Volume 124, number 1 CHEMICAL PHYSICS LETTERS 7 February 1986

EFFECT OF THREE-BODY INTERACTIONS ON THE EARLY STAGES OF ATOMIC CLUSTER GROWTH

I.L. GARZÓN and Estela BLAISTEN-BAROJAS

Instituto de Física, Universidad Nacional Autónoma de México,
Apartado Postal 20-364, 01000 Mexico, D.F., Mexico

Received 3 June 1985; in final form 15 November 1985

The sequence of conformations a cluster assumes as it grows from a trimer into a thirteen-atom aggregrate under a given model potential has been studied. The model potential proposed is a construction composed of a van der Waals pairwise term and a three-body term composed of the triple dipole contribution and the exchange overlap contribution. A parametric study of the thermodynamically preferred structures is given. After reaching a boundary between regions in the parameter space, equilibrium mixtures of isomers with different packings are obtained. The normal frequency spectrum is given for clusters up to thirteen atoms.

1. Introduction

The effects of dispersive three-body interactions have been analyzed [1] and abrupt changes in the energetically most stable structures were predicted in the early stages of atomic cluster aggregation. On the other hand, analytical functions have been developed to represent the short-range region of a three-atom potential energy surface [2,3]. The prime purpose of this Letter is to describe and extend our knowledge of the important configurations of monoatomic systems of up to thirteen atoms subject to non-additive interactions. Particular emphasis is laid on the effect of two types of three-body interactions, the triple dipole term and the exchange overlap term, on the early stages of cluster growth at low temperature. The study is a parametrical analysis of the three-body interaction that allows us to identify regions of the parameter space for which very different aggregations can be modeled. The second purpose of this Letter is to point out the extreme importance that a non-additive interaction potential (or family of potentials) has on stabilizing structures other than close packed. It therefore allows for the possibility of modeling mixtures of isomers of different packings.

2. Three-body potential

Let us consider a system of N identical atoms or molecules whose total potential energy function $\phi(r_1, r_2, ..., r_N)$ is expanded as a sum of n-body potentials V_n:

$$\phi(r_1, r_2 \dots r_N) = \frac{1}{2!}\sum_{\substack{i,j \\ i\neq j}}^{N} V_2(r_i, r_j) + \frac{1}{3!}\sum_{\substack{i,j,k \\ i\neq j\neq k}}^{N} V_3(r_i, r_j, r_k) + \dots + \frac{1}{n!}\sum_{\substack{i,j,k,\dots m \\ i\neq j\neq k\dots\neq m}}^{N} V_n(r_i, r_j, \dots, r_m) + \dots . \quad (1)$$

It is believed that this series is convergent and that the main contribution to the potential energy is given by the pair potentials V_2. Then, higher-order terms may be treated as corrections to the former. Nevertheless, these "corrections" are responsible for the saturation of the chemical bonds [4]. In this calculation the first two terms in the expansion of ϕ are kept: the two-body interaction is represented by a sum of Lennard-Jones potentials, whereas the model for V_3 is a construction based on an analysis of the overlap

0 009-2614/86/$ 03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

repulsion for trimers of closed-shell atoms [2,5] to which the usual triple dipole energy [6,7] is added. Specifically, the dimensionless form of the model potential proposed is

$$\phi = \sum_{i<j}^{N} \left(\frac{1}{r_{ij}^{12}} - \frac{2}{r_{ij}^{6}} \right) + \sum_{i<j<k}^{N} V_3(r_{ij}, r_{ik}, r_{jk}) , \qquad (2)$$

where

$$V_3(r_{ij}, r_{ik}, r_{jk}) = \{-A \exp[-\alpha(r_{ij} + r_{ik} + r_{jk})] + C_9/(r_{ij} r_{ik} r_{jk})^3\} f_{ijk} \qquad (3)$$

and

$$f_{ijk} = 1 + 3 \cos\theta_{ijk} \cos\theta_{jki} \cos\theta_{kij} , \qquad (4)$$

where A and α are positive parameters measuring the intensity and range of the exchange overlap term. The positive constant C_9 stands for the intensity of the triple dipole term. The θ_{ijk} are the angles in a triangle formed by three atoms: between i and k subtended at vertex j, etc. Reduced variables are used throughout, such that distances are measured in units of $r_0 = 2^{1/6}\sigma$ and energies in units of ϵ, where σ and ϵ the Lennard-Jones constants.

