Orbital-free molecular dynamics simulations of melting in Na₈ and Na₂₀: melting in steps.

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The melting-like transitions of Na₈ and Na₂₀ are investigated by ab initio constant energy molecular dynamics simulations, using a variant of the Car-Parrinello method which employs an explicit electronic kinetic energy functional of the density, thus avoiding the use of one-particle orbitals. Several melting indicators are evaluated in order to determine the nature of the various transitions, and compared with other simulations. Both Na₈ and Na₂₀ melt over a wide temperature range. For Na₈, a transition is observed to begin at ∼110 K, between a rigid phase and a phase involving isomerizations between the different permutational isomers of the ground state structure. The “liquid” phase is completely established at ∼220 K. For Na₂₀, two transitions are observed: the first, at ∼110 K, is associated with isomerization transitions between those permutational isomers of the ground state structure which are obtained by interchanging the positions of the surface-like atoms; the second, at ∼160 K, involves a structural transition from the ground state isomer to a new set of isomers with the surface molten. The cluster is completely “liquid” at ∼220 K.

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I. INTRODUCTION

Recent experimental advances have made possible the study of the melting phenomenon in metal clusters. Martin measured the melting temperatures Tm of large sodium clusters by observing the disappearance of the atomic shell structure with increasing temperature, and determined the dependence of Tm on cluster size. More recently, Haberland and coworkers determined the heat capacity and melting temperature of free sodium clusters containing from 50 to 200 atoms by studying the temperature dependence of the photofragmentation mass spectrum. Electron diffraction patterns of trapped clusters may be useful for distinguishing different stages in the melting process.

For many years, computer simulations have been the main guide to an understanding of melting-like transitions in small finite systems. Molecular dynamics (MD) calculations based on phenomenological potentials have been used to study the solid-like to liquid-like phase transitions in rare gas, alkali halide, and metal clusters. The unification of density functional theory (DFT) and molecular dynamics formulated by Car and Parrinello allows for an explicit treatment of the electronic degrees of freedom. Such ab initio molecular dynamics calculations have been performed by Röthlisberger and Andreoni for Naₙ (n=2–20) microclusters at several temperatures, and very recently, Rytkönen et al. have presented results for the melting of Na₄₀. These studies make use of the Kohn-Sham (KS) version of DFT, but large computational savings can be obtained if an orbital-free method, based solely in the electronic density n(⃗r), is used instead. Madden and coworkers have demonstrated the value of orbital-free methods for the study of bulk metallic systems. Shah et al. and Govind et al. have applied the approach to study the structures of small metal and covalent clusters. Blaise et al. have performed orbital-free calculations of some static and dynamic properties of sodium clusters with sizes up to 274 atoms, and Vichare and Kanhere have studied the melting of Al₁₃. In this paper we describe the study of solid-like to liquid-like phase transitions of Na₈ and Na₂₀ microclusters using constant energy orbital-free molecular dynamics simulations.

In the next section we present the theoretical details of the method. The results are presented and discussed in section III. Section IV summarizes the main conclusions from this study.

II. THEORY

A. Car-Parrinello Molecular Dynamics with Orbital-Free Energy Density Functionals

The orbital-free molecular dynamics method is a Car-Parrinello total energy scheme which uses an explicit kinetic-energy functional of the electron density, and has the valence electron density as the dynamic variable. Now we describe the main features of the energy functional. The orbital-free calculation scheme has been described at length in Refs. 14 22 so we will give just a brief description here.

The ground state energy is a functional of the valence electron density n(⃗r), and a function of the ion positions Rn (n = 1, 2, … N), with the following form (Hartree atomic units will be used through the paper):

\[ E[n, ⃗R] = T_s[n] + \frac{1}{2} \int \int \frac{n(⃗r)n(⃗r')}{|⃗r - ⃗r'|} d⃗r d⃗r' + \int n(⃗r)V_{ext}(⃗r)d⃗r + E_{XC}[n] + E_{ion-ion}[⃗R], \]  

(1)
where the different terms are: the kinetic energy functional for a noninteracting inhomogeneous electron gas, the classical electron-electron interaction energy, the interaction energy between the valence electrons and the external potential provided by the instantaneous ionic configuration, the exchange-correlation energy functional, and the classical Coulomb repulsion between positive ions. Three key approximations in the energy functional involve \( T[n], \ E_{XC}[n], \) and the electron-ion interaction. The electronic kinetic energy functional used in this work corresponds to the gradient expansion around the homogeneous limit through second order.

\[
T_s[n] = T^{TF}[n] + \lambda T^W[n],
\]

(2)

where the first term is the Thomas-Fermi approximation,

\[
T^{TF}[n] = \frac{3}{10} \left( 3 \pi^2 \right)^{2/3} \int \frac{n(\vec{r})^{5/3}}{\rho(\vec{r})} d\vec{r},
\]

(3)

and \( T^W \) (the Weizsäcker term) is the lowest-order gradient correction to \( T^{TF} \)

\[
T^W[n] = \frac{1}{8} \int \Omega \frac{\nabla n(\vec{r})^2}{n(\vec{r})} d\vec{r},
\]

(4)

taking some account of inhomogeneities in the electron density. Different values have been proposed in the literature for the constant \( \lambda \). The value adopted here, \( \lambda = \frac{1}{4} \), corresponds to the limit of a slowly varying \( n(\vec{r}) \) and has a number of desirable properties.

