

First principles calculations of melting temperatures for free Na clusters

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Density-functional simulations have been performed on Na_{55} , Na_{92} , and Na_{142} clusters in order to understand the experimentally observed melting properties [M. Schmidt *et al.*, *Nature (London)* **393**, 238 (1998)]. The calculated melting temperatures are in excellent agreement with the experimental ones. The calculations reveal a rather subtle interplay between geometric and electronic shell effects, and bring out the fact that the quantum mechanical description of the metallic bonding is crucial for understanding quantitatively the variation in melting temperatures observed experimentally.

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I. INTRODUCTION

There is currently great interest in the statistical mechanics of finite-sized versions of systems that display phase transitions in the infinite-size limit. Recently, atomic clusters have provided an example of a finite system whose caloric curve may be measured, yielding evidence for a “melting” transition over a broad range of temperatures.^{1–4} The clusters involved in these experiments were both small (containing from a few atoms to several hundreds of atoms) and free (not supported on a surface). Now, according to old thermodynamic models,^{5,6} a small particle should melt at a lower temperature than the bulk because of the effect of the surface, with the reduction in melting temperature being roughly proportional to $1/R$, where R is the radius of the particle. This effect has been verified quantitatively for particles of mesoscopic size (upwards of several thousand atoms) supported on a surface.^{6,7} More recently, however, in a series of experiments on free Na clusters in the size range 55 to 350, Haberland and co-workers^{1–3} found that the simple $1/R$ scaling is lost; they did observe a substantial lowering (by about 30%) of the melting temperature compared to bulk sodium, but accompanied by rather large size-dependent fluctuations in the melting temperatures. In spite of considerable theoretical effort,^{8–13} the precise form of the observed fluctuations remains unexplained to date.

As is well known, metallic clusters (such as sodium) possess the same first few “magic” sizes as atomic nuclei, $N=2, 8, 20, \dots$,¹⁴ corresponding to particularly stable systems in which the delocalized valence electrons form closed fermionic shells. Unlike nuclei, however, metallic clusters also contain positively charged ions, which are much heavier than electrons and may be treated classically to a good approximation, leading to the possibility that geometric packing effects may enter into competition with electronic shell effects in determining certain properties. The precise pattern of melting points observed experimentally^{1,3} shows maxima at sizes that correspond neither to magic numbers of valence electrons nor to complete Mackay icosahedra of ions, thereby suggesting a subtle interplay between geometric and quantum electronic effects.^{1,3,8,9}

Reliable simulations to determine the melting properties of clusters are made difficult by a combination of two crucial requirements: the need to compute the ionic potential-energy surface accurately, and the need for high statistics to converge the features in the caloric curve. Good statistics have been obtained using a variety of *parametrized* interatomic potentials,^{9,10} as well as with a treatment of the valence electrons in the extended Thomas-Fermi (ETF)¹¹ and related density-based (DB) approximations.^{12,15} But these attempts have failed to reproduce crucial features of the experimental results, such as the precise pattern of observed melting temperatures. An interesting observation is that in all earlier simulations the melting temperature of Na_{55} has been considerably underestimated (by about 100 K lower than the experimental value).

Clearly, what is required is a more realistic treatment of interacting electrons, in particular, one that incorporates correctly electronic shell effects, which are explicitly excluded from the above-mentioned work using parametrized, ETF, or DB potentials. We have recently demonstrated the power of *ab initio* density-functional theory (DFT), in the Kohn-Sham (KS) formulation, for simulating the melting properties of small Sn (Ref. 16) and Ga (Ref. 17) clusters in the size range 10–20. Unfortunately, the computational expense of the KS approach, combined with the relatively large sizes of the Na data ($N=55$ –350), have so far made it difficult to perform KS simulations with high statistics in the size range of the experiment. Recently, a KS simulation of Na_{55}^+ ,^{8,9} performed with limited statistics, shows encouraging results, with an estimated melting temperature T_m between 300 and 350 K [$T_m(\text{expt}) \approx 290$ K for Na_{55}^+].

