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Structural effects of three-body interactions on atomic clusters

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A study of the structure of 13,54 and 147 atom microclusters was performed using molecular dynamics at constant temperature. A special emphasis was given to the calculations of those quantities that could be sensitive to the effect of adding 3-body interactions to the usual pairwise additive potentials. Thus, a topologycal approach for analyzing the radial distribution function second peak is presented. The effects of 3-body interactions of the triple-dipole and exchange overlap type on the aggregation of microclusters are: 1) to diminish the coordination number resulting in a global expansion of the microclusters; 2) to increase internal desorder in such a way as to lower the crystallization temperature; 3) in the temperature range $0.25 \leq T^* \leq 0.4$, to favor certain features characteristic of random close packing of spheres at the expenses of destroying locally paired tetrahedra.

I. INTRODUCTION

In the last decade, structural phenomena in small systems such as drops and dense aggregates of atoms have deserved various degrees of attention. We are interested in this work to analyze the importance of three body interactions versus pair-wise additive interactions in what concerns the structure of atomic microclusters. Experimentally it has been difficult to obtain direct studies on isolated microsystems. In addition, findings in condensed phase microclusters deposited on substrates or trapped in matrices might not be good candidates for comparison with available theoretical approaches because of the complexity of experimental setups.

In between theory and experiment are the computer simulations that have proved to be fundamental in various research lines such as liquid theory or nucleation phenomena. Two approaches have been used in this direction, the atomistic building up of clusters(1,2) and the Monte Carlo or molecular dynamics methods(3). The first group of works is based on

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several criteria for packing atomic clusters. Generally in this atomistic procedure one follows conventions with respect to minima of the potential energy surface or of the spatial occupation. The second group uses two powerful simulation techniques that were focused on atomic cluster problems such as: the local density of small systems(4,5,6), vaporization(5), the local potential energy(7,8), the structure of a microcrystal in the process of a phase transition(9), the free energy and surface energy(9,10) dependence on the number of atoms, the structure and interference functions(8,11) among others.

On the other hand much effort is paid in the aggregation of molecules to n-body effects. These contributions to the energy, although small, do play an important role on the theoretical determination of the best molecular geometry.

It is our purpose to review some of the previous calculations with the use of molecular dynamics at constant temperature(12) for clusters of 13,54 and 147 atoms. In addition we will incorporate to the Newton equations of motion the non pair-additive forces resulting from a 3-body potential V_3 for every triplet of atoms in the cluster. At least partly because of limited information in the literature, V_3 has frequently been approximated by the triple-dipole energy of Axilrod, Teller(13) and Muto(14). However, more extensive information on V_3 is available al present and models based on Hartree-Fock(15) and dispersion energy results(13) have been constructed for weakly bound trimers(16,17). It is our intention to incorporate into the molecular dynamics calculation one of these models.

The organization of the paper is as follows. In section II we define the clusters and discuss the methods used. In section III we present the results of adding the 3-body potential to the dynamics. In particular we discuss and analyze the structure of the 147 atom cluster as a function of temperature. We present a novel approach to interpret the profile of the radial distribution function g(r). In section IV we discuss a phase transition for the 2-body system and conclude with a brief discussion.

II. MODEL AND METHODS

Historically it has been difficult to give a unique definition of a physical cluster and much work in this direction is due to Abraham, Lee and Barker(3-5). Here we define a cluster as that aggregate of N atoms held together only by the intermolecular forces themselves. The range of interaction between atoms has a finite cutoff radius, r_c, mainly because of computational requirements. We keep a configuration as an aggregate if the atoms are not further away than a distance d_2 from at least one other atom in the cluster. Whenever the kinetic energy of an atom is large enough to push it outside this cutoff, we stop the simulation. This restrictive condition allows us to study clusters at low temperatures and presumably only in the solid phase.