The local density approximation (LDA) is used for the exchange-correlation functional. We use the Perdew and Zunger parametrization of the electron gas results of Ceperley and Alder. The external field contains the electron-ion interaction, \( V_{ext}(\vec{r}) = \sum_i v(\vec{r} - \vec{R}_i) \), where we take for \( v \) the local pseudopotential of Fiolhais et al. which reproduces very well the properties of bulk sodium and has shown good transferability to sodium clusters. Although some progress has been made recently for including the effects of nonlocality in the pseudopotential in orbital-free schemes, these effects are expected to be small for sodium. The ion-ion interactions are treated using the usual Ewald method.

For a given set of ion positions \( \{ \vec{R}_i \} \), that is for a given external potential \( V_{ext} \), the ground state is obtained from the variational principle:

\[
\frac{\delta}{\delta n(\vec{r})} \left( E[n, \vec{R}] - \mu \int n(\vec{r}) d\vec{r} \right) = 0,
\]

(5)

where \( \mu \) is the electron chemical potential chosen to give the desired number of electrons \( N_e \). We have found it convenient to work in terms of a single effective orbital \( \psi(\vec{r}) \) rather than \( n(\vec{r}) \), where

\[
n(\vec{r}) = |\psi(\vec{r})|^2,
\]

(6)

and to vary \( \psi \) rather than \( n \). This has the advantage of maintaining \( n \) nonnegative if \( \psi \) is real. The cluster of interest is placed in a unit cell of a superlattice of volume \( \Omega \), and the set of plane waves periodic in the superlattice is used to expand \( \psi \). The expansion coefficients \( C_{G} \) (where \( \vec{G} \) is a reciprocal lattice vector of the superlattice) are considered as generalized coordinates of a set of fictitious classical particles each of mass \( m \). The Lagrangian for the whole system of electrons and ions is

\[
L(C, \dot{C}, \vec{R}) = \sum_\vec{G} \frac{1}{2} m | \dot{C}_{\vec{G}} |^2 + \sum_{i=1}^N \frac{1}{2} M_i \dot{R}_i^2 - E[n, \vec{R}],
\]

(7)

and the constraint to be considered is

\[
\int d\vec{R} n(\vec{r}) = \Omega \sum_\vec{G} C_{\vec{G}}^* C_{\vec{G}} = N_e,
\]

(8)

where \( N_e \) is the number of electrons per supercell, and \( M_i \) is the mass of the \( i \)th ion.

The explicit functional of the density we have used for the electronic energy is much superior in computational speed and memory requirements to the conventional KS orbital approach, allowing the treatment of larger systems for longer simulation times. Those computational savings can also be used to perform simulations for a larger number of different temperatures, allowing better identification of transition temperatures. The present restriction to local pseudopotentials being not a serious matter for sodium, the most important difference between the orbital-free and KS approaches is the treatment of the independent particle kinetic energy. \( T_s[n] \) is computed exactly in the KS approach, whereas the orbital-free approach draws on approximate density functionals based on a few known limiting cases. Our choice for \( T_s[n] \) with \( \lambda = \frac{1}{4} \) is appropriate for a slowly varying density, whereas \( T_s[n] = T^W[n] \) is believed to give the limit of rapidly varying density. Linear response theory gives \( T_s[n] \) when the variations in electron density about the mean density are small, and some functionals attempt to combine these different limits. Our functional would seem to be appropriate for the smooth pseudoelectron density of a Na cluster, but since little is known about the range of validity of the various functionals, we have performed test calculations on some simple Na systems and compared the results with those of other approaches.

