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# Probing the liquid-gas like phase transition in the mixed Ar$_x$Ne$_{13-x}$ clusters?

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**Abstract.** The solid-liquid and the liquid-gas like phase transitions have been identified in the case of "caged" mixed atomic Ar$_x$Ne$_{13-x}$ clusters with $0 \leq x \leq 13$. An artificial repulsive potential of spherical symmetry prevents the loss of atoms from the cluster. The thermodynamical functions have been calculated for different values of the radius of the sphere. The sensitivity of heat capacity to the radius of the sphere allows to assign the nature of the phase transitions observed. Around the energy associated to the liquid-gas transition, molecular dynamics simulations have been performed in order to analyse the evaporation dynamics of the corresponding free clusters. The analysis of $MD$ trajectories shows that the occurrence of "boiling" is related to the tendency of the cluster to undergo multiple evaporation events. The kinetic energy release in this regime is analysed in an attempt to check its capability to probe the phase transitions.

**PACS.** 36.40.Ei Phase transition in clusters – 36.40.Qv Stability and fragmentation of clusters

## 1 Introduction

The study of the equivalent of bulk phase transitions in free clusters has been a subject of intense activity the last decade [1–3]. The solid-like to liquid-like "melting" transition has been well characterized thanks to clear dynamical criteria, which are reflected in the caloric curve. This has allowed the experimental observation of "melting" in Na$_n^+$ clusters [4,5]. Although some experimental results have characterized liquid/gas phase transition [6], the characterization of liquid-like to gas "boiling" transition is not as simple. Specific problems arise from the essential lack of constant pressure or constant volume gas phase in evaporating clusters.

We present here a simulation procedure which allows to unambiguously discriminate the signature of such a liquid-gas like transition in the plot of heat capacity *versus* temperature $C_v(T)$. It is applied to the case of mixed rare gas clusters Ar$_x$Ne$_{13-x}$, in which the change of $x$ between 0 and 13 allows to explore various situations for the occurrence of "melting" and "boiling" in these small clusters. The choice of this particular system has been governed by a recent simulation of the evaporation process in mixed atomic clusters performed by Parneix and Bréchignac [7] and also by the theoretical work of Frantz [8] on the thermodynamical properties of the Ar$_x$Ne$_{13-x}$ cluster. Previous works have shown that the evolution of the kinetic energy release with the clus-

ter internal energy is able to reflect the occurrence of the "melting" transition [9,10]. Can it similarly be used as a probe of the liquid-gas like phase transition in appropriate experiments?

## 2 Theoretical approach

The thermodynamical properties of the mixed Ar$_x$Ne$_{13-x}$ atomic clusters have been obtained from microcanonical molecular dynamics (MD) simulations. The microcanonical density of states has been calculated by applying the multiple histogram method to the potential energy distributions that are obtained during MD simulations, for several values of the internal energy [11]. For each cluster, a grid of 50 or more internal energies was considered. At a given energy, the potential energy was calculated every 1 fs along a trajectory whose the duration was long enough (15 ns) in order to avoid problems related to quasi-ergodicity which can appear in such mixed clusters. The potential energy surface has been built as a sum of pairwise atom-atom Lennard-Jones (LJ) potentials [$\sigma_{\mathrm{Ar-Ar}} = 3.405$ Å, $\sigma_{\mathrm{Ne-Ne}} = 2.749$ Å, $\epsilon_{\mathrm{Ar-Ar}} = 83.26$ cm$^{-1}$ and $\epsilon_{\mathrm{Ne-Ne}} = 24.74$ cm$^{-1}$]. The LJ potential parameters for the Ar-Ne interaction were deduced from:

$$\sigma_{\mathrm{Ar-Ne}} = (\sigma_{\mathrm{Ar-Ar}} + \sigma_{\mathrm{Ne-Ne}})/2$$

$$\epsilon_{\mathrm{Ar-Ne}} = \sqrt{\epsilon_{\mathrm{Ar-Ar}}\epsilon_{\mathrm{Ne-Ne}}}. \tag{1}$$

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To obtain potential energy distributions for large vibrational energy, the cluster was constrained to evolve inside an artificial sphere [12] the center of which coincides with the center-of-mass. The density of states has been calculated for 4 different values of the radius $R_s$ of the sphere ($R_s = 20, 25, 30$ and $35$ Bohr) for each cluster. The sensitivity of the thermodynamical functions with respect to $R_s$ is directly correlated to the gaseous character of the cluster. Indeed if these functions are dependent on $R_s$ at a given temperature, it means that some atoms start to separate from the cluster and can be viewed partially as a gas at this particular temperature. Such an approach allows to easily discriminate between solid-liquid and liquid-gas like phase transitions. It has to be noted that the influence of the container size on the shape of the caloric curve of a 13-atom Morse cluster has been already analysed by Moseler and Nordiek [13].