The cluster N atoms have coordinates $\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N$, such that the potential energy is given by:

$$V(\vec{r}^N) = \sum_{i<j}^{N} V_2(r_{ij}) + \sum_{i<j<k}^{N} V_3(r_{ij}, r_{ik}, r_{jk}) \tag{1}$$

and the Hamiltonian is

$$H(\vec{r}^N, \vec{p}^N) = \sum_{i=1}^{N} p_i^2/2m + V(\vec{r}^N) \tag{2}$$

where $\vec{r}_{ij} = |\vec{r}_i - \vec{r}_j|$ and $\vec{r}_i$, $\vec{p}_i$, are conjugated variables

$$\dot{\vec{r}} = \frac{\partial H}{\partial \vec{p}_i} \;; \qquad \dot{\vec{p}}_i = -\frac{\partial H}{\partial \vec{r}_i} \;. \tag{3}$$

The interaction between two atoms is calculated by using a truncated Lennard-Jones potential which is zero at a cutoff distance d_2

$$\begin{aligned} V_2(r) &= 4\varepsilon\{[(\sigma/r)^{12} - (\sigma/r)^6] - [(\sigma/d_2)^{12} - (\sigma/d_2)^6]\} && \text{if } r \leq d_2 \\ &= 0 && \text{otherwise} \end{aligned} \tag{4}$$

The three-body contribution to the potential energy is represented by a model(16,17) that fits well the quantum mechanical data for noble gas and beryllium atoms:

$$V_3(r,s,t) = \{-A \exp[-\alpha(r+s+t)] + Z/(rst)^3\}(1 + 3\cos\theta_r\cos\theta_s\cos\theta_t) \tag{5}$$

where r, s, t, are the three sides and Θ_r, Θ_s, Θ_t the three angles of the triangle formed by a triplet of atoms. The first term on the RHS stands for the exchange overlap contribution of intensity A and range measured by α. This contribution is short range, and so it modifies the repulsion introduced by the pair potential. The second term is a dispersion energy result(13) of intensity(7) obtained from third order perturbation theory. For the calculations, the three-body potential V_3 goes to zero at a cutoff distance d_3 much in the same way as V_2.

The density of the cluster is defined as

$$\rho = \frac{N_c}{\Omega_c} \tag{6}$$

where N_c denotes the number of atoms contained in a sphere of radius

$$R_c = \sum_{i=1}^{N} |\vec{r}_i - \vec{r}_{cm}|/N$$

with $\vec{r}_{cm}$ being the cluster center of mass radius vector and Ω_c is the volume of a sphere with radius R_c. This definition gives an idea of which is the density at the cluster core. The atoms outside the core make up the cluster surface.

Hans C Andersen introduced the constant temperature molecular dynamics method and we refer to his work(12) for details. The main ingredient for this dynamics is that the equations of motion of the N particles in the volume Ω are the Hamiltonian equations supplemented by a stochastic collision term in the equation for $\vec{p}_i$. The trajectory average $\bar{F}$ of a function $F(\vec{r}^N, \vec{p})$ is equal to an ensemble average. Here we are concerned with the canonical ensemble $(N\,\Omega\,T)$, so that the average is for fixed volume Ω:

$$\bar{F} = F_{n\Omega T}(N\Omega T) \equiv [N!Q(N\Omega T)]^{-1} \int_\Omega d\vec{r}^N \int d\vec{p}^N \exp[-H(\vec{r}^N,\vec{p}^N)/k_B T]\, F(\vec{r}^N,\vec{p}^N) \tag{7}$$

where

$$Q(N\Omega T) = (N!)^{-1} \int_\Omega d\vec{r}^N \int d\vec{p}^N \exp[-H(\vec{r}^N, \vec{p}^N)/k_B T] \tag{8}$$

and k_B is Boltzmann's constant.