Table I presents results for equilibrium bond lengths and binding energies per atom for the Na dimer and an octahedral Na_{6} cluster calculated within three different approximations. All the calculations use the LDA for exchange and correlation, but differ in their treatment of the electron-ion interaction and the electron kinetic energy. The results of KS all-electron calculations are given along with those of KS calculations which use our choice of local pseudopotential, and comparison of these results tests the pseudopotential of Fiolhais. We see that the use of the pseudopotential overestimates the bond lengths by 2–3 percent, but the increased bond length in Na_{6} over that in the dimer is reproduced. The binding energies, with respect to spin-polarized free atoms, are also in reasonable agreement. The third set of calculations uses the same pseudopotential and the orbital-free kinetic energy functional. Comparison of the second and third sets of results tests the orbital-free \( T_s[n] \). The approximate \( T_s[n] \) overestimates the bond
length of the dimer by 4% but the results for Na$_6$ are in very good agreement. The binding energies (with respect to spin-polarized free atoms) are overestimated but the increased binding in Na$_6$ is reproduced. The agreement between orbital-free and KS calculations for the ground state structure and the energetic ordering of the low lying isomers of Na$_8$ which is detailed in section III, and the reasonably accurate interatomic distances we obtain, provide additional support to our approach for studying the melting-like transitions of Na clusters. This agreement suggests that the orbital-free approach gives a potential energy surface with the correct features for interatomic separations near the equilibrium distances, and this is enough to determine the details of the melting transition. The discrepancies in the binding energies are less important for the dynamics provided we do not consider evaporation events.

The main approximation of an orbital-free method is the neglect of quantum shell effects. Specifically, the method gives energies that vary smoothly as a function of cluster size, without showing the oscillations associated with electronic shell closures. On the other hand ionic shell effects due to the geometrical arrangement of ions are present. The experimental results of Haberland et al. seem to indicate that both effects are relevant to the melting of sodium clusters, although their relative importance is not yet known. Nevertheless, the good performance of the orbital-free method mentioned above, together with the good agreement between the melting dynamics of Na$_8$ and Na$_{20}$ predicted by our model and that obtained from the KS calculations of Röthlisberger and Andreoni (see section III), support the orbital-free method as a valuable starting point. Extended Thomas-Fermi models usually give equilibrium structures that are quite spherical, and do not have the deformations found in small clusters of size intermediate between two electronic shell closures. By restricting our study to closed-shell clusters, which are known to be quite spherical, we minimize the probability of finding wrong zero-temperature isomers.

The calculations for Na$_8$ and Na$_{20}$ have been performed using a cubic supercell of edge 63.58 a.u. with a 64 $\times$ 64 $\times$ 64 mesh and a plane wave energy cut-off for $\psi$ of 10 Rydbergs. The test calculations performed for Na$_2$ and Na$_{16}$ showed that with this cutoff, equilibrium bond lengths are converged within 0.01 Å and binding energies within 0.002 eV, which we consider sufficient for our purposes. The equations of motion were integrated using the Verlet algorithm for both the electrons and the ions with a time step ranging from $\Delta t = 1 \times 10^{-15}$ sec. for the simulations performed at the lowest temperatures, to $\Delta t = 0.85 \times 10^{-15}$ sec. for those performed at the highest ones. The fictitious electron mass ranged from 1.15 $\times$ 10$^8$ a.u. for the shorter time steps, to 1.75 $\times$ 10$^8$ a.u. for the longest. These choices resulted in a conservation of the total energy better than 0.1%. The first step in the simulation was the determination of the low temperature ground state structures (GS) of Na$_8$ and Na$_{20}$ using the dynamical simulated annealing technique by heating the clusters to 600 K and then slowly cooling them. Next, several molecular dynamics simulation runs at different energies were performed in order to obtain the caloric curve. The initial relative positions of the atoms in the cluster for the first run were taken by slightly deforming the equilibrium geometry. The final configuration for each run served as the starting geometry for the next run at a different energy. The initial velocities for every new run were obtained by scaling the final velocities of the preceding run. The total simulation times were 8 ps for the lowest temperatures for which the clusters are very rigid (T < 60 K), and 20−22 ps for temperatures larger than 60 K. Longer runs of 50−60 ps were performed for specific temperatures. The first 2 ps of each run were not included in the various time averages. After the velocity scaling performed at the beginning of each new trajectory, the internal cluster temperature (see next section) was always an oscillating function of time with a decreasing envelope during approximately the first 2 ps of the simulation, after which equilibration is achieved. The reason for such a short equilibration time seems to be that the velocity scaling never increased the cluster temperature in more than 20 K, at least in the transition region. Equilibration was also checked by comparing the caloric curve and the specific heat curve (see following section). The locations of the specific heat peaks were in coincidence with the slope changes in the caloric curve, which is a sign of correct equilibration.

**B. Analysis of the Molecular Dynamics**

In order to characterize the thermal behavior of the clusters as a function of increasing internal energy, and the solid-like to liquid-like transitions, we monitor: (a) global quantities that are calculated from time averages over a whole trajectory at a given energy; (b) time dependent quantities that are calculated from averages over well separated time origins along a single trajectory.

