ON THE ORIGIN OF THE OCCURRENCE OF "MAGIC NUMBERS" IN CLUSTER SIZE DISTRIBUTIONS OF XENON IN THE COMPRESSED GAS PHASE

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The formation of clusters in compressed argon and xenon gases is studied with the molecular dynamics simulation technique using two-body Lennard-Jones and three-body Axilrod–Teller potentials. It is suggested that the occurrence of clusters corresponding to the "magic number" $n = 13$ for xenon and the absence of such stable clusters for argon is due to the dispersion forces that result from triple-dipole interactions.

In recent experiments Echt et al. [1,2] have shown, by measuring time-of-flight mass spectra of argon and xenon clusters, that the xenon spectra show distinct maxima for clusters Xe_n with $n = 13, 19, 25, 55, 71, 87$ and 147 corresponding to the so-called "magic numbers". These clusters possess an icosahedral symmetry [3] and are especially stable in computer simulations in which isolated clusters were built and their properties studied [4–8]. On the other hand no such stable clusters have been observed for argon although the basic geometric structure anticipated for such clusters is the same as that for xenon. Echt and coworkers have already raised the question of why clusters corresponding to the "magic numbers" are only observed experimentally for xenon [2]. On the basis of their experimental data alone they were unable to give a satisfactory answer to that question.

Based on our recent work on the formation of argon clusters in the compressed gas phase [9] we have undertaken a comparison of cluster formation for argon and xenon gases by means of the molecular dynamics (MD) simulation technique. In this communication we present preliminary results obtained on systems of 108 atoms regarding the influence of the chosen interaction potential on cluster formation. A detailed analysis will be published elsewhere [10]. In ref. [9] it was shown that the inclusion of the three-body Axilrod–Teller (AT) potential to the interaction potential between argon atoms gives argon clusters an additional stability causing longer average lifetimes of these clusters in comparison with clusters formed under the influence of a two-body Lennard-Jones (LJ) potential alone. However, no particular maxima were registered in the distribution of clusters according to size, in accordance with the experimental data of Echt et al. [2].

In order to explore the formation of argon clusters in more depth and simultaneously compare argon with xenon cluster formation, we have performed calculations at temperatures ranging from 270 to 90 K with number densities of 1.40×10^{21} cm^{-3} and 1.27×10^{20} cm^{-3} for argon and xenon respectively. By keeping the volume constant and at the same time lowering the temperature, our system always remained in the gaseous phase. This was also reflected in the structure of the radial distribution function which showed a broad maximum at all temperatures. For each temperature we have monitored the distribution of cluster density as a function of cluster size as well as the average lifetime of each cluster size. As before a cluster was defined as that aggregate in which each atom is no further away than a given distance $R_{cl} = 2.00\sigma$ from at least one other atom in the aggregate. In addition, we have imposed the restriction that the set of atoms forming an aggregate fulfils the above criterion at least for a time interval of a full period of

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oscillation of two atoms of the system under consideration. The frequency of one oscillation for an internuclear distance of 2.00σ was 0.73 ps^{-1} ($\approx$ 500 integration steps) and 0.30 ps^{-1} ($\approx$ 1000 integration steps) for argon and xenon respectively. The average lifetime was obtained by dividing the cluster distribution obtained for all possible clusters being formed by the distribution of unique (different) clusters that appear only once during the simulation [9]. The potential parameters we have used for argon were σ = 3.405 Å, ϵ/k = 119.8 K and $\nu = 73.2 \times 10^{-84}$ erg cm^9. Further details of these calculations are given in ref. [9]. The trend we had observed in our previous work was confirmed, i.e. no maxima in the cluster distribution of argon at any temperature, and stabilization of clusters through inclusion of the AT potential. Similar calculations for xenon (σ = 4.1 Å, ϵ/k = 221 K, $\nu = 705.0 \times 10^{-84}$ erg cm^9) have shown that, besides the stabilizing effect due to the three-body potential, xenon clusters have in general a lifetime at least twice as long as that of argon, and that at 120 and 90 K xenon distributions show a distinct maximum at cluster Xe_n with n = 13. Typical cluster density versus cluster size distributions and the corresponding average lifetimes at 120 K for both argon and xenon are shown in fig. 1. It can clearly be seen that stable Xe_{13} clusters are built only under the influence of the combined LJ + AT potential. We have repeated the xenon calculations three times, each time beginning from different initial conditions and have always obtained similar distributions. The maximum at Xe_{13} did not always have the same height but it was clear that clusters Xe_{12} and Xe_{14} showed a lesser density and had a shorter average lifetime than cluster Xe_{13}. Inspection of the atom coordinates composing the X_{13} clusters indicate a compact structure which, however, does not necessarily show icosahedral symmetry.