As the liquid-gas transition in a free cluster is intrinsically linked to the evaporation process, we have been interested to follow the microcanonical dynamics of such mixed clusters when they are free and vibrationally excited in the energy range where the "caged" clusters exhibit the liquid-gas like phase transition. Classical $MD$ trajectories were propagated using a Verlet algorithm with an integration time step equal to 1 fs. The dissociation process of the non-rotating parent cluster was followed during 4 ns and a set of 2000 trajectories was considered to obtain confident statistical results. Along a given trajectory, structural informations were extracted from a geometrical criterion. The rate constant for the loss of atoms could thus be easily obtained. The energetics of the sequential evaporation processes has been analysed by calculating the kinetic energy of the released atoms in the center-of-mass frame.

## 3 Results and discussion

First of all, before analysing results of the thermodynamics and dynamics of these mixed clusters, it is important to note that our analysis of the topology of the potential energy surface has confirmed the results obtained by Frantz [8] for the first lowest isomers. For any composition of the $Ar_xNe_{13-x}$ mixed clusters, the minimum energy configuration has an icosahedral structure.

We analyse now the results obtained for the heat capacity $C_v$ of the $Ar_xNe_{13-x}$ clusters as a function of $R_s$. It should be noted at this point that only classical simulations have been performed in order to fully compare our results with those of Frantz [8]. As demonstrated by Neirotti et al. [14], a quantum description of neon clusters has shown that the classical description overestimates the melting temperature by about 10%.

In Figure 1, $C_v$ is plotted for 4 different 13-atom clusters ($x = 0, 3, 10$ and $13$) and for two values of $R_s$. In the case of neat clusters, $Ar_{13}$ and $Ne_{13}$, these results are found in excellent agreement with the work of Frantz [8]. Obviously, as LJ potentials have been used, the simple scaling law: $T(Ne_{13})/T(Ar_{13}) = \epsilon_{Ne-Ne}/\epsilon_{Ar-Ar}$ holds for the pure $Ar_{13}$ and $Ne_{13}$ clusters. Consequently, the phase transition is observed at lower temperature in the case
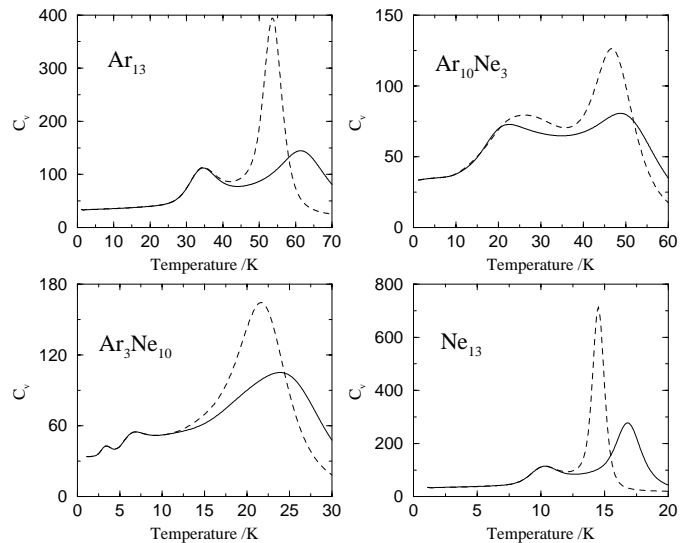


**Fig. 1.** Heat capacity $C_v$ of the $Ar_xNe_{13-x}$ cluster (with $x = 0$, 3, 10 and 13) as a function of temperature. Solid line: $R_s = 25$ Bohr, dashed line: $R_s = 35$ Bohr.

of $Ne_{13}$ ($T = 10.1$ K) in comparison to the case of $Ar_{13}$ ($T = 34.1$ K). Although the liquid phase is stable on a wide domain of temperature (about 15 K) for $Ar_{13}$, the stability of the liquid phase is strongly reduced for the $Ne_{13}$ cluster (only 5 K).