First, we define the “internal temperature” $T$ of the cluster as

$$T = \frac{2}{3N-6} <E_{\text{kin}}>_t,$$  

where $k_B$ is the Boltzman constant, $E_{\text{kin}}$ is the ionic kinetic energy, and $<\cdot>_t$ represents the time average over a whole trajectory. All the global quantities described below will be plotted as functions of this internal temperature.

The degree of mobility of atoms - a sort of index of rigidity of the cluster - can be characterized by the relative root-mean-square (rms) bond length fluctuation $\delta$, defined by

$$\delta = \frac{2}{N(N-1)} \sum_{i<j} \left( <R_{ij}^2>_t - <R_{ij}>_t^2 \right)^{1/2} <R_{ij}>_t,$$  

where $R_{ij} = |\vec{R}_i - \vec{R}_j|$. This quantity changes abruptly at isomerization or melting transitions, and for the bulk, a sharp increase in $\delta$ gives the Lindemann criterion for melting.

As another indicator of the melting-like transition we calculate the specific heat defined by
The mean square displacement, $R(t)$, defined by
$\begin{align*}
R(t) = \frac{1}{Nn_t} \sum_{n=1}^{n_t} \sum_{i=1}^{N} [\mathbf{r}_i(t_0, t) - \mathbf{r}_i(t_0)]^2,
\end{align*}$
(12)

where $n_t$ is the number of time origins ($t_0$) considered along a trajectory, is a time-dependent quantity that also serves as a measure of the rigidity of the cluster. The slope of $R(t)$ for large $t$ is proportional to the diffusion coefficient. Thus, a flat $R(t)$ curve is indicative of a solid-like character with the constituent atoms vibrating about their equilibrium positions; when diffusive motion of the atoms starts, the slope of $R(t)$ becomes positive. We shall see in the next section that it is useful to separate the atoms of Na$_{20}$ into two subsets of $N_s=2$ “core” and $N_s=18$ “surface” atoms. We can then define partial $R(t)$’s, restricted to core ($R_c(t)$) and surface ($R_s(t)$) atoms, respectively, and the differences between these will be indicators of different degrees of rigidity in the two groups of atoms for a given internal cluster temperature.

Recently, the “atomic equivalence indexes”
$\begin{align*}
\sigma_i(t) = \sum_j | \mathbf{r}_i(t) - \mathbf{r}_j(t) |,
\end{align*}$
(13)

which contain very detailed structural information, have been introduced. The degeneracies in $\sigma_i(t)$ are due to the specific symmetry of the isomer under consideration, and the variations in the time evolution of $\sigma_i(t)$ allow for a detailed examination of the melting mechanism.

III. RESULTS AND DISCUSSION

A. Na$_8$

The calculated GS structure of Na$_8$ is shown in Fig. 1(a). It is a dodecahedron ($D_{3d}$ symmetry), a result which is in agreement with the KS-LDA calculations. The stellated tetrahedron ($T_d$ symmetry) is the GS structure in all-electron SCF-CI calculations, although the energy difference between the isomers is very small indeed. It is noteworthy that the orbital-free-LDA calculations lead to the same energetic ordering of isomers (and also to similar energy differences between isomers) as the KS-LDA.

Figure 2 shows the results for the calculated global quantities $C$ (fig. 2(a)) and $\delta$ (fig. 2(b)) as functions of internal cluster temperature, and the time evolution of the mean square displacement, $R(t)$, for three representative temperatures (fig. 2(c)). The specific heat shows a peak centered at a temperature $T_{m_1} \approx 110$ K, which correlates with the temperature region in which $\delta$ experiences an almost stepwise increase, and marks the onset of the melting transition. This is followed by a steady increase of $\delta(T)$, until a leveling off occurs at $T_{m_2} \approx 220$ K, indicating that the liquid state is fully developed. The melting transition of Na$_8$ from a rigid form, in which the atoms merely oscillate about the equilibrium configuration, to a “fluid” form characterized by uncorrelated motion of the atoms, is spread over a range of temperatures $T=T_{m_1}-T_{m_2}$. Fig. 2(c) shows that for a temperature $T=34$ K, $R(t)$ has zero slope at long times, reflecting the oscillatory motion of the atoms. At $T=111$ K the diffusive motion of the atoms in the cluster begins, resulting in a positive slope which increases with temperature.

