures and the thermal stability of two interacting magic clusters. Our results show that, as two clusters come close to each other, the cluster dimer can be formed at low temperatures, while the initial structure of the isolated clusters remain unchanged. Several structures for cluster dimers have been observed, but the most stable dimer is the same for various interaction strengths, which is shown in Fig. 1. By heating the most stable cluster dimer, we have studied the thermal stability of a cluster dimer. The cluster dimer is only stable under a certain temperature  $T_c$ . The dependence of  $T_c$  on  $\gamma$  is observed, for small values of  $\gamma=0.5$ ;  $T_c$  is very high, but drops quickly; a flat appears near  $\gamma=0.9$ , and, for  $\gamma$  larger than 1.0,  $T_c$  drops again.

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