Geometric Size Effects in the Melting of Sodium Clusters

F. Calvo and F. Spiegelmann

*Laboratoire Collisions, Agrégats, Réactivité (UMR 5589, CNRS) and Laboratoire de Physique Quantique
(UMR 5626, CNRS), IRSAMC, Université Paul Sabatier, 118 Route de Narbonne, F-31062 Toulouse Cedex, France*

Melting of neutral and singly charged sodium clusters Na_n and Na_n^+ is investigated for several sizes ($8 \leq n \leq 139$) using both Monte Carlo and molecular dynamics simulations with an empirical many-body potential. Up to $n = 75$, we find that the solid-liquid-like phase change is a multistage process initiated by "premelting." The equilibrium structure is found to play an important role in the thermodynamics, in particular when such premelting features are induced by diffusion processes at the surface. However, larger sizes $n \geq 93$ exhibit preferentially a single process similar to bulk melting. [S0031-9007(99)08675-5]

The thermodynamics of finite systems is an important part of the clusters' chemical physics. Understanding how phase changes occur far below the bulk limit has motivated a lot of theoretical work on various species [1–10] as well as experimental investigations [11–13]. Size affects the thermal properties of nanoscale materials in several ways. A first-order phase transition, such as the solid-liquid transition, becomes "rounded," spread over a finite temperature range. As the size decreases from the bulk, the melting point and the latent heat of fusion also decrease, and the transition region itself widens. When the size gets low enough, it has been observed both in simulations [14] and in experiments [13] that the melting point could undergo strong, nonmonotonic variations with size, even if only a single atom is added or removed. In the case of argon clusters, these differences have been attributed to the underlying geometrical "magic numbers" governing the extra stability of icosahedral clusters [14]. In the case of metal clusters, electronic shell effects are also expected to play a significant role [13].

The experimental approaches to phase changes in free clusters, as developed, e.g., in the group of Haberland [12], are macroscopic in that they try to access thermodynamical indicators such as the heat capacity or the melting temperature. Theoretically, the most relevant numerical approaches, although they can also provide the thermodynamic functions, generally attempt to relate the solidlike or liquidlike character of a cluster to its microscopic dynamics, especially to the details of its potential-energy surface (PES) [4,10,15,16]. Solid and liquid phases cannot, however, always be identified unambiguously with a single peak in $C(T)$. Indeed, for small clusters, the concept of phases and phase changes is often related to isomerization phenomena, and many theoretical studies seem to show an intricate, multimodal behavior of $C(T)$. Bumps in $C(T)$ may be due to preliminary isomerization processes [16], partial melting [17,18], orientational disorder in molecular clusters [4], or to more complex features such as multiple funnels on a PES landscape [10]. In some cases, such as ionic [16,19] or metallic [5,20,21] clusters, the solidlike-liquidlike transition may involve intermediate phases fluctuating between several isomers. These phases cannot be fully described with the macroscopic tool $C(T)$, and they require other conventional microscopic indicators: the Lindemann parameter δ, the diffusion constant D, the principal momenta of inertia, the Liapunov exponents, etc., not all of them having the same level of significance. For instance, Liapunov exponents cannot make a clear distinction between the solid and liquid states in Lennard-Jones (LJ) clusters smaller than 38 atoms [22], whereas they are able to detect premelting in small alkali-halide clusters [16]. Even the Lindemann criterion, which states that matter melts when the thermal fluctuations of the interatomic distance gets over 10%–15%, is not fulfilled in the same way, depending on the microscopic details of the model.

Another problem is structure. During a heating simulation, one may wish to follow the deformation of a cluster. This requires a fairly good knowledge of the global minimum, as starting from a higher-energy isomer is likely to induce erroneous variations of the thermal properties, especially for pathological systems such as LJ_{38} [10]. Knowing the equilibrium structure even appears mandatory when studying size effects in the small sizes regime. Unfortunately, performing a realistic global optimization search is exponentially difficult ("*NP* hard") as size increases, so it is still necessary to choose potential-energy functions that can be efficiently computed while remaining meaningful.