The trigonometric part of eq. (3), f_{ijk}, discriminates in favor of linear arrays of three atoms if the function in braces is positive. On the contrary, when in eq. (3) the combination of exchange overlap plus triple dipole terms is negative, then the equilateral triangle characteristic of close packed structures is the most stable trimer. By varying the intensities of the two contributions to V_3, A and C_9, the effect of non-additive potentials on minimum energy cluster configurations can be analyzed parametrically.

The function approximated by a combination of sums of pair and triple potentials is indeed an extrapolation of the quantum results for clusters larger than trimers, since typical cluster distances are longer than those used in the ab initio calculations [5]. The conclusions based on the use of this construction, i.e. eqs. (2)–(4) are thus stated subject to these qualifications.

3. Cluster conformations

The aggregation atom by atom yielding the sequence of three- to seven-atom clusters plus the thirteen-atom cluster reported here corresponds to a fixed value of $\alpha = 4.5$ (reduced units). This is an intermediate value among those fitted for Be, Ne [2] and He [8] based on ab initio calculations, i.e. 4.1, 5.2 and 5.8, respectively. Once a value for the parameter α is chosen, then the range of variation of A, the exchange overlap intensity, was determined such as to give a positive and monotonically decreasing repulsive term for each pair in a trimer. An upper bound of $A \leqslant 4.3 \times 10^4$ is reached. Larger A values yield a well in the function made up by the sum of the pair $1/r^{12}$ term plus the

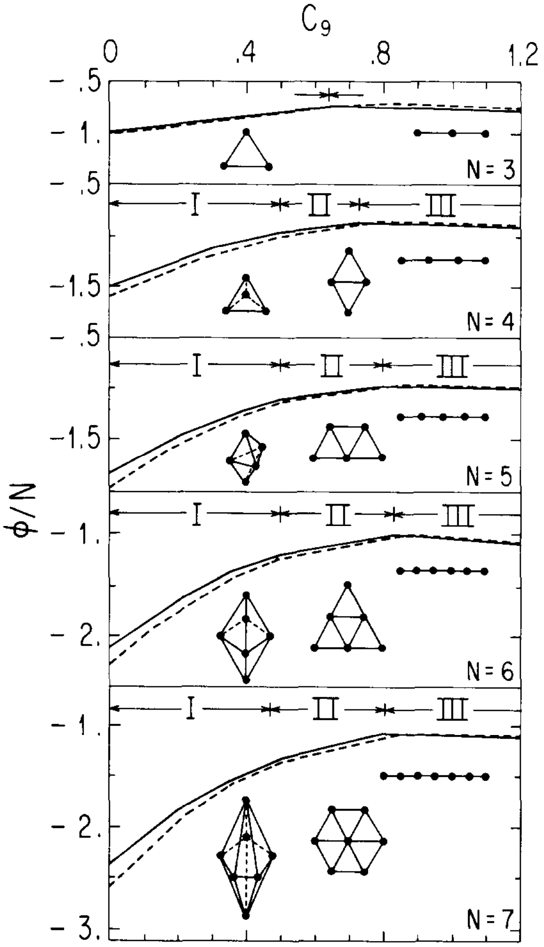

Fig. 1. Minimum potential energy per atom, as a function of the three-body parameter C_9 of eqs. (2)–(4). Plots show the sequence of three- to seven-atom clusters. Full lines correspond to the value $A = 0$, dotted lines to the value $A = 42373$. The structures drawn in region I indicate a 3-D cluster growth. Region II is made up of 2-D clusters. Region III shows a linear aggregation.

