RELAXATION OF COLLECTIVE EXCITATIONS IN LJ-13 CLUSTER

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We have performed classical molecular dynamics simulation of Ar_{13} cluster to study the behavior of collective excitations. In the solid “phase” of the cluster, the collective oscillation of the monopole mode can be well fitted to a damped harmonic oscillator. The parameters of the equivalent damped harmonic oscillator – the damping coefficient, spring constant, time period of oscillation and the mass of the oscillator – all show a sharp change in behavior at a kinetic temperature of about 7.0\,^o\,K. This marks yet another characteristic temperature of the system, a temperature \( T_s \) below which collective excitations are very stable, and at higher temperatures the single particle excitations cause the damping of the collective oscillations. We argue that so long as the cluster remains confined within the global potential energy minimum the collective excitations do not decay; and once the cluster comes out of this well, the local potential energy minima pockets act as single particle excitation channels in destroying the collective motion. The effect is manifest in almost all the physical observables of the cluster.

I. INTRODUCTION

The study of collective excitations in finite systems originated in Nuclear Physics and subsequently were carried out in free atoms and metal clusters as well. It is understood that in case of atomic nuclei, the coherent motion of shell nucleons driven by a sufficiently confining short-range interaction potential gives rise to collective resonances in specific modes, and these long-lived, large amplitude oscillations are termed “giant resonances”. While single particle excitations are adequately described by Hartree-Fock approximation, its time-dependent extension accounts for the collective behavior of the constituent fermions \[1,2\], and the damping of the giant resonances is explained by the non-perturbative treatment of the residual collisions of quasi particles \[3\]. In case of atoms and metal clusters the valence electrons execute the resonance motion. Though long-ranged, the screening makes the Coulomb potential effectively short-ranged, enabling the local confinement of the electrons that is necessary for the resonance to occur \[4\].

In this article we present some results of the study of collective motions of yet another finite system – a 13 particle inert gas atom cluster. Being a classical, non-fermionic and very weakly interacting system, the situation is quite different here. In nuclei and metal clusters, the collective excitations are essentially given by the poles of the Green’s function corresponding to the response of the charge density fluctuations, and are amenable to detection by the electro-magnetic probe, whereas the constituents of the system under present investigation are charge-neutral point particles, so there is no possibility of charge fluctuations. Nevertheless, the particles do exhibit coherent motion owing to the presence of interaction potential between them, and these are simply the normal modes of the mass density fluctuations. In section II we will describe how the normal mode components of the cluster can be projected out of the complex dynamics that it undergoes.

It is well know that molecular dynamics simulations of Ar_{13} cluster display solid-liquid phase transitions. The cluster has a near-rigid regular icosahedron structure in the solid-like “phase”, the individual atoms executing vibrational motions about their mean positions, whereas in the liquid-like phase the cluster does not have any regular shape and the individual atoms exhibit largely diffusive motion. In addition, the cluster also shows a “coexistence phase”, wherein after spending some time in one of the phases the cluster spontaneously switches to the other and eventually back again.

The “phase changes” in Ar_{13} have been well charac-
The three phases are best illustrated by the curve of caloric equation of state- the plot of long time ($\sim 10^6$ time steps) average of kinetic energy against that of total energy. The plot distinctly shows three regions- the solid-like region towards low kinetic/total energy, the liquid-like region on the higher end, and the coexistence phase in between. Another good diagnostic of the phase change is the root mean square bond length fluctuations, which shows a steep rise at the “melting point”, indicating that there is a large increase in the mobility of the atoms of the cluster as it enters in to the liquid-like region. There are few other diagnostics given in detail in Ref. 5 which demonstrate the occurrence of the change of phase.

The original motivation behind this work was to study the collective excitations in $Ar_{13}$ cluster as it passes through the phase changes. It was naively expected that in the transition region the system would show a marked change in behavior, much like the bond length fluctuations. However, this effort had to be abandoned as it was soon realized that the results obtained from different runs in the liquid-like region show a very large spread in values and hence it becomes hard to arrive at an unambiguous result. On the other hand, we have had some surprising results in the solid-like region itself. We found that there is yet another, much lower characteristic temperature of the system, much more sharply demarcated on the total energy axis than the solid-liquid phase change. We shall argue that at this temperature the single particle excitations begin to destroy the collective excitations, and the effect is manifest as a qualitative change in behavior of almost all the physical observables of the cluster.