In this Letter, we present a theoretical study of the thermodynamical behavior of neutral and singly charged sodium clusters in the size range $8 \leq n \leq 139$ atoms, emphasizing the microscopic changes underlying the macroscopic phase transitions. In order to carry out extensive global optimizations and simulations, we have adopted an empirical many-body potential instead of time-consuming quantal Hamiltonians. For the neutral clusters, the form and parameters ($\varepsilon_0 = 1.5955$ eV, $\zeta_0 = 0.29113$ eV, $p = 10.13$, $q = 1.30$, and $r_0 = 6.99$ bohr) were those recently given by Li *et al.* [23]. These authors have also used this model for charged clusters, assuming a uniform partial charge on each nucleus, the charge interacting through

Coulombic and polarization forces. However, this latter model overestimates the repulsive contributions, especially for small sizes, due to the use of a discrete charge distribution instead of the real continuous one. Because of this, the resulting ionic clusters are less bound than the neutrals, which is contrary to the known experimental data [24]. Therefore we have slightly modified the potential used for ions, setting $\varepsilon_0^+ = \gamma \varepsilon_0$ and $\zeta_0^+(n) = \gamma \zeta_0 (1 + \alpha/n^\beta)$ with $\alpha = 6.6$, $\beta = 1.27$, and $\gamma = 1.0055$. To search for the lowest-energy structures, we have used the "basin-hopping" global optimization technique of Wales and Doye [25]. This method has been one of the most successful (along with genetic algorithms) in finding the global minima of clusters. In order to cover a variety of situations (magic or nonmagic clusters either for neutrals or ions), we have chosen the set of sizes $n = 8, 20, 40, 59, 75, 93$, and 139. The smaller ones have been previously studied by several authors using different potential surfaces [5,18,26,27]. The thermodynamical analysis was performed with standard isothermal Monte Carlo (MC) simulations improved by the q-jumping method of Andricioaei and Straub [28] to reduce nonergodicity problems (with a Tsallis parameter $q = 3/2$ and a probability to attempt a jump move $P_q = 0.1$), and with the multiple histogram method [2]. The Lindemann index δ was also calculated from these MC simulations. Complementary to this, we conducted some isoergic molecular dynamics (MD) simulations to investigate atomic mobility. As shown by López and Jellinek [29], fragmentation may occur at high temperatures. To avoid extra spurious peaks in the heat capacity, we enclosed the clusters inside a spherical repulsive wall [2]. Finite-temperature simulations were carried out with 40 temperatures between 10 and 400 K, each trajectory involving 5×10^5 MC cycles whose 2×10^5 first cycles were discarded for thermalization. The full range of energies obtained from these MC runs was discretized into 1500 bins forming the histograms. Such conditions were checked to ensure stable caloric curves for all sizes.

The lowest-energy structures of all of the neutral and charged clusters are found to be the same. They are reported in Fig. 1 as well as the heat capacities per nucleus $C(T)/nk_B$. It must be noticed that, for Na$_8$ and Na$_{20}$, the global minima in our model potential are close, but not identical, to the structures found in more realistic tight-binding [30] or density-functional theory [31] studies. Although we can never be sure that we have fully explored the PES of the cluster, we are rather confident we have not missed any important structure, at least up to 59 atoms. Binding energies of neutrals [$V_0(n)/n = 0.59, 0.73, 0.82, 0.86, 0.88, 0.90$, and 0.93 eV for increasing n] and adiabatic ionization potentials calculated as $\mathrm{IP}(n) = V_0^+(n) - V_0(n) + \mathrm{IP}(\mathrm{Na})$ (4.01, 3.81, 3.70, 3.61, 3.54, 3.47, and 3.26 eV) are in reasonable agreement with experimental data [24]. Nevertheless, we are aware that electronic shell effects are not included in the present simple model.