exchange overlap contribution of a third atom placed at unit distance form both atoms in the pair. Other α, A combinations were also tried; the results obtained were all qualitatively the same. The chosen range of variation of the triple dipole term C_9 is $0 \leqslant C_9 \leqslant 1.2$, to ensure three-body energies not larger than 15% of the two-body energies in a triplet of atoms. In figs. 1 and 2 we display the results of minimizing the potential energy of the various clusters under the two-parameter family of V_3 potential functions given in eqs. (2)–(4). A quasi-Newton algorithm was used for finding the minima [9]. For $A = 0$ (full lines) three regions of the parametrical space were already reported by Halicioglu [1,10]. For $A \neq 0$ (dashed lines) these regions are shifted towards larger values of C_9. Region I is characteristic of the close packed cluster growth, resulting in a cluster sequence extensively explored by Hoare and Pal [11,12], i.e. equilateral triangle, tetrahedron, bipyramid, octahedron, pentagonal bipyramid, ... icosahedron. This growth sequence is stabilized with increasing A and destabilized with increasing C_9. Region II is reached in the interval $0.4 \leqslant C_9 \leqslant 0.8$ leading to a two-dimensional aggregation of clusters under triangular symmetry. Again in this region the exchange overlap ($A \neq 0$) effect is to stabilize the various 2-D clusters. Region III is typical of a one-dimensional growth, all clusters aggregate in a linear fashion. Here the exchange overlap effect reverses, producing more unstable clusters with increasing A, as is shown in fig. 1. The thirteen-atom cluster remains planar up to $C_9 = 1.2$.

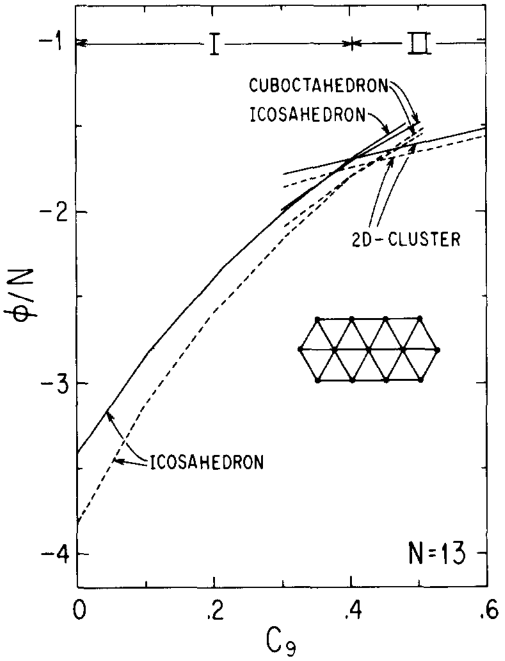

Fig. 2. Minimum potential energy per atom of the thirteen-atom cluster as a function of the three-body parameter C_9 of eqs. (2)–(4). Full lines correspond to the value $A = 0$, dotted lines to the value $A = 42373$. Regions I and II are shown.

The above observations on the cluster aggregation are based on the minimization of the potential energy per particle (or binding energy) valid only at zero temperature. At finite temperatures the entropy contribution to the Helmholtz free energy F might not be negligible [13], since the system has enough kinetic energy as to visit many minima of the potential energy surface. The vibrational contribution to the free energy arising from only the lowest minima analyzed in this work can give an insight at very low temperatures of how this function changes. For large T values more minima will contribute to the free energy producing deviations from the very low T limit [3]. In the harmonic approximation and in reduced units, the free energy is

$$F = E_0 + \sum_{i=1}^{N} \{\tfrac{1}{2} h^* \omega_i^* + T^* \ln[1 - \exp(-h^* \omega_i^* / T^*)]\} , \quad (5)$$