Details of the computational procedure are discussed in section II. The main results are presented in section III followed by a discussion. Finally we summarize the results and conclude.

II. COMPUTATIONAL PROCEDURE

We perform isogenic molecular dynamics simulation of the 13-particle Argon cluster choosing the pairwise 6-12 Lennard-Jones interaction

$$V_{ij}(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$

with parameters $\sigma = 3.4 \times 10^{-8}$cm and $\epsilon = 1.67 \times 10^{-14}$erg. The classical equations of motion were solved using Verlet algorithm 6 with a time step of $2.0 \times 10^{-13}$sec. The total energy is found to be conserved to within 0.001%.

In an interacting many body system, we know that the average potential of the static system contributes to the single particle excitations, and the interaction treated dynamically gives rise to collective excitations. Similarly it should be possible to think of the complex dynamics of the cluster to be composed of collective motions in addition to the single particle undulations. Then we need to identify the collective modes of the cluster. In view of the nuclear deformations, it has been recognized 8 that collective variables of an arbitrary density distribution can be parametrized in terms of the moments of density distribution, and in particular for small deviations from spherical symmetry, expansion in terms of spherical harmonics components is the most natural description of the normal modes. Adapting the same idea, the contributions to different normal modes of the cluster as a function of time can be projected out as

$$C_{lm}(t) = \int \rho(\mathbf{r}, t) Y^m_l(\theta, \phi) r^2 d\mathbf{r}$$

where $\rho(\mathbf{r}, t)$ is the density distribution, which is discrete in the present case.

Obviously the collective oscillations here are the shape oscillations. The monopole ($\ell = 0$) mode component is projected out simply as the average radius of the cluster as a function of time, hence it corresponds to the uniform radial motion of the particles (“breathing” mode). It should be noted at this point that in charged systems like the atomic nuclei or the metal clusters, the dipole mode ($\ell = 1$) usually is the strongest and the monopole is always very weak. In contrast the inert gas atom cluster $Ar_{13}$ has monopole mode as the strongest and the dipole mode simply does not exist. The reason is the following: A dipole motion in general corresponds to the vibration of the centroid of the distribution about its mean position, and in case of charged systems, it is the out of phase motion of the centroids of the opposite charge distributions that stabilizes the dipole oscillation. But there is no negative polarity for the mass distribution, so a dipole oscillation is ruled out, and so are all the modes with odd $\ell$, as they would correspond to the oscillation of the center of mass of the system about its origin.

Here we present some observations made on the monopole oscillations of the cluster. A monopole excitation is given to the cluster as follows: The system equilibrated at any temperature performs shape oscillations of its own accord owing to the interplay of its kinetic and potential energies. First, a reference time $t=0$ is chosen such that at that time the cluster has expanded to its maximum, and is just about to start contracting. At this stage, when most of its energy is in the potential energy form, the cluster is given a sudden, radially uniform expansion, so as to raise the total potential energy of the cluster by a predetermined value. The velocities and hence the kinetic energies of the atoms are left unchanged, therefore the sudden expansion has the effect of instantaneous increase of total energy by a predetermined value. The cluster responds to the increase in the amplitude and sets itself into oscillation in a pure mode and this amounts to giving a monopole excitation to the cluster. We will add more on the method of giving the excitation to the system later in the discussion.