Both Na$_8$ and Na$_8^+$ change from a rigid, solidlike form to a disordered phase below 100 K, the heat capacity exhibiting a continuous sharp rise near 80 K for Na$_8$, near 100 K for Na$_8^+$. This jump can also be seen in the results of Bulgac and Kusnezov [5], and is also present in recent time-dependent Thomas-Fermi models [27]. The Lindemann index, not plotted here, strongly rises above 15% at the onset of isomerization. Quenching along MC trajectories shows that, in each case (Na$_8$ or Na$_8^+$), only one single isomer is involved in the disordered phase, in addition to the solid state. This isomer lies 0.04 eV above this state for Na$_8$, 0.06 eV for Na$_8^+$. As the heat capacity nearly reaches its maximal value, two isomers higher in energy ($\Delta E > 0.09$ eV in both cases) can be found.

The equilibrium geometry of Na$_{20}$ and Na$_{20}^+$ is a double icosahedron with a capped atom over the central pentagonal belt of atoms. Heating this structure up to about 80 K makes two new isomers appear, the capped atom merging now into the meridian belt. The heat capacities for both the neutral and charged clusters show a clear jump near this temperature, and the Lindemann parameter also rises sharply above 10%. There, the phase is similar to the fluctuating phase of Sawada and Sugano [20], and disappears near 160 K as the number of accessible isomers increases. Between 140 and 200 K, δ and C continuously rise, C reaches its peak near 210 K, which corresponds to melting. The case of Na$_{40}$ and Na$_{40}^+$ is similar. These clusters go through a fluctuating state made of a dozen isomers
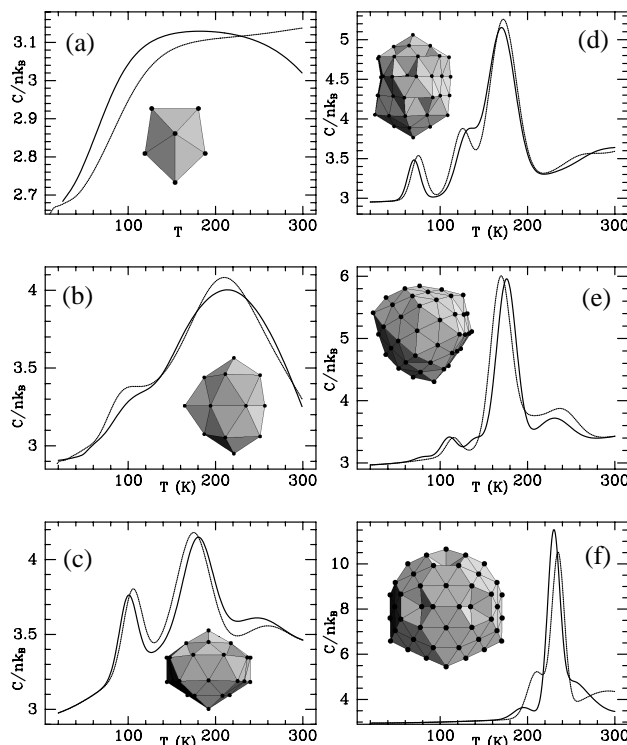

FIG. 1. Canonical heat capacities $C(T)$ from Monte Carlo simulations; for Na$_n$ (solid lines) and Na$_n^+$ (dashed lines). The lowest-energy structures are also plotted. (a) $n = 8$; (b) $n = 20$; (c) $n = 40$; (d) $n = 75$; (e) $n = 93$; (f) $n = 139$.

when the temperatures comes to 100 K. C exhibits a rather narrow peak, although δ only gets slightly over 7%–8%. Above 100 K, the increase of δ with T is stronger, but still continuous. Finally, the heat capacity exhibits a larger and broader peak near 180 K, whereas the Lindemann parameter reaches 15%. The number of isomers visited on the PES is also very large.