For computational purposes we adopt reduced units: $r^* = r/\sigma$, $\rho^* = \rho\sigma^3$, $T^* = k_BT/\varepsilon$, $V^* = V/\varepsilon$, $t^* = t/\tau$ with $\tau = \sqrt{m\sigma^2/\varepsilon}$. The equations of motion were solved using a time step of 0.01τ in all cases and the atoms were initially arranged as those in a sphere cut from a well equilibrated 500 atoms configuration of the bulk liquid phase at high temperatures. Other initial conditions were also considered and we detected a certain reminiscence in the results on those initial configurations when they had a defined point symmetry. Typically runs lasted 120τ for 2-body systems and between 30 to 60τ when 3-body forces were added.

III. THE THREE-BODY INTERACTION

The effects on the structure of the three body term in the potential energy can be seen in several ways. When we analyze the first peak ot the radial distribution g(r), we see that the effect of the dispersive term is to shift the maximum towards larger distances. The exchange overlap term opposes this effect, although slightly. The coordination number n_c is also modified by V_3. If r_o^* is the maximum g(r), then

$$n_c = \int_0^{r_o} 4\pi r^2 \rho g(r)dr \ . \tag{9}$$

For a 54 atom cluster we can see in Fig. 1 the variation of n_c as a function or A^* and Z^* for two different temperatures 0.35 and 0.42. The exchange overlap contribution alone is quite sensitive to the temperature, while combined with the dispersion term results in small charges of n_c. The overall effect of both terms is to shift the maximun of the g(r) function from $r^* = 1.095$ to 1.105 and to give a 5 to 10% smaller coordination number. The situation is about the same for the 147 atom cluster. At $T^* = 0.35$ there is a shift of g(r) first maximum form $r_o^* = 1.085$ to $r_o^* = 1.095$ and a change of n_c from 2.65 to 2.5 for the V_3 parameters $A^* = 2 \times 10^4$, $Z^* = 0.15$. Summing up, in this range of variation of the three-body intensities, the effect of these interactions is to increase slightly the nearest neighbor distances between atoms in the cluster and consecuently to reduce the coordination number in about 10% with respect to values obtained with pairwise interactions alone. This effect is true in the temperature range $0.25 \leq T^* \leq 0.42$ and for finite number of atoms.

A more interesting effect is pictured by the second peak of the radial distribution function which presents a splitting. The g(r) second peak for clusters is splitted(8,11) for a Lennard-Jones system. This

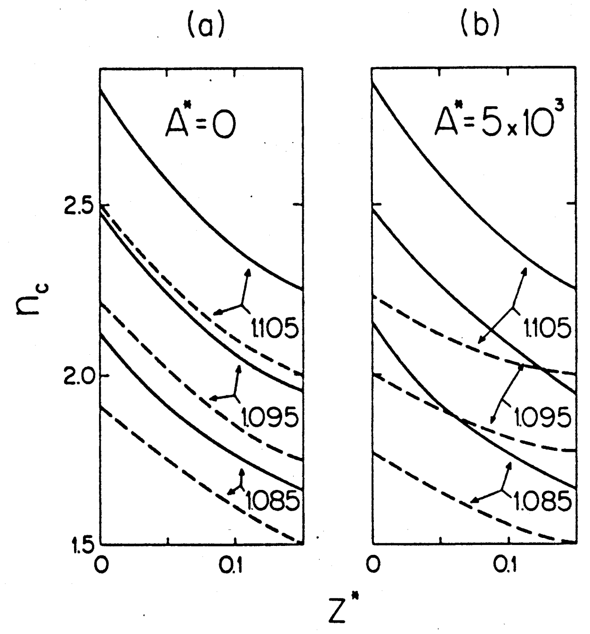

Figure 1. Coordination number as a function of Z* for two temperatures T* = 0.35 (full lines) and T* = 0.42 (dotted lines), and for two values of A*, a) and b) plots. The arrows point to curves obtained by integrating Eq. (9) up to the r_0^* values indicated in the figure.