Fig. 1 shows the time evolution of the monopole component of the cluster at three different temperatures- the
first one at 5°K, the second at 20°K, and the last at 30.5°K which is very close to the melting point (∼34°K). A monopole excitation corresponding to an excitation energy of ∆E = 0.05 × 10^{-14} \text{ erg/atom} is given at time t=0. The solid curve shows the time evolution of the cluster and one can immediately recognize that the relaxation of the excitation resembles the time evolution of a damped harmonic oscillator. The dotted curve in the plot actually is a fit to a damped oscillator

\[ y(t) = y_0 + Ae^{-\lambda t} \cos(\omega t + \delta) \]  

where \( \lambda \) is the decay constant and \( \omega' \) is the reduced frequency of the damped oscillator. It should be mentioned here that the curves shown are actually not the ones obtained out of single runs, but in fact are the averages over 500 independent runs. Though the excitation is given at a configuration at which the cluster is in a state of maximum expansion, in general not necessarily would all the constituents of the cluster be at their respective maximum displacements from the origin. As a consequence the response of the system to the excitation is quite sensitive to the initial configuration, and the quantities derived out of different runs show a spread in value about their mean, increasingly so at higher temperatures. Hence it becomes necessary that some kind of ensemble averaging be done in order that good consistency is obtained. Note that the monopole oscillation of the cluster is essentially simple harmonic at very low temperatures, and the oscillations are progressively damped as the temperature is increased. The fit is remarkably good, suggesting that one may map the monopole mode motion of the cluster to a 1-dimensional under-damped harmonic oscillator. A plot of the potential energy of the cluster as a function of its radius as it evolves deviates very little from a perfect parabola [Fig. 2], giving further justification to the mapping. Hence we shall carry out further analysis in terms of the parameters of the equivalent harmonic oscillator, an exercise which would prove very fruitful.

From the fit to the time evolution of the excitation [Fig. 1] we already have the values of two of the parameters of the equivalent harmonic oscillator, the damping coefficient \( \lambda \) and the reduced frequency \( \omega' \). From Fig. 2 we notice that the oscillator potential can well be taken to be parabolic with respect to the cluster radius, so we could make use of the Hooke’s law to obtain the spring constant \( k \) of the oscillator. We can go further. The reduced frequency \( \omega' \) of a damped harmonic oscillator is related to its natural frequency \( \omega \) by

\[ \omega' = \sqrt{\omega^2 - \lambda^2} \]  

and from the value of the natural frequency we can obtain the mass \( m \) of the equivalent oscillator from the relation \( \omega = \sqrt{k/m} \). Thus, we now have the values of all the parameters of the equivalent oscillator, and henceforth we find it more convenient to discuss in terms of these parameters. We use the term “reduced mass” \( m \) to refer to the mass of the equivalent oscillator to distinguish it from the actual mass \( M \) of the Argon atom.

### III. RESULTS AND DISCUSSION

The results are summarized in Fig 3. The data are completely in the solid-like domain of the cluster (The last four points are from the coexistence region). The abrupt change in qualitative behavior of the oscillator parameters at \( E_{\text{tot}} = -5.444 \times 10^{-14} \text{ erg/atom} \), which corresponds to a kinetic temperature of \( T_s \approx 7.0^0\text{K} \) is quite puzzling. The damping coefficient is zero for \( T < T_s \) and then has a linear rise throughout the solid phase (Fig 3(a)); the period of oscillation changes slope at \( T_s \) (Fig 3(b)) ; the spring constant has a slow linear rise at low temperatures but shows a dramatic \( \sqrt{E_{\text{tot}}} \) rise beyond \( T_s \) (Fig 3(c)) ; and finally, the reduced mass drops drastically at \( T_s \) (Fig 3(d)). Some observations :

1. Of the four parameters of the damped harmonic oscillator, three (viz. the spring constant, the reduced mass and the damping coefficient) are completely independent of each other and only the frequency of oscillation is a derived quantity. However, the transition at \( T_s \) brings a qualitative change in all of them.

2. It is on the total energy axis that these parameters indicate a clear-cut transition. Therefore it is the total energy and not the kinetic temperature that is the most relevant parameter to study the system.

3. The change of behavior along the total energy axis at this transition is much too sharp compared to that in the case of solid-liquid phase change.

4. Other dynamical properties like the rms bond-length fluctuations, velocity autocorrelation function, specific heat and Lyapunov characteristic exponent should also manifest the signature of this transition.

The sharpness of the transition at \( T = T_s \) is unprecedented for a system of its size. Earlier investigations do not seem to have paid much attention to the system at such low temperatures. From Fig 3(a) we find that at temperatures below \( T_s \) the oscillations are completely undamped, which means that the collective mode is very stable and the individual atoms of the cluster perform periodic motion without losing coherence. However, it should be noted that anharmonicity is inherent in the underlying interaction potential, and manifests itself as a slow linear rise in the time period of oscillation with the increase in total energy.