In this paper, we report the first *ab initio* KS thermodynamic calculations up to size $N=142$, within the size range of the experiment. We present simulations for Na_N with $N=55, 92$, and 142, each with total sampling times of the order of 2–3 ns. For each size there is a pronounced peak in specific-heat curve, whose position agrees with the experimental finding to better than 8%. This error is also the approximate level of statistical error for the simulation times

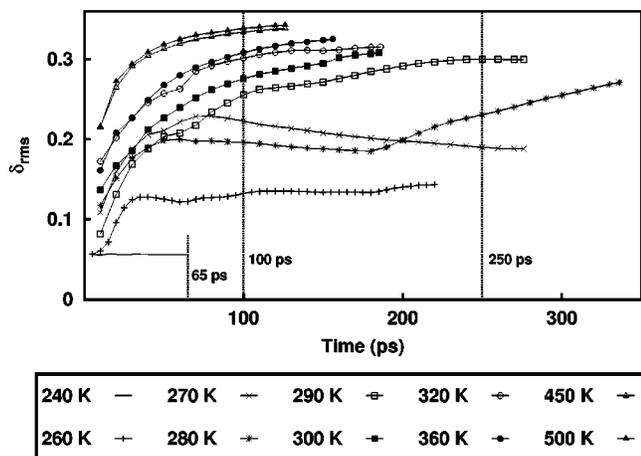


FIG. 1. The root-mean-square bond-length fluctuations δ_{rms} for Na_{55} , as a function of the total time used to compute the average value.

used, suggesting that a KS approach is capable of quantitative predictions of melting temperatures at this level of accuracy or better. Analysis of the structural and dynamical information in these simulations sheds new light on the respective roles of geometric and electronic effects in this intriguing problem.

II. COMPUTATIONAL DETAILS

Our simulations have been carried out using isokinetic Born-Oppenheimer molecular-dynamics with ultrasoft pseudopotentials in the local density approximation, as implemented in the VASP package.¹⁸ We have carried out calculations for up to 17 temperatures for Na_{55} and 14 temperatures for Na_{92} and Na_{142} in the temperature range 100 to 500 K. The simulation times are 90 ps for temperatures below T_m , and between 150–350 ps for temperatures near the melting transition or higher. Such high statistics must be performed in order to achieve good convergence of thermodynamic indicators such as the root-mean-square bond-length fluctuation δ_{rms} .¹⁹ In Fig. 1, we show δ_{rms} for Na_{55} as a function of the total time used to compute the time averages. We have discarded at least the first 25 ps at each temperature to allow for thermalization. This plot shows that, for lower temperatures (below the transition temperature, that is, $T \leq 240$ K) simulation times of the order of 60–70 ps are sufficient for convergence. (For a discussion of melting temperatures T_m , see Sec. III.) For the higher temperatures (300 K and above), at least 100–300 ps are required to achieve proper convergence. However, near the melting transition, namely, around 270 and 280 K, δ_{rms} is rather poorly converged even up to about 300 ps, indicating the need for higher statistics at these temperatures. Further, with increase in the cluster size, these averaging times may increase, making the *ab initio* simulations of larger clusters very difficult.

An energy cutoff of 3.6 Ry is used for the plane-wave expansion of the wave function, with a convergence in the total energy of the order of 0.0001–0.0005 eV. Increasing the energy cutoff to, say, about 22 Ry causes a change of

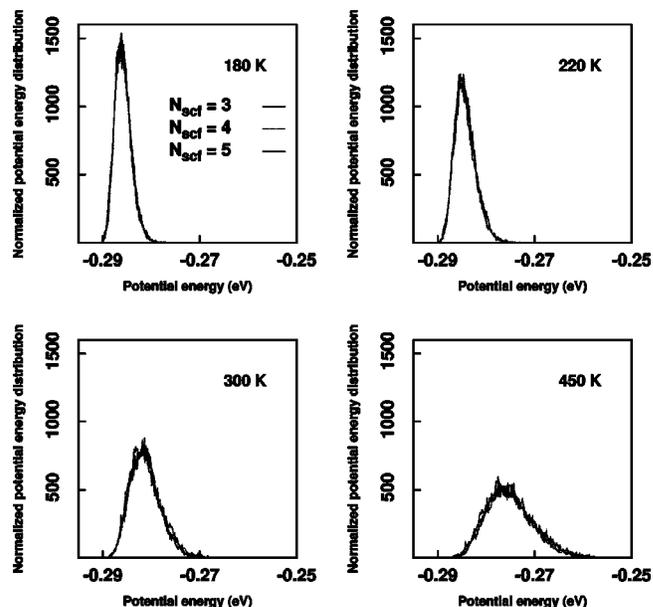


FIG. 2. Comparison of the potential-energy distributions of the Na_8 cluster at 180, 220, 300, and 450 K, computed with minimum $N_{scf}=3,4,5$ iterations (Ref. 21) used for obtaining the self-consistent-field solution of the Kohn-Sham equations.

only 0.31% and 0.28%, respectively, in the binding energy and bond length of