splitting is affected by V_3, especially by the dispersive term which tends to smooth it as shown in Fig. 2. In an attempt to study what is the cause of this smoothing of g(r) second peak, we propose a classification of the distances composing this peak in the following way. Let us classify the second neighbor distances between atoms A and B as belonging to geometrical arrangements formed by A and B and by at most 3 common nearest neighbors. Only 5 structures containing second-neighbor distances are obtained using this procedure (see Fig. 3): 1) half octahedra; 2) double tetrahedra sharing one face (DT); 3) double equilateral triangles with one common side; 4) double isosceles triangles sharing the unequal side, and 5) linear arrays of 3 atoms with 2 nearest-neighbor distances.

Structures (1) and (2) involve five atoms while (3) and (4) are formed by four atoms. Interestly enough, these five smallest atomic arrays are the only structures into which all second neighbor distances can be distributed (Fig. 3b). We can thus classify the distances into

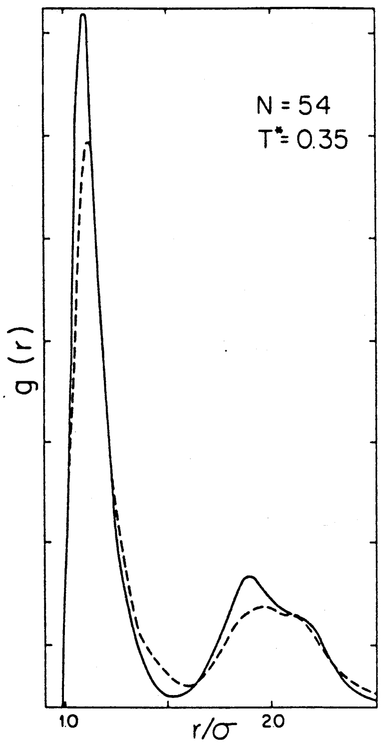

Figure 2. Radial distribution function of a 54 atom cluster at $T^* = 0.35$.

partial contributions to g(r), each one picturing one type of geometrical array of atoms

$$g(r^*) = \sum_{\alpha=1}^{5} g_\alpha(r^*) \qquad 1.35 \le r^* \le 2.3 \qquad (10)$$

In Fig. 4 we show an example of this pictorial decomposition of g(r) for the range of distances corresponding to second-neighbors.

Once the three-body forces are plugged into the system, atoms tend to rearrange with the eventual outcome of a system in which certain favored triplet configurations are larger in number. This can be quantified by defining a frequency of ocurrence for each of the five geometrical arrays of atoms

$$\nu_\alpha = n_\alpha / n_T \qquad (11)$$

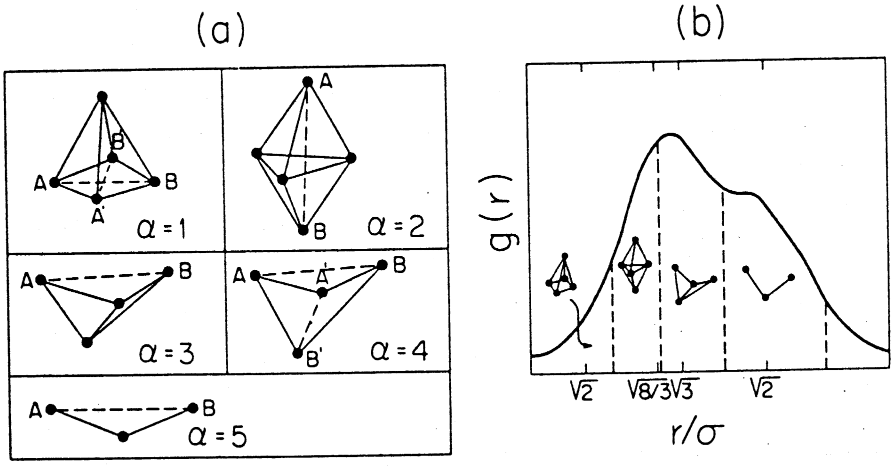

Figure 3. (a) The five geometrical arrays with second-neighbor distances (dotted lines). Full lines join nearest neighbor atoms; (b) The decomposition of second-neighbor distances in g(r). The array $\alpha=4$ is very spread, giving contributions up to distances $r^* \sim \sqrt{3}\, r_o^*$.