Then the question is what causes the damping of the collective mode at temperatures above \( T_s \). Looking at the plot of the reduced mass, Fig 3(d), it is curious to note that below \( T_s \) the mass of the equivalent oscillator...
is smaller by a factor of 12 against the mass of the Argon atom, a factor same as the number of surface atoms. In addition, the value of the reduced mass drops drastically at \( T_s \) and reaches an asymptotic value of 1 at higher temperatures. This leads us to the picture of a set of a coupled oscillators, which continues to oscillate without losing strength if set-in in one of its normal modes; and the normal mode gradually decays if one or a few of the constituents are given additional independent disturbances. Based on this reasoning, we infer that for \( T < T_s \) collective modes are stable whereas above \( T_s \), particles somehow begin to make independent motions and these independent motions cause the damping of the collective mode. One can then argue that as the temperature is raised, these independent particle motions become more and more prominent, destroying the collective oscillations faster than before.

If this argument is indeed correct, a Fourier analysis of motion of the particles should reflect this behavior. We took the power spectra of individual radial motion of the particles and plotted in Fig 4, adding them together. The plot clearly shows that for \( T < T_s \) (Fig 4(a)), the spectrum has a single sharp peak at the frequency component \( \omega = 1.13 \times 10^{10} \text{ Hz} \), and at \( T_s \) (Fig 4(b)), additional components have just begun to appear. At a slightly higher temperature (Fig 4(c)), the spectrum shows a continuum at low frequencies, with a considerable reduction in the strength of the collective mode. The presence of an almost flat continuous spectrum is a clear indication of the incoherent motion of the particles. However, it should be noted that there are also additional peaks in the spectrum, which could mean the presence of other collective modes. Indeed, most of the individual spectra do show prominence at these peaks. This may lead us to another scenario, that anharmonicity sets in at \( T_s \); as a consequence of which other modes are excited due to mode-mode coupling, and thus causing the decay of the original pure mode. But it was found that the strengths are never the same at any component from the spectra of any two of the particles. On the other hand the individual spectra of all the particles are stunningly identical at \( T < T_s \). This gives a convincing evidence to the proposition that it is the onset of the independent particle motions that damps the collective oscillations at \( T > T_s \). Finally, at still larger temperatures (Fig 4(d)), there is no trace of any collective mode.

What remains to be explained then is how is it that these independent particle motions are triggered and why are they absent below \( T_s \). Interestingly, the situation is quite similar to some of the interacting quantum many body systems, like for example the case of a system with magnetically ordered ground state, wherein the interaction gives rise to a finite gap in the single particle excitation spectrum, besides the formation of low lying collective modes.

Another surprising feature is the behavior of the spring constant above \( T_s \). We know that the potential energy surface gets widened as the energy is increased, so we would expect the spring constant to decrease as the energy is increased. Instead, we notice that the spring constant increases, as square root of the total energy. To gain a better understanding, we plot the potential energy curves corresponding to different energies on the same graph in Fig 5. Observe that for \( T < T_s \), the oscillations at all temperatures lie on the same potential energy curve, only the amplitude increases with the increase in energy, just as in the case of an actual harmonic oscillator. On the other hand, above \( T_s \), the oscillations of the cluster trace different potential energy curves at different temperatures. This implies that it is not the same harmonic oscillator any more at different temperatures. We reason that this happens because the potential energy hyper-surface of the cluster in the 3N dimensional co-ordinate space has a global minimum, and so long as the cluster is confined within this well the cluster sustains collective oscillations, individual particles retaining their relative phase coherence. Total energy \( TE = 5.44 \times 10^{-14} \text{ ergs/atom} \), corresponding to \( T_s \) can now be seen as the depth of this global minimum well, within which pure normal mode of the cluster is stable. Above \( T_s \), the cluster has sufficient energy to come out of this global minimum, and the particles find local minima pockets in the potential energy hyper-surface accessible to them. Once they start making excursions to such local minima pockets, the motion of different particles become asynchronous, causing them lose coherence, and this has the effect of damping the collective oscillation. These excursions are the “single particle excitations” of this classical system. Different particles now go through the potential energy minimum at different instances of time, and that is the reason why the potential energy curve is much raised and the amplitude of the monopole mode is much smaller (Fig 5). However, it is not clear yet as to why, with the increase in total energy, the potential energy curve becomes narrower and the spring constant increases as square root of total energy.