where $h^* = h/\tau\epsilon$, $\tau = (m r_0^2/\epsilon)^{1/2}$, $T^* = k_B T/\epsilon$ and $\omega_i^* = \omega_i \tau$ are the normal-mode frequencies about the E_0 minimum of the potential energy surface. Low-frequency modes produce a temperature-dependent negative contribution to the free energy. Therefore clusters possesing low-frequency modes have a tendency to be preferred at high temperatures versus other isomers presenting high-frequency modes. Such statement is reinforced if h^* is the smallest from a set of values corresponding to materials treated under the same model potential. The tendency of the C_9 term in the three-body potential is in fact to produce low-frequency modes. This behavior is clearly shown in fig. 3, where the normal-mode frequencies of the clusters shown in figs. 1 and 2 are plotted for different cluster sizes, $A = 0$, and four values of the C_9 parameter. In all cases the dashed lines how the normal-mode frequencies for the same N and C_9 and $A = 42373$. Thus, the effect of the exchange overlap term

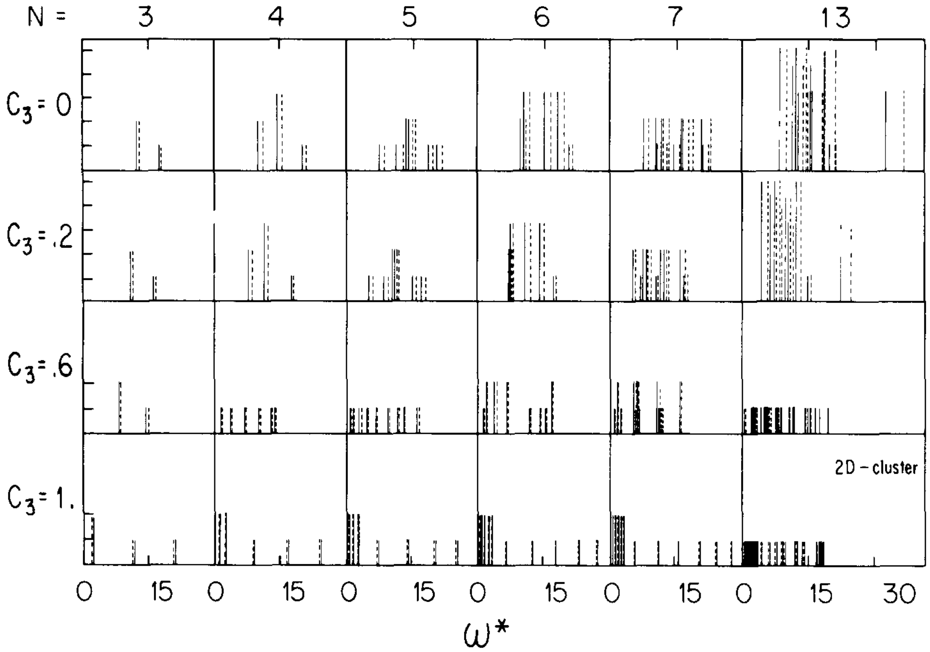

Fig. 3. Normal-mode frequencies about the minima described in figs. 1 and 2, for different values of the C_9 parameter characteristic of regions I to III. The heights 1 to 5 indicate the degeneracy of the modes. Full lines correspond to the value A = 0 and dotted lines to A = 42373. The thirteen-cluster is 2-D for both C_9 = 0.6 and 1.0