For $Ar_3Ne_{10}$, Frantz [8] found a single peak at $T = 6.8$ K ($C_v = 58.5$) for temperatures lower than 20 K. In the present work, we find two peaks, the first one appears at $T_1 = 3.4$ K ($C_v = 43$) and the second one at $T_2 = 6.9$ K ($C_v = 54.8$). These two features in the $C_v(T)$ curve do not depend on $R_s$ and can be assigned to solid-liquid like transitions. The first and the second transitions correspond respectively to the melting of the Ne sub-cluster (premelting) and the melting of the whole cluster. Around $T = 20$ K, an other maximum in the $C_v(T)$ curve appears, which is now clearly dependent on the radius of the sphere. This can be viewed as a liquid/gas like transition. This last feature had not been clearly seen in the work of Frantz: only some increase of the $C_v(T)$ curve between $T = 10$ and $20$ K could be seen.

For the $Ar_{10}Ne_3$ cluster, Frantz [8] found one peak at $T = 22.0$ K ($C_v = 73.9$) although we find 2 peaks that both depend on the radius of the sphere. The first peak appears at $T = 22-26$ K ($C_v = 73-79$) and the second peak at $T = 49-46$ K ($C_v = 81-126$). The general trend observed for the phase transition involving a gas phase in these Ar/Ne mixed clusters is a slight increase of the temperature where $C_v$ peaks when $R_s$ decreases. On the other hand, the height of the peak strongly increases when the container radius increases, which is in agreement with the work of Moseler and Nordiek [13].

The first transition around $T = 22$ K corresponds to the onset of the gas phase for the Ne atoms. Indeed for lower temperature (around 5 K), the analysis of the isomerization dynamics has shown that the $Ne_3$ sub-cluster can be seen as a liquid-like sub-cluster. The absence of
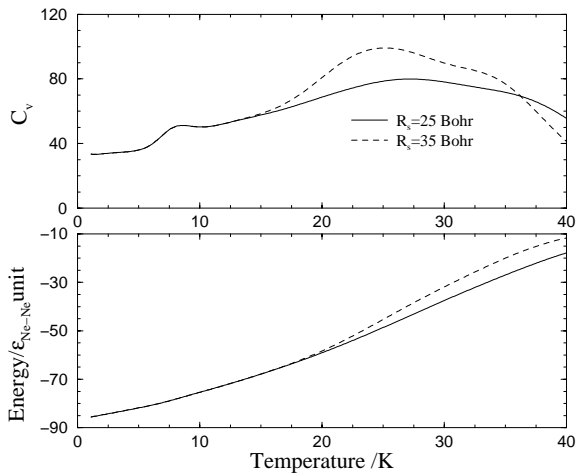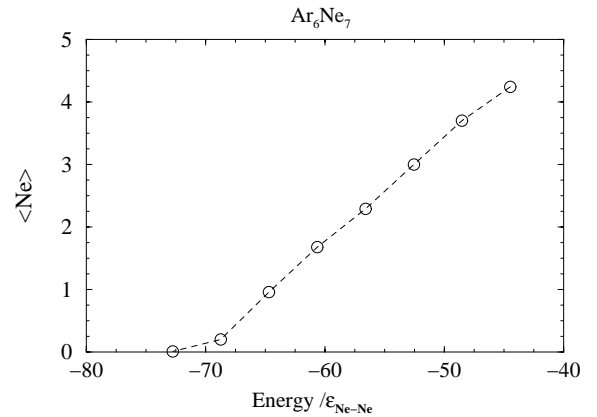
**Fig. 2.** Top panel: heat capacity $C_v$ of the $Ar_6Ne_7$ cluster as a function of temperature for two values of $R_s$. Bottom panel: energy of the $Ar_6Ne_7$ cluster as a function of temperature with the same values of $R_s$.