The existence of a global minimum in the potential energy surface has long been known, the local minima are termed “particle-hole structures". It has been accepted that the cluster has icosahedron structure so long as it is inside the global minimum and attains liquid-phase the moment it comes out of this well. Our results do not agree with this view, in fact the depth of this global minimum is found to be just about \( 3.2 \times 10^{-14} \text{ erg} \), whereas it requires about \( 15.6 \times 10^{-14} \text{ erg} \) of energy to take the cluster to the coexistence phase.

At temperatures below \( T_s \), since all the 12 surface atoms on the icosahedron execute coupled oscillations, the reduced mass \( m \) of the normal mode is given by

\[
\frac{1}{m} = \sum_{i=1}^{12} \frac{1}{M_i} = \frac{12}{M}
\]

or

\[
\frac{M}{m} = 12
\]
in agreement with the results of the simulation (Fig 3(d)). The transition temperature $T_s$ corresponds to the situation wherein the motion of only one of the 12 surface atoms on the average becomes incoherent with the motion of the rest. This is reflected in the reduced mass, which at this temperature drops to one eleventh of the mass of the Ar atom, as can be seen from the figure. With the increase in temperature the reduced mass drops drastically and reaches an asymptotic value of 1. Since $(1/m)$ is a measure of the coherence of motion of the particles in the normal mode, the value of the ratio $(M/m)$ being 1.0 amounts to the constituents executing independent incoherent motion just as in the case of a viscous fluid. This transition to a liquid-like behavior at $T_s$, which is far below the melting temperature is a phenomenon new to the clusters, and is absent in case of bulk solids. Hence it is expected that it will be more difficult to observe this phenomenon with the increase in cluster size.

As has already been mentioned we expect the transition at $T_s$ to manifest itself in other observables as well. Here are the other results:

- The rms bond length fluctuation (not shown here) starts from a value of zero and shows a quick rise in value till the kinetic temperature $T_s$, and only then settles down to the slow linear rise with temperature, as shown in Ref. [3].
- Fig 6 is the plot of velocity autocorrelation – the solid curve just below $T_s$ and the dotted one just above. This once again demonstrates the qualitative change in the dynamics of the cluster at $T_s$, there being a complete reversal of velocities at temperatures below $T_s$, and only a partial reversal the moment the temperature goes above $T_s$. A Fourier transform would show similar features as that of single particle radial coordinates.
- The average radius of the cluster has a linear temperature dependence all along the solid-phase; nevertheless shows a sudden though small increase in the value at $T_s$.
- The maximal Lyapunov exponent (MLE) is close to zero at $T < T_s$ and shows a sudden rise at $T_s$ (Fig 7).

It is quite satisfying that an independent dynamical quantity, MLE, gives yet another illustration of the effect we have observed. It was shown earlier that MLE data indicates solid-liquid phase change by a sharp jump in its value [3], and now we see that the same dynamical quantity once again shows a steep rise – starting from a value of zero this time – to mark the presence of another transition. The MLE data implies that the system is integrable at $T < T_s$, and becomes chaotic above $T_s$. In other words, the onset of single particle excitations drives the system into ergodicity.

Finally a few words about the method of giving excitation to the cluster. It is essential that the cluster is set into a pure mode oscillation to observe all the effects we have presented. In particular, if one starts from a cluster equilibrated at $T > T_s$ and cools it below $T_s$, it is unlikely that such a system would show the features as distinctly as is presented here. The reason being that the single particle excitations present in the system above $T_s$ continue to be present while the system is cooled and get proportionately amplified by the radial displacement of the particles meant to provide the monopole excitation. If started from low temperature side, this problem would not arise until the temperature $T_s$, as the system continues to perform monopole oscillations without losing strength. However, beyond $T_s$, there is no way one could get rid of the presence of single particle excitations to begin with, so we take recourse to the option of taking statistical average over many independent runs, with the hope that the effects of the independent particle motions are averaged out, leaving behind the systematics. The essence of the analysis is the presence of a kinetic temperature $T_s$, below which the cluster can sustain pure monopole oscillation for ever and above which the particles suffer a loss of memory, invariably.