These observations lead us to believe that the stabilization effect and the appearance of the maximum in our distribution are caused by the physical context inherent in the potential we have used (LJ + AT), and in particular by the inclusion of the non-additive AT

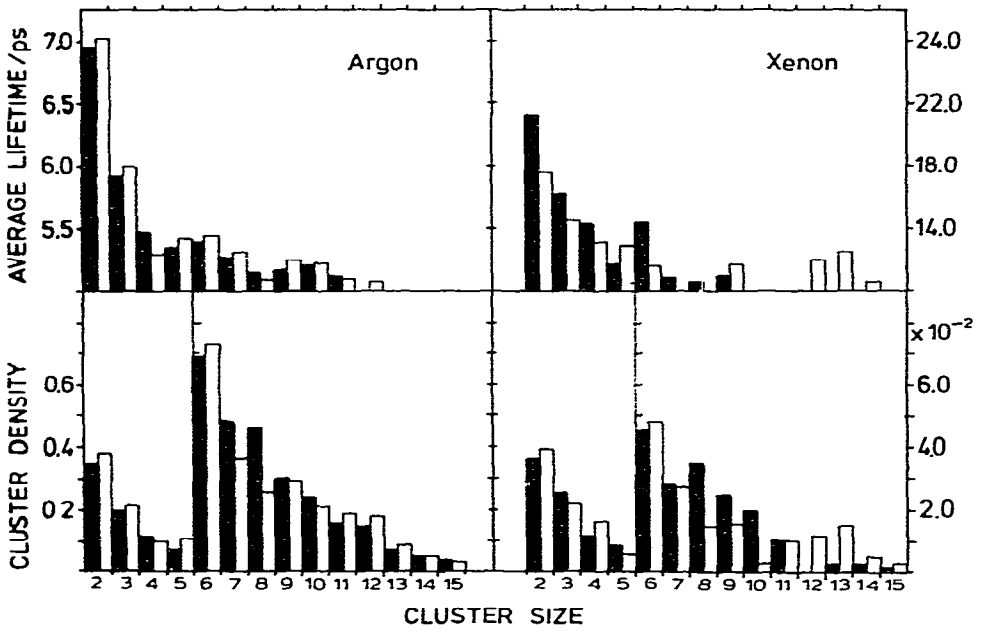

Fig. 1. Cluster density versus cluster size distribution (bottom) and average lifetimes (top) at 120 K. Cluster configurations being formed with the same atoms at different times are counted only once. The density of clusters 2–5 and the average lifetime of Ar clusters are given on the left-hand side while the density of clusters 6–15 and the average lifetime of Xe clusters are given on the right-hand side of the figure. Dark columns represent clusters being built under the influence of a LJ potential; light columns represent clusters being built under the influence of a LJ plus AT potential. Average cluster lifetimes equal to or less than one period of oscillation of Ar_2 clusters (5.0 ps) or Xe_2 clusters (10.0 ps) are not shown in the figure.

contribution. An analysis of the contributions of these two potentials gives a plausible explanation of why stable icosahedral structures corresponding to the "magic numbers" may only be observed for xenon and not for argon.

The LJ potential contains the potential of the dispersion force for the dipole–dipole interaction. This contribution is approximately four times as big for xenon as for argon [11]. However, it is not sufficient to give stable Xe_{13} clusters in our dynamic simulations of cluster formation. The AT potential on the other hand represents the potential of the dispersion force for the triple-dipole interactions and is proportional to the third power of the polarizability of the species. The polarizability of xenon is approximately 2.5 times as big as that of argon [12]. This non-additive contribution has been shown by Etters and Danilowicz [13] to be between 5 and 10% of the total energy for argon clusters. Our calculations for xenon give similar results [14]. A comparison of the non-additive contribution to the potential has shown that the contribution for xenon is approximately four times as big as for argon [12,14]. The occurrence of stable Xe_{13} clusters suggests that this contribution is indeed important, and that the observation of clusters corresponding to the "magic numbers" depends on the polarizability of the system under consideration and, thus, on the dispersion forces that result from triple-dipole interactions. These conclusions are also reflected in the work of Halicioglu [15,16] and Oksuz [17] who have studied the effect of three-body forces on the structure of isolated microclusters.

Since the system we have studied represents a compressed gas phase, that is, the step prior to the expansion into vacuum in the experimental procedure of Echt et al. [1,2], we believe that we are justified in posing the question of whether clusters, and in particular stable ones corresponding to the "magic numbers", are already built in the gas phase and thereafter remain stable throughout the expansion and identification.

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