The quantities shown in Fig. 2 indicate that Na$_8$ undergoes a melting-like transition in the temperature range 110-220 K. In order to get a better understanding of the melting, the short-time averages of the “atomic equivalence indexes”, $< \sigma_i(t) >_{sta}$, have been calculated and the cluster evolution during the trajectories has been followed visually using computer graphics. The $< \sigma_i(t) >_{sta}$ curves are presented in Fig. 3 for three representative values of $T$. At the lowest temperature $T=34$ K (fig. 3(a)) there are two distinct groups of nearly equivalent atoms in the $D_{2d}$ GS structure: four atoms with coordination 4, and four with coordination 5. The curve crossings within a group of nearly equivalent atoms display oscillations of the atoms around their equilibrium positions, but there are no crossings of curves from different groups. At a higher temperature $T=78$ K (not shown), but still lower than $T_{m_1}$, the oscillations have larger amplitudes, but the two types of atoms do not yet mix. At $T=111$ K, which marks the beginning of the step in $\delta$, interchanges between atoms with different coordination begin, but are still scarce. The dynamics over 60 ps (fig. 3b) illustrates that the atoms in the cluster can still be separated into two sets with 4 and 5 coordination during most of the simulation time, there being just four interchange events. The movies show that the onset of melting in Na$_8$ is associated with isomerization transitions between the different permutational isomers of the $D_{2d}$ GS structure, which come with significant distortions of the cluster from the GS geometry. The transitions become more frequent and the distortions increasingly severe with increasing temperature giving rise to the steady increase observed in $\delta$, until at $T \approx 220$ K (fig. 3c) and higher temperatures the ground state isomer is seen only occasionally in the movies. Snapshots of the trajectories at these temperatures show that the cluster sometimes adopts elongated configurations with Na or Na$_2$ subunits joined to the cluster by a single bond. This is reflected in figure 3c by the larger values of $< \sigma_i >_{sta}$. All the atoms diffuse across the cluster volume so that the different $< \sigma_i >_{sta}$ curves are all mixed and the “liquid” phase is fully established. While we have not observed evaporation of fragments at this temperature (at least within 20 picoseconds), the trajectories suggest that Na or Na$_2$ subunits may evaporate at higher temperatures from the ends of a “cigar-like” cluster. However, our energy functional may not be reliable for such events.

Detailed simulations of the melting-like transition of
Na₈ have been performed by Bulgac and coworkers using constant-temperature MD simulations with a phenomenological interatomic potential, and by Poteau, Spiegelmann and Labastie using Monte Carlo (MC) simulations with a tight-binding Hamiltonian to describe the electronic system; recently, Calvo and Spiegelmann (CS) have performed also MC simulations employing an empirical potential. Aside from the differences between MC and MD methods, the main difference between those calculations and our work is the interatomic potential. That employed by Bulgac has free parameters fitted to properties of bulk sodium, and while the tight-binding calculations of PSL deal explicitly with the electronic system, our overlap integrals were fitted to ab initio results for the sodium dimer and tetramer. Since we consider the electronic degrees of freedom explicitly and find the forces on ions through the Hellman-Feynman theorem, the present calculations should be considered an advance over empirical or semiempirical methods. Bulgac predicts a transition temperature of about 100 K from a solid-like to a glassy phase of the cluster in which the atoms stay close to their equilibrium positions for relatively long periods with occasional atom interchanges. The tight binding treatment gives a melting-like transition at ~200 K, whereas CS give an approximate value of 80–100 K for T_m, more similar to the values of Bulgac and ourselves. Bulgac also predicts a boiling transition at 900 K but we do not expect our approach to be reliable at such high temperatures where evaporation is a factor. However, the “solid-to-glassy” transition is similar to the behaviour we have found at the onset of melting at ~110–130 K, where the atoms remain in their equilibrium positions for relatively long periods, only swapping positions from time to time with a frequency which increases with temperature. For temperatures above 220 K where the value of δ increases smoothly with T, we find that the atoms are very mobile and the cluster can be considered liquid.

Röthlisberger and Andreoni (RA) have performed finite temperature simulations for Na₈ using the ab initio Car-Parrinello MD method with pseudopotentials for the electron–ion interaction and the LDA for the exchange-correlation energy functional. Thus, the main difference from the present calculations is our use of an approximate electronic kinetic-energy functional. They deduced from a simulation at T=240K a value of δ still less than the 0.1 value which is taken to indicate the onset of melting according to the Lindeman criterion. The full KS method gives a more accurate description of the electronic structure than our orbital-free approach, but we feel that the apparently contradictory results for δ can be reconciled. The total simulation time of RA for Na₈ was t=6 ps, corresponding to about ~10 vibrational periods for sodium. Our calculated value of δ at T=230 K, if we average over the first 6 ps of the simulation is 0.098, in agreement with the full KS results. Due to the nature of the melting transition in Na₈, involving a repeated swapping of the atom positions, 6 ps may not be long enough to obtain a converged value for δ. In fact, we chose the total simulation time of t=20 ps after recognizing that preliminary simulations performed with t=8 ps did not yield a converged result for δ. With t=20 ps, further increases only lead to minor changes in δ, at least when the cluster is clearly liquid-like. Nevertheless, we can not guarantee that fully converged values of δ have been obtained in the transition region.