**Fig. 3.** Mean number of evaporated Ne atoms after 4 ns as a function of the internal energy in the parent cluster.

thermodynamical characterization in the caloric curve is certainly due to the very small energy difference of the isomeric structures explored by the system in this temperature domain. Thus the phase transition at $T = 22$ K can be viewed as a liquid/gas transition of the $Ne_3$ sub-cluster. The second transition at higher temperature (around $T = 43$ K) is linked to the onset of Ar atoms in the gas phase. This peak should thus correspond to a liquid-gas like transition for the $Ar_{10}$ sub-system. This seems to indicate that the solid-liquid transition for the $Ar_{10}$ sub-system and the liquid-gas one for the $Ne_3$ sub-system occurs at around the same temperature, *i.e.* $T = 22$ K. This can effectively be seen in Figure 1 because the increase of the $C_v$ value between 10 K and approximatively 17 K is not sensitive to a change of $R_s$.

Finally the heat capacity curve $C_v(T)$ of the $Ar_6Ne_7$ cluster is plotted in Figure 2, together with the caloric curve $E(T)$ (the caloric curve is only shown to explicit the energy-temperature correspondence which will be useful for the following discussion on the multi-evaporation dynamics from MD trajectories). The two phase transitions can be clearly characterized in this case: the solid-liquid like one occurs at $T = 8.5$ K and the liquid-gas like one occurs near 25 K ($E \approx -45\epsilon_{Ne-Ne}$). The liquid phase appears to be stable between 8 and 15 K ($-78\epsilon_{Ne-Ne} < E < -68\epsilon_{Ne-Ne}$). It has to be noted that the shape of the second broad peak can be seen as a superposition of two peaks: the first one appears at around 25 K and the second one at around 35 K. These peaks correspond to the liquid-gas transitions of the $Ne_7$ and $Ar_6$ sub-clusters respectively.

Up to now, we have calculated the heat capacity of atomic clusters for which atoms are restricted in a given volume. Earlier works have shown that the solid-liquid like transition in free clusters could be characterized from the analysis of the mean kinetic energy release in the evaporation process [7,9,10]. In the case of the liquid-gas transition, the evaporation process is intrinsically linked to the appearance of the gas phase. Thus, it is important to explore if the same physical observable could also be used to characterize such a phase transition in a free cluster, as it could be the basis of future experiments. We have done that in the second part of this work, by simulating through classical dynamics the sequential evaporation of the $Ar_6Ne_7$ *free* cluster. In this way we correlate its thermodynamical properties with the evaporation processes.

At a given energy, a large set of initial conditions (2000 trajectories) has been considered. The classical dynamics of the cluster was propagated as a function of time and multiple evaporation events were analysed during 4 ns. The mean number of evaporated Ne atoms after 4 ns is plotted in Figure 3 as a function of the internal energy in the parent cluster. For energies smaller than approximatively $-65.0\epsilon_{Ne-Ne}$ ($T = 16.8$ K), only evaporation of a single Ne atom takes place. This particular energy corresponds approximately to the onset of the bump in the $C_v(T)$ curve. For higher energies, a regime of sequential evaporations takes place and a change in the dynamical behavior of the free cluster with respect to the evaporation process occurs. Indeed, above this particular energy, the evolution of the mean number of evaporated Ne atoms becomes fairly linear as a function of the vibrational energy in the cluster, and it can be found that the inverse of the slope of the straight line is equal to the mean binding energy (characterizing the separation of a Ne atom from the cluster), *i.e.* $E_0 = 6.3\epsilon_{Ne-Ne}$. This plot is essentially similar to those which have been experimentally obtained by Bréchignac *et al.* [15] for $K_n^+$ clusters. In each evaporation event the internal energy left in the sub-cluster is reduced by $E_0$ until it reaches the value characteristic of the unimolecular decay for a given time window (4 ns here). The time evolution of the mean number of evaporated Ne atoms is plotted in Figure 4 for three values of the energy chosen in the range where the effect of the gas phase in the $C_v(T)$ curves is maximum (note that the caloric curves in the bottom panel of Fig. 2 may be used for the correspondence between temperature and energy). No Ar atom evaporation has been observed in these trajectories. The number ($\approx 3$) of evaporated Ne atoms is typically close to half the total number (= 6) of Ne atoms