We now come to the largest sizes studied here, $n = 59$, 75, 93, and 139. The $n = 59$ case is illustrated with more details in Fig. 2. As for Na_{40}, the heat capacity in Fig. 2(a) is bimodal, with a preliminary peak smaller than in the former case. In Fig. 2(b) we have plotted the spectrum of isomers obtained from periodic quenching along MC trajectories as a function of temperature. Each of the peaks in $C(T)$ appears to be correlated with a sudden increase in the number of isomers, a signature of an opening of the configuration space. The first peak (near 100 K) leads to a fluctuating state made of about ten topologically different structures, and the second and larger peak (near 160 K) leads to a truly melted state. For both Na_{59} and Na_{59}^{+}, the Lindemann index δ (Fig. 3) displays a continuous increase between 140 and 300 K, besides a common small rise at $T = 100$ K. With the present model potential, Na_{75} and Na_{75}^{+} are not found to be decahedral, but instead are made of a 71-atom compact structure of C_5 symmetry with four surface adatoms. These atoms exhibit an enhanced mobility, responsible for the small peak in $C(T)$ seen near 80 K in Fig. 1(d). We have investigated this phenomenon by estimating in MD simulations the time evolution of the mean square nuclear displacement, whose slope gives the diffusion constant. Figure 4 shows, at the kinetic temperature $T = 100$ K, these functions for the 71-atom subcluster, for the four surface atoms, and for the whole cluster Na_{75}. It is striking that the surface atoms have a much higher mobility than the inner part. No such diffusive motion could be observed in the clusters previously studied. In the range $120 < T < 200$ K, the phase change again shows a bimodal character with a shoulder in $C(T)$ near 140 K.

The 93- and 139-atom clusters show quite a different thermodynamical behavior. The heat capacities are mainly unimodal, a small hump occurring near 100 K for Na_{93} and Na_{93}^{+}, and another one near 210 K for Na_{139} and Na_{139}^{+}. In contrast to the smaller sizes, δ abruptly increases when C reaches its maximal value, near 180 K for $n = 93$ and

near 230 K for $n = 139$. A small rise in δ above 5% is also seen for $n = 93$ at $T = 100$ K. The corresponding fluctuating state is made of a larger number of isomers, but this results from the complexity of the PES at this size. Concerning Na_{139} and Na_{139}^{+}, the small preliminary hump can be interpreted thanks to quenches in terms of the enhanced mobility of the outer atoms. This mobility is due to the eight missing atoms on the surface of the third Mackay layer of the 147-atom icosahedron. However, it remains that, for both sizes, the large peak of the heat capacity can be attributed to global melting.

The results described above show that, below the approximate size of 75 atoms, it is not possible to define unambiguously a solid-liquid transition temperature. Premelting turns out to be a general phenomenon, not limited to the smallest sizes. The fluctuating state, previously observed on transition metal [20] and ionic [9,16] clusters, is seen in all of our model sodium clusters as large as 139 atoms. These effects involve a multistage, hierarchical opening of the configuration space, although the Lindemann index does not necessarily rise suddenly at any time new isomers are visited on the PES. The occurrence of defects (missing or extra atoms) favors the existence of premelting, as first noted by Jellinek and Garzón [21]. Indeed, no premelting can be observed on Na_{19} or Na_{55}. The premelted state can be diffusive (such as in Na_{75}) or not (Na_{20} and Na_{20}^{+}). Interestingly, the tight-binding Hamiltonian of Poteau et al. [18] displays some common features with the present many-body empirical potential. In particular, surface melting of the external atoms was detected for Na_{20} in a range of temperature, with a shoulder in the heat capacity. Considering that most model potentials exhibit various premelting characteristics for some sizes [10,16–18,20,21,27], it is therefore quite possible that similar behaviors may be found in more complicated descriptions.