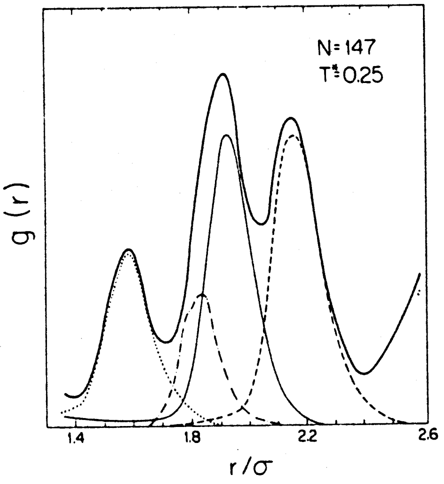

Figure 4. Decomposition of the radial distribution function second peak. The lower curves indicate the contribution of the five structures shown in Fig. 3a: =1(...), =2(-·-·), =3(____), =5(---). The array $\alpha=4$ gives a contribution not seen in the scale.

where $n_T = \Sigma n_\alpha$ and $\alpha = 1$ to 5. In Fig. 5 we have represented the ν_α's as functions of temperature. Changes in the packing, as we can infer from this picture are not drastic. There are though some effects of the 3-body interactions. At lower temperatures, when the ratio of 3-body to 2-body energies is larger, we find that tetrahedra shearing one face ($\alpha = 2$) are favored at the expenses of double triangles shearing one side ($\alpha = 3$). When temperature is rised in the system, the ratio 3- to 2-body energies diminishes. But between $T^* = 0.25$ and $T^* = 0.3$ the 2-body system is suffering a structural change. Even though the 3-body contributions at these temperatures is small, it is enough to inhibit the structural change enhanced by the 2-body interactions alone. This fact suggests a possible criterion for scaling the 3-body effects into effective 2-body parameters. Yet, we must keep in mind that the ratio 3-body to 2-body potential energy per particle is a function of temperature and cluster size.

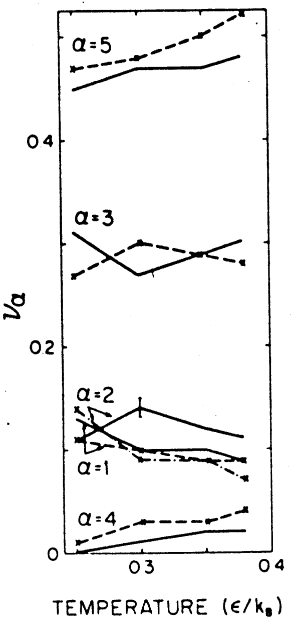

Figure 5. Frequency of ocurrence of the five geometrical arrays as a function of temperature. Full lines correspond to the 2-body calculation and dotted lines are the result when 3-body interactions are added. A typical error bar is shown.

Concerned with the packing of these five fundamental geometrical arrangements of atoms, and specially with the possibility of locating motifs with five-fold symmetry, we searched for the mutual arrangement of the double tetrahedra into pairs. Let us define correlations coefficients C_μ in the following way. Consider one DT_i and ask for the number of its atoms that are shared with any other DT_j.