**IV. SUMMARY**

In this article we have presented some results of the detailed analysis of monopole excitation in $Ar_{13}$ cluster. Ensemble average of time evolution of the monopole excitation is found to fit very well with a damped harmonic oscillator. The parameters of the equivalent oscillator show a marked change in behavior at kinetic temperature $T_s = 7.0^\circ K$ which marks the existence of yet another characteristic temperature in the system. Below $T_s$ the cluster remains confined within the global minimum of the potential energy surface, due to which the normal mode oscillations remain undamped. The velocity autocorrelation function shows a complete bounce-back revealing that there is absolutely no loss of coherence. The system moves out of the global minimum well at $T_s$, above which the local minima pockets in the potential energy surface act as single particle excitation channels in damping the collective modes. A continuous, flat power spectrum of the radial motions of the particles at low frequency components confirms the onset of these single particle excitations. The system is naturally driven into ergodicity at this point due to the availability of local energy minima pockets.

This work paves way for many interesting questions. First of all, one may like to investigate to see whether or not the presence of $T_s$ is a generic feature of small clusters, irrespective of the interaction potential used- including the ab initio dynamics. We obviously do not expect this phenomenon to occur in large clusters. A closed shell structure plays a vital role in this phenomenon, so we might still see it in 55 atom icosahedron cluster. One could also analyze higher angular momentum com-
ponent in the same fashion.

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**Figure captions:**

**Figure [1]**. Time evolution of the monopole oscillation at three different temperatures: (a)at 5°K, (b)at 20°K and (c)at 30.5°K. Average radius of the cluster as a function of time simply projects out the time evolution of the monopole mode. A monopole excitation is given at $t=0$. Oscillations are simple harmonic and are undamped for $T < T_s (\approx 8.4°K)$.

**Figure [2]**. Potential energy of the cluster as a function of its radius. The dotted curve is a perfect parabola.

**Figure [3]**. Behavior of the parameters of the equivalent 1-d damped harmonic oscillator as a function of total energy of the cluster. The data are completely in the solid-like phase of the cluster (the last four points are in the coexistence region). (a)Damping coefficient. There is no damping for $T < T_s$ and a linear rise in damping coefficient with the total energy for $T < T_s$. (b)Time period of oscillation. Shows a change of slope at $T = T_s$. (c)The “spring constant” $k$. It is a constant for $T < T_s$ but shows a dramatic $\sqrt{E_{tot}}$ rise for $T > T_s$. (d)The ratio of the mass of the Ar atom to the “reduced mass” of the oscillator. The value of the ratio drops rapidly at $T = T_s$ and reaches an asymptotic value of 1.0 at high temperatures. The solid line is only a guide to the eye.

**Figure [4]**. Power spectrum of the time sequence of the radial coordinates of the particles. Power spectra of the surface atoms are added together and plotted. $P(\omega)$ is in arbitrary units and total energy is in units of $1.0 \times 10^{-14}$ ergs/atom. The onset of continuous spectrum coincides with the damping of the monopole excitation.

**Figure [5]**. Potential energy curves of the cluster at various temperatures (°K): (a) 1.40 (b) 2.85 (c) 4.25 (d) 5.64 (e) 7.04 (f) 8.40 (g) 9.81 (h) 11.24 (i) 12.68 (j) 14.10 (k) 15.48. For $T > T_s$, the cluster deviates away from the curve soon after one period.

**Figure [6]**. The normalised autocorrelation function. The solid curve is at temperature just below $T_s$ and the dotted one just above $T_s$. The curves are averages over 500 independent runs.

**Figure [7]**. The maximal Lyapunov exponent. The system is integrable at temperatures below $T_s$ and chaos sets in at $T_s$. (Data from V. Mehra and R. Ramaswamy, private communications).