B. Na₂₀

We find the ground state structure of Na₂₀ to be a single-capped double icosahedron (fig. 1(b)), again in good agreement with the KS-LDA calculations of RA, who found this structure as an isomer almost degenerate with their GS structure. The variation of the specific heat with temperature, which is shown in fig. 4(a), displays two maxima around 110 K and 170 K. The relative rms bond length fluctuation is given in fig. 4(b). For small temperatures the curve δ(T) has a small positive slope reflecting the thermal expansion of the solid-like cluster, but at higher temperatures there are two abrupt increases at T_{m₁} ≈ 110K and T_{m₂} ≈ 160K, and a levelling off at T_{m₃} ≈ 220K, indicating that the melting of Na₂₀ occurs in several stages over the range of temperatures T_{m₁}–T_{m₃}. The two peaks in the specific heat are in rough correspondence with the two steps in δ(T), but the levelling off in δ does not seem to be associated with any pronounced feature in the specific heat. The mean square displacement for the particles in the cluster is plotted as a function of time in Fig. 4(c) for four different temperatures. The curve corresponding to T=55 K shows a clear levelling off after a small initial rise, reflecting the solid-like nature of the cluster at that temperature. For T = 109 K and higher temperatures, R(t) shows a linear increase implying a finite diffusion coefficient and the emergence of liquid-like properties.

In order to investigate the nature of the transitions we divide the 20 atoms of the cluster into two subsets: the two internal “core” atoms of the ground state structure, and the 18 peripheral “surface” atoms. The partial R_c(t) and R_s(t) for the temperature at which the first step in δ begins are shown in fig. 5. The R_c(t) curve shows the typical diffusive behavior of liquid-like phases, whereas R_s(t), after the initial rise, oscillates with an average slope near zero. Differences in the mobility of the surface and core atoms are clearly indicated, the surface atoms undergoing diffusive motion at a lower temperature (T_{m₁} ≈ 110 K) than the core atoms. Snapshots at regular time intervals for the runs between T=T_{m₁} and T=T_{m₃} show the two central atoms oscillating around their initial positions, while surface atoms interchange their positions in the cluster without destroying the double-icosahedral symmetry. The picture is similar to the onset of melting in Na₈. The swapping of surface atom positions causes significant distortions of the double-icosahedral geometry, but after each interchange the cluster returns to the ground state structure. Therefore, we identify the transition at T_{m₁} ≈ 110 K as an isomerization-like transition in which the cluster begins to visit those permutational isomers of the ground state which involve the interchange of positions between surface atoms. In our view, this fluctuating phase of
Na$_20$ can not be associated with surface melting, because the double-icosahedral symmetry persists and the surface disorder is temporary.

The next stage is seen in snapshots from the runs performed at temperatures between $T_{m2}$ and $T_{m3}$. The second transition involves the motion of one of the central atoms out to a peripheral position, the double-icosahedral symmetry is lost, and most of the snapshots show a structure with a single central atom (see an example in fig. 1c). The central core atom exchanges with one of the 19 surface atoms at a slower rate than the interchanges between surface atoms, and so converged values of $\delta$ require longer simulations (50–60 ps). The 19 surface atoms are very mobile and the structure of the cluster fluctuates a great deal. The exploration at these temperatures of a new structure leads to the second peak in the specific heat, and we identify $T_{m3} \approx 160K$ with an isomerization-like transition in which new (19+1) structures are explored. As the temperature is increased from $T_{m2}$ to $T_{m3}$, the interchanges of a core atom and a surface atom become more frequent, leading to the steady increase in $\delta$, and a cluster surface which has melted in the sense that the structure is now very fluid, and the surface disorder is large.

In fig. 6 we show the short-time averaged $\sigma_i(t)$ for several representative temperatures. At $T=32$ K (fig. 6(a)) the cluster is solid-like and $<\sigma_i(t)>_{sta}$ serves to identify groups of "nearly" equivalent atoms. Starting from the bottom, these are: the two central atoms, the five atoms of the central pentagon, the 10 atoms in the upper and lower pentagons, and finally the two axial atoms and the capping atom. At $T=72$ K (not shown) the different groups can still be recognized, but fig. 6(b) shows that at 137 K there is a group of two central atoms, but the rest are no longer distinguishable. At $T=163$ K (fig. 6(c)) we see that the cluster has a single central atom for most of the simulation time (56 ps), the 19 atom surface is melted, and occasionally an interchange between the central atom and one of the surface atoms occurs. At higher temperatures the interchange rate increases.