$$C_\mu = 2\left[n_{DT}(n_{DT} - 1) \right]^{-1} \sum_{i<}^{n_{DT}} \quad (DT_j \text{ with } \mu \text{ atoms shared by } DT_i) \qquad (12)$$

$$\mu = 1,\ 2,\ 3,\ 4.$$

If μ atoms are shared between DT_i and DT_j , then DT_j is accounted only once *i.e.*, into that C_μ with highest μ. From Table I it is clear that the highest correlation values are those of paired DT's sharing one atom. Moreover 3-body effects are not producing dramatic breaking of correlation among pairs of double tetrahedra. The presence of many locally interconnected icosahedra, or polyicosahedral model(8,11), is not confirmed. Another correlation of interest is a measure of the twinning of half octahedra to give full octahedra:

$$C_o = \frac{\text{No. of half octahedra forming full octahedra} \times 100}{\text{No. of half octahedra}} \qquad (13)$$

This coefficient measures the ratio of cubic packing present in the cluster, its values being cast in Table I as well. The effect of 3-body interactions on C_o is to restrain the formation of local f.c.c. motifs.

The overall effect of 3-body interactions is therefore to produce desorder, as if an extra source of temperature would be plugged to the cluster. At $T^* = 0.25$ they tend to enhance the formation of double tetrahedra at the expences of other arrangements. At higher temperatures they point towards a destruction of all structures with a tendency to favor more planar ($\alpha = 4$) and linear arrays ($\alpha = 5$) as well as triplets with sides larger than 2.3σ.

The analysis of $g(r)$ second peak can be performed on the components of $g(r)$ when we break this function into partial functions associated to the core, surface and intermediate regions in the cluster (see section II for definition). Except for the distances within the core being shorter than those in the core-surface and in the surface

Table I

Correlation coefficients measuring the extent of pairing between DT's (C_μ, $\mu = 1-4$), n_{DT} is the number of half octahedra and C_o is the correlation coefficient indicating the % of HO that form full octahedra.

	T*	n_{DT}	$C_1 \times 10^3$	$C_2 \times 10^3$	$C_3 \times 10^3$	$C_4 \times 10^3$	n_{HO}	C_o (%)
v_2	0.25	196 ± 7	106.5 ± 0.7	14 ± 2.1	20 ± 1.7	13.4 ± 0.8	240 ± 5	49 ± 6
	0.3	264 ± 22	100 ± 1.3	22 ± 3.9	22 ± 2.8	13 ± 1.4	189 ± 12	32 ± 6
	0.35	210 ± 26	90 ± 2.6	40 ± 11	27 ± 7	16 ± 3	166 ± 14	12 ± 4
	0.38	191 ± 30	90 ± 2.6	40 ± 12	28 ± 8	17 ± 4	161 ± 14	12 ± 4
$v_2 + v_3$	0.25	248 ± 25	100 ± 1.6	22 ± 4.7	22 ± 3.7	13 ± 1.8	194 ± 12	29 ± 5
	0.3	161 ± 27	100 ± 3.9	40 ± 18	31 ± 11	19 ± 5	168 ± 12	11 ± 4
	0.35	148 ± 23	90 ± 3.3	40 ± 16	34 ± 11	21 ± 4.8	145 ± 14	7 ± 3
	0.38	118 ± 21	90 ± 3.3	40 ± 17	33 ± 13	24 ± 6.4	138 ± 18	7 ± 4

regions, the distribution of geometrical arrays as well as frequencies and correlation coefficients in the three regions are very much like those previously discussed for the whole cluster. The surface region contains the largest proportion of arrays $\alpha = 4$ and triplets with at least two sides larger than 2.3σ.

IV. TWO-BODY CONFORMATIONAL TRANSITION AND DISCUSSION

Let us present here one other computer experiment for the 147 cluster with only 2-body interactions among the atoms of the system. Brian and Burton(9) reported a phase transition from solid to liquid in a 100 atom cluster at $T^* = 0.31$ to 0.33. They detected the transition only when the cluster was prepared by heating slowly form a lower energy.