Clusters containing as much as typically a hundred atoms undergo mainly a global melting similar to bulk melting. In this state, the solid-liquid phase transition is a well-defined process occurring with a narrow and high peak in the heat capacity and a sharp jump in the Lindemann parameter above 15%. Because of premelting,
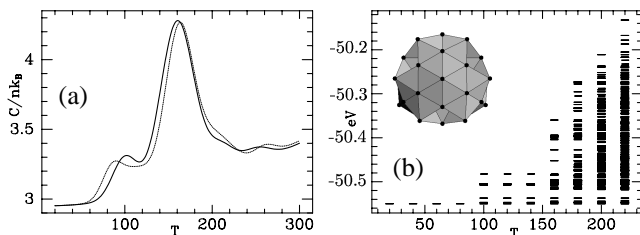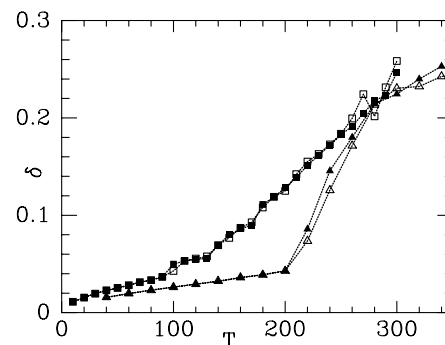

FIG. 2. (a) Heat capacity of Na_{59} and Na_{59}^{+}. (b) Energetic spectra of isomers obtained by regular quenching of Na_{59} during MC simulations.

FIG. 3. Lindemann parameter δ for neutral (solid symbols) and singly charged (open symbols) clusters, either for $n = 59$ (squares) or for $n = 139$ (triangles).
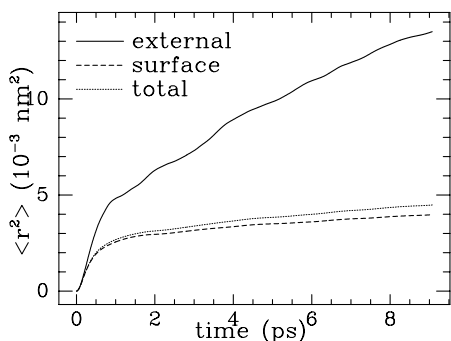
FIG. 4. Mean square nuclear displacement from molecular dynamics simulations of Na_{75} for various parts of the cluster, at the kinetic temperature $T = 100$ K.

it is not obvious to easily assign a value of the solid-liquid transition temperature to each cluster. However, we have seen that the size effects in the thermodynamics of our model sodium clusters were important. Direct quantitative comparison with the experimental results of Schmidt et al. [12,13] should be taken cautiously, since the numerical parameters of the potential are indeed size dependent. For the largest clusters, $n = 93$ and 139, the melting temperatures are quite in agreement with the values given in [13]. However, the observed enhancement of the melting temperature at $n \sim 59$ [32] is not reproduced here, perhaps also due to the neglect of explicit electronic shell effects. Besides size effects, the thermodynamics of sodium clusters also appears to be strongly correlated to the equilibrium structure. The influence of the starting geometry on the dynamical behavior of alkali clusters was recently shown on the Li_8 cluster, using *ab initio* MD simulations [33]. In the larger clusters investigated here, these effects account for, in large part, the geometric size effects responsible for the size variations in the melting temperature. A similar behavior was seen in LJ clusters such as LJ_{38} [10]. Hence a proper investigation at finite temperature requires a preliminary study at $T = 0$ that is a search for the global minimum on the energy surface, especially when unexpected geometries are found (Na_{75}). As a matter of fact, neutrals and ionic clusters have the same equilibrium structure in the present model, which results in very similar calorific curves, nearly identical for $n \geq 20$.

The transition from a microscopic thermal behavior toward a more macroscopic behavior is clearly seen in the results presented here. It would now be very interesting to know if such a transition could be seen in clusters modeled by a less crude potential. In particular, the fact that premelting is a general phenomenon exhibited by realistic quantal models instead of only a simple many-body potential would definitely provide a clue for further experimental studies on the thermodynamics of sodium clusters.

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