is to increase the normal-mode frequencies in regions I and II and to decrease them in the linear cases. This behavior is expected since square frequencies depend linearly on the repulsive core of the potential. In regions I and II there are very few three-atom "collineations", the f_{ijk} of eq. (3) is a positive function and therefore the exchange overlap term softens the repulsive core. In region III all triplets of atoms are collineations producing a harder potential core. The heights of the lines at the vibrational frequencies indicate the degeneracy of the modes (1 to 5 depending on the cluster). Near the boundary between two of the parametric regions in figs. 1 and 2, several isomers may have minimum potential energies very close among them. For instance, let us consider the $N = 13$ cluster with parameter $C_9 = 0.4$ and $A = 0$. This is a crossing point in the ϕ versus C_9 plot where three isomers coexist, the icosahedron, the cuboctahedron and the 2-D triangular cluster, as shown in fig. 2. When $C_9 < 0.4$, the cuboctahedron is not a minimum conformation of the potential energy surface. The icosahedron stops to be a minimum structure for $C_9 \geqslant 0.5$, whereas the 2-D triangular cluster is a minimum conformation starting at $C_9 > 0.3$. The exchange overlap term with $A = 42373$ shifts the crossing point from $C_9 = 0.4$ to 0.43.

It is interesting to see under what circumstances a relative concentration of several stable forms can coexist in thermal equilibrium at low temperatures. In fig. 4a is shown the Helmholtz free energy per particle as a function of temperature for the same $N = 13$ clusters as in fig. 2, with $C_9 = 0.4, A = 0$ (full line). In the temperature range studied the free energies of the three isomers are very close. The exchange overlap term contributes more to the 3-D conformation and at very low temperatures. Indeed, in fig. 4a the dashed line shows the free energy of the icosahedron for A = 42373, the cuboctahedron is not shown since it is not a minimum. The 2-D curve for $A \neq 0$ is almost indistinguishable from the case $A = 0$. The relative concentration of two different isomers α and β, can be expressed in terms of the difference in the free energy F as

$$c_\alpha/c_\beta = \exp(-\Delta F/kT) . \qquad (6)$$

Eq. (6) can be generalized for more than two isomers.