Simulations of the melting-like transitions of Na$_20$ have also been performed by Bulgac and CS. As for Na$_8$, the ground state structure of Na$_20$ predicted by PSL is different from that of KS-LDA calculations, although it may also be divided in "core" and "surface" atoms. They also predict surface melting at a temperature of $T_s=190$ K, and a melting temperature of $T_m=300$ K. The discrepancies between these quantities and the corresponding quantities we obtain should again be attributed to the differences in the interatomic interactions. Once more our detailed description of the onset of the melting transition and the full establishment of a liquid-like phase are in better agreement with the results of Ju and Bulgac. CS predict the same ground state structure found in this work for Na$_20$. Their calculations also predict a two-step melting mechanism, with $T_{m1} \approx 100$ K and $T_{m2} \approx 200$ K. RA have performed two short ab initio KS-LDA molecular dynamics simulations of Na$_20$. At $T=350$ K, the lowest temperature they considered, they found that the mobility of the atoms in Na$_20$ is already quite high within the 3 ps of their simulation, but such a short simulation time led to a value of $\delta \approx 0.1$. If we average over the first 3 ps of our run performed at $T=324$ K, we obtain $\delta=0.15$, in contrast with the converged value $\delta=0.29$. A simulation time of 3 ps, corresponding to $\sim 5$ vibrational periods, does not allow for enough jumps to obtain a converged value of $\delta$.

The melting-like transitions in both Na$_8$ and Na$_20$ are found to be spread over a broad temperature range, and in the case of Na$_20$ we have identified a stepwise melting mechanism. Recently, Rey et al. in a study of the melting-like transition of a 13 particle cluster associated the occurrence of melting in steps to the softness of the repulsive core interaction rather than any many-body character of the interactions. For the softer potentials considered, two abrupt increases of $\delta$ were found: the first corresponding to the onset of isomerization transitions involving only surface atoms, and the second to complete melting. The stepwise melting mechanism was less clearly defined for the harder interatomic potentials. We have used our approximate functional in a series of static calculations for Na$_2$ at several interatomic distances in order to construct the binding energy curve, and have compared to the interatomic potentials considered by Rey et al. We find that the repulsive part of the binding energy curve obtained using the GEPS is softer than their softest interatomic potential, and so the stepwise melting we have found is consistent with their findings.

Jellinek et al. have demonstrated for Li$_8$ that the temperature at which exploration of low-lying isomers begins is estimated more accurately in MC than in MD simulations. This is because the J-walk MC sampling of the configurational space is not hindered by the presence of energy barriers. If the energy in a microcanonical MD simulation is just slightly higher than the energy needed to surmount a barrier, exceedingly long simulation times will be needed in order to achieve an efficient sampling. Thus, the real temperatures at which the onset of melting occurs may be slightly lower than those determined in our "short" simulations. The location of the specific heat peaks, however, should be more accurate, because these occur for a temperature higher than that corresponding to the onset of melting, where the energy is already large enough to easily surmount the barriers. In summary, the width of the specific heat peaks may be underestimated in MD simulations.

We have studied the melting of clusters upon heating, but some differences might be observed if the clusters were cooled from a high temperature simulation. The details of the melting transition, such as the number and location of the steps in the $\delta$ curve, depend on the specific isomer from which the dynamics is started, and thus may differ from those obtained through a cooling procedure. This is worthy of further study.

IV. SUMMARY

We have applied an ab initio, density-based, molecular dynamics method to the study of melting transitions in finite atomic systems. The computational effort which is required is modest in comparison with that required
by the traditional CP-MD technique based on the use of the KS one-particle orbitals. The computational effort to update the electronic system scales linearly with the system size N, in contrast to the N^3 scaling of orbital-based methods. This saving allows the method to be used in the study of large clusters, and also for performing extensive MD simulations in much the same way as the usual procedures involving phenomenological potentials.

The method has been applied here to study the melting-like transitions in Na_8 and Na_20 clusters. Na_8 melts in a broad temperature range from 110–220 K. The transition at \( T \approx 100 \) K is from a rigid cluster in which the atoms are vibrating around their fixed equilibrium positions to a phase in which the different permutational isomers of the GS structure are visited. For higher temperatures the cluster distorts more and more from the GS structure and can be considered fully liquid at \( T \approx 220 \) K. Na_20 undergoes several successive transformations with increasing temperature, and the melting transition is also spread over a wide temperature range. In the first transition at \( T_{m_1} \approx 110 \) K surface atoms swap positions without destroying the underlying icosahedral symmetry. At \( T_{m_2} \approx 160 \) K, one of the inner atoms becomes surface-like, the other remains in its central position for most of the simulation time, and the surface of the cluster has melted. Swapping between the central atom and one of the surface atoms is more frequent upon heating, until at \( T_{m_3} \approx 220 \) K the value of \( \delta \) saturates. As expected, the temperatures of the melting intervals are lower than the experimental melting temperature of bulk Na (\( T_{m}^{bulk} = 371 \) K). Preliminary calculations to simulate the melting of bulk Na give a melting temperature in very good agreement with experiment, which gives us confidence in the quantitative results we obtained for the melting temperatures of the clusters.