From our 2-body data discussed in the previous section, Fig. 5 and Table I, we can say that at $T^* = 0.3$ there is a structural change. At lower temperatures we have larger occurrance of half and full octahedra at second neighbor distances $\sqrt{2}r_o^*$ which is an indication that a f.c.c. quasi crystalline phase is favored. At $T^* = 0.3$ and higher temperatures, may more "twinned" tetrahedra are formed, possibly indicating the presence of incomplete icosahedra or hexagonal close packed regions. There is a reasonable indication that a conformational transition is taking place in this range of temperatures. In order to locate such transition, and in view of our constant temperature dynamics we proceed as follows. First, let us start from an initial configuration chosen as explained at the end of section II. Secondly, let us cool at a very slow rate of $\Delta T^* = 0.01$ every 120τ and sweep the region $0.25 \leq T^* \leq 0.38$.

The results are shown in Fig. 6 where we plot the average potential energy per atom as a function of temperature. The curve has definitely two slopes at $T^* = 0.29 - 0.30$. The low temperature side of the transition corresponds again to a system crystallizing. The high temperature side of the transition is a system too structured to be a liquid. In fact the pair distribution function second peak presents the splitting that we analyzed before in terms of the geometrical arrangements of atoms. We can say that we are seeing a transition from an amorphous with ingredients of random close packing phase to a quasi f.c.c. phase. We locate the transition at a somehow lower temperature T_c than Brian and Burton. According to them T_c should increase with increasing number of atoms in the cluster. This suggests that possibly the transition is reversible but there is a hysteresis loop.

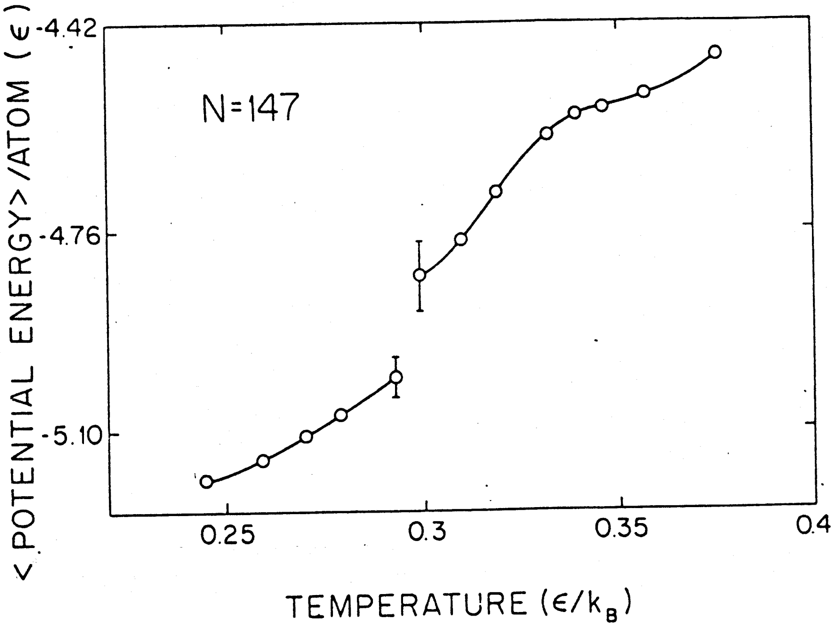

Figure 6. Average potential energy per atom as a function of temperature. Typical error bars are shown.

We have demonstrated that for finite systems when the exchange overlap term is small the effect of 3-body interactions is to increase slightly the nearest neighbor distances and decrease the coordination numbers. We have also shown that 3-body interactions favor the less crystalline packing and no temperature-activated transition seems to appear (at least in the range $0.25 \leq T^* \leq 0.38$). In the range of temperatures of this study, there is little evidence of a large number of icosahedral motifs for the 147 cluster with 2- and 3-body potentials. Finally, let us say that the analysis of the radial distribution function second peak might be interesting for the study of amorphous phases of metals and alloys. Further work is needed to search for effects of the non pair-additive effects on pair potential other than the Lennard Jones, of how pairs of different geometrical arrays pack together (crossed correlation coefficients) and how the internal pressure changes during a slow cooling or slow heating experiment.

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