Ar$_6$Ne$_7$
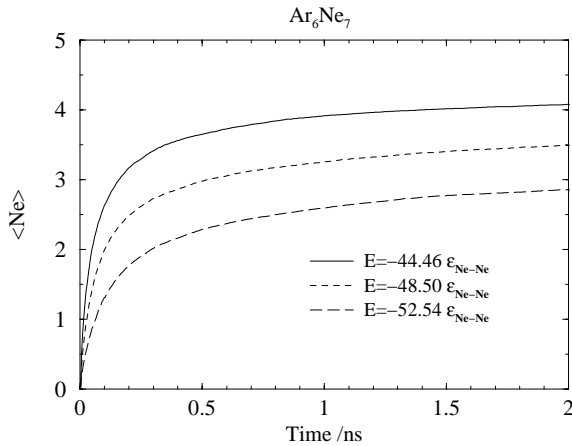


**Fig. 4.** Mean number of evaporated Ne atoms as a function of time for 3 different energies.

Ar$_6$Ne$_7$



**Fig. 5.** Mean kinetic energy release of the Ne atoms as a function of the initial energy in the parent Ar$_6$Ne$_7$ cluster.

in the parent cluster. The first evaporation event appears in a very short time (less than 100 ps). The average time it takes for the next atom to be ejected is a few times larger than for the previous one during the cascade, but gets much larger for the last step.

We come now to the analysis of the kinetic energy release. Along the dissociative trajectories, we have also calculated the kinetic energy of the evaporated Ne atoms in the center-of-mass frame, and evaluated their mean value $\langle \epsilon \rangle$. The results are plotted in Figure 5 as a function of the initial energy in the parent cluster. In the same plot the predictions of the Engelking model and of the RRK approach are also shown. Previous studies aimed at showing that the solid-to-liquid like phase transition in the product cluster was reflected in the behavior of the kinetic energy release [7,9,10] have been reported, which involved analysis of the dynamics in an energy domain where a single evaporation occurs. It was found that $\langle \epsilon \rangle$ first follows the Engelking line at low energy above threshold, then deviates with a reduced slope, but remains between Engelking and RRK predictions. In the present case for which several Ne atoms are consecutively ejected, we observe that the values of $\langle \epsilon \rangle$ go below the RRK line, exhibiting (most probably) a kind of accident near $E = -60\epsilon_{\mathrm{Ne-Ne}}$. Interpretation of this behavior is delicate for several reasons. First of all, as the successive Ne atoms are ejected, the size of the remaining cluster is progressively reduced, and there may be a size dependence of the transition temperature. At the same time the cluster undergoes evaporative cooling and there is no reason for the evolution of the cluster temperature to match that due to the size dependence. On the other hand the kinetic energy going into the recoil of the sub-cluster (expected to be small due to the mass of the 6 argon atoms) has not been considered. Finally the $C_v(T)$ curves show that the solid/liquid and the liquid/gas phase transitions are not fully separated. However, considering that the stability of the liquid phase extends up to $-70\epsilon_{\mathrm{Ne-Ne}}$ and that the "anomalous"
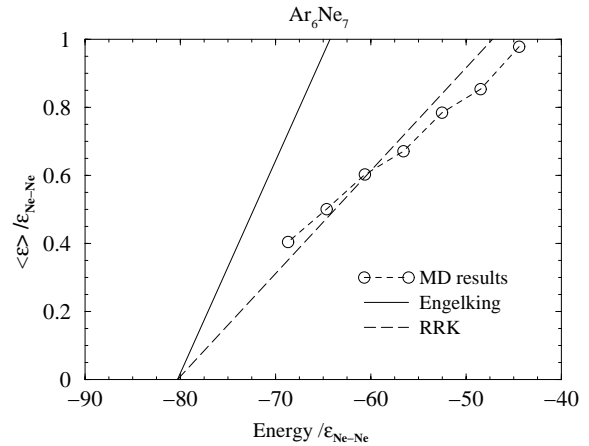
behavior of $\langle \epsilon \rangle$ occurs above $-60\epsilon_{\mathrm{Ne-Ne}}$, we think that these results are a good indication that the kinetic energy release is sensitive to the occurrence of the liquid-gas like phase transition. It will be interesting to confirm this conclusion by more extensive calculations. As a final remark the capability of using $\langle \epsilon \rangle$ as an experimental probe is probably very dependent on the specific properties of the chosen system. Interestingly an experimental study of the translational kinetic energy release in successive evaporation events from Sr$_n^+$ has just been published [16].

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