Our findings suggest that it is important to study several melting indicators when disentangling the details of melting-like transitions. If a stepwise mechanism is present, the location of the different steps are clearly indicated in \( \delta \). The variation of the diffusion coefficient with temperature obtained from the \( R(t) \) curves is also useful in this respect. The “atomic equivalence indices” are valuable for understanding the nature of the structural transitions associated with each step in \( \delta \). We conclude that the specific heat alone may not be a sensitive indicator of all the “structural” information contained in the \( \delta \) curve. Specifically, the final levelling off in \( \delta \), marking the end of the transition region and the temperature at which the liquid-like phase is completely established, does not have any appreciable feature associated with it in the specific heat.

Comparison with other theoretical calculations performed at different levels of theory suggests that our results agree with the \textit{ab initio} KS-LDA calculations of Röthlisberger and Andreoni if the same simulation times are considered. This agreement is strong validation of our model. However, we found it necessary to lengthen the simulation times to at least 20 ps (and sometimes to 50–60 ps) in order to obtain converged global quantities. With the improved statistics, our results for Na_8 and Na_20 are in better agreement with those of Bulgac and coworkers and of Calvo and Spiegelmann than with those of Poteau \textit{et al.}

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**Captions of Figures and Tables.**

Figure 1 Geometries of the ground state isomers of (a) Na_8 and (b) Na_20; (c) is an example of the (19+1) structure that appears after the second phase transition in Na_20 (see text for details).

Figure 2 (a) Specific heat and (b) relative rms bond length fluctuation of Na_8 as functions of the internal temperature. The deviation around the mean temperature is smaller than the size of the circles. (c) Mean square displacement as a function of time for three representative values of \( T \).

Figure 3 Short-time averaged atomic equivalence indices as functions of time for Na_8 at \( T= 34 \) K (a), 111 K (b), 220 K (c). Note the different simulation times for different temperatures.

Figure 4 (a) Specific heat and (b) relative rms bond length fluctuation of Na_20 as functions of the internal temperature. The deviation around the mean temperature is smaller than the size of the circles. (c) Mean square displacement as a function of time for four representative values of \( T \).

Figure 5 Partial mean square displacements for core \( (R_c(t)) \) and surface \( (R_s(t)) \) atoms in Na_20, for \( T=109 \) K.

Figure 6 Short-time averaged atomic equivalence indices as functions of time for Na_20 at \( T=32 \) K (a), 137 K (b), 156 K (c). Note the different simulation times for each temperature.

**Table 1** Bond length and binding energy per atom for Na_2 and Na_6, calculated by Perdew and coworkers using Kohn-Sham all electron (KSAE), and Kohn-Sham pseudopotential (KSPPS) methods, compared to our results of the gradient expansion functional of eq. (13) with the same pseudopotential (GEPS).

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| Bond Length (a.u.) | Binding Energy (eV) |
|---------------------|---------------------|
| Na$_2$            | KSAE  | KSPS | GEPS |
|                    | 5.64  | 5.77 | 5.99 |
|                    | 6.51  | 6.87 | 6.81 |
|                    | 0.44  | 0.46 | 0.55 |
| Na$_4$            | 0.63  | 0.53 | 0.69 |
| Na$_6$            | 0.63  | 0.53 | 0.69 |

**TABLE I.**
Specific Heat ($k_B$) vs. T(K)

- The specific heat increases significantly around 200 K, reaching a peak.
- There are fluctuations in the specific heat around this peak temperature.
- The specific heat decreases as the temperature increases further.

**Data Points**
- At 2.5 K, specific heat is approximately 2.5 $k_B$.
- At 3.0 K, specific heat is approximately 3.0 $k_B$.
- At 3.5 K, specific heat is approximately 3.5 $k_B$.
- At 4.0 K, specific heat is approximately 4.0 $k_B$.
- At 4.5 K, specific heat is approximately 4.5 $k_B$.
Specific Heat ($k_B$)

| T(K) | Specific Heat ($k_B$) |
|------|-----------------------|
| 2.8  |                       |
| 3.3  |                       |
| 3.8  |                       |
| 4.3  |                       |

![Graph showing specific heat vs. temperature (T(K))](image-url)
\[ \langle \sigma \rangle_{\text{sta}} \text{ (a.u.)} \]

\[ 0 \quad 5000 \quad 10000 \quad 15000 \]

\[ -300 \quad -250 \quad -200 \quad -150 \quad -100 \quad -50 \quad 0 \quad 50 \quad 100 \quad 150 \]

\[ t \text{ (fs)} \]