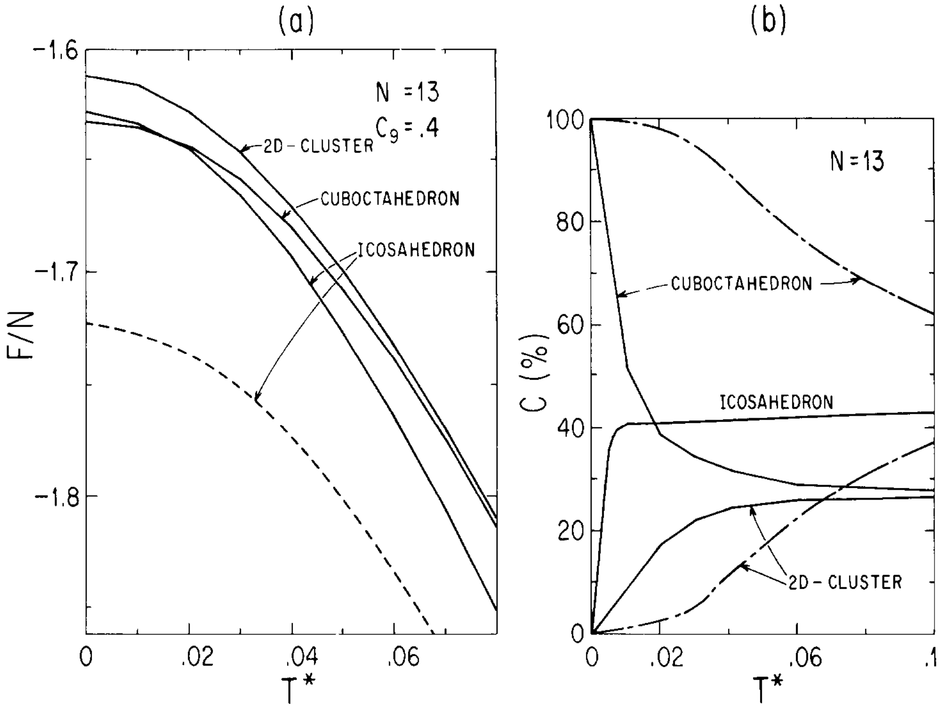

Fig. 4. (a) Helmholtz free energy as a function of temperature for the three isomers of the thirteen-atom cluster and a fixed value of $C_9 = 0.4$. Full lines correspond to the value $A = 0$ in eqs. (2)–(4), dotted lines are obtained when $A = 42373$. (b) Relative concentrations of the three thirteen-atom cluster isomers as a function of temperature for $C_9 = 0.4$ and $A = 0$ (full lines). Dotted lines correspond to the two isomers that survive when $C_9 = 0.5, A = 0$ (the icosahedron is not a minimum structure of the model potential for this couple of parameters).

In particular for three isomers α, β, γ with normalized concentrations $c_\alpha + c_\beta + c_\gamma = 1$, it is shown in fig. 4b how their relative concentrations change with temperature. The curves reported correspond to $C_9 = 0.4$ and $A = 0$. At very low temperatures there are drastic changes in a narrow temperature interval of the relative concentration between icosahedra and cuboctahedra. As temperature rises, the 2-D cluster is more abundant resulting in a mixture of the three isomers. If C_9 is increased to $C_9 = 0.5$, the icosahedron is not a stable structure and only two isomers are left, as indicated by the broken lines of fig. 4b. At very low temperatures the cuboctahedron is more abundant than the 2-D cluster, but at $T = 0.1$ an equilibrium mixture of about 50% of each component is reached.

The three-body model examined in this paper seems to be qualitatively successful in representing mixed samples of condensed clusters in different structural phases. For several values of the parameters this model is able to predict mixtures of close packed clusters with 2-D clusters or "rafts" [14] as other authors have called the latter.

The possibility of having materials where these mixtures are thermodynamically allowed and where the relative concentration of species changes abruptly with temperature, might explain discrepancies between some experimental observations. In this line of work Yacaman et al. [15] report that 10 Å clusters of Rh supported on SiO_2 have icosahedral (or decahedral) structure, whereas Yates et al. [14] propose that the very same clusters are rafts.

Acknowledgement

We want to thank Dr. T. Halicioglu for interesting discussions. We acknowledge J.L. Dounce for help in the numerical calculations. The work was partly supported by the CONACYT, Mexico, under contract PCCBBNA-022643.

References

[1] T. Halicioglu and P.J. White, Surface Sci. 106 (1981) 45.
[2] L.W. Bruch, E. Blaisten-Barojas and O. Novaro, J. Chem Phys. 67 (1977) 4701.
[3] E. Blaisten-Barojas and H.C. Andersen, Surface Sci. 156 (1985) 548.
[4] O. Novaro, Kinam 2 (1980) 175.
[5] L.W. Bruch, O. Novaro and A. Flores, J. Chem. Phys. 67 (1977) 2371.
[6] B.M. Axilrod and E. Teller, J. Chem. Phys. 11 (1943) 299.
[7] Y. Muto, Proc. Phys. Math. Soc. Japan 17 (1943) 629.
[8] E. Blaisten-Barojas, O. Novaro and L.W. Bruch, Mol. Phys. 37 (1979) 599.
[9] R. Fletcher, Report R7125 AERE, Harwell, UK.
[10] T. Halicioglu and P.J. White, J. Vacuum Sci. Technol. 17 (1980) 1213.
[11] M.R. Hoare and P. Pal, Advan. Phys. 24 (1974) 645.
[12] M.R. Hoare, Advan. Chem. Phys. 40 (1979) 49.
[13] T.P. Martin, Phys. Rept. 95 (1983) 167.
[14] D.J. Yaters, L. Murrel and E. Prestidge, J. Catal. 57 (1979) 41.
[15] M.J. Yacamán, D. Romeu, S. Fuentes and J.M. Domínguez, J. Chim. Phys. 78 (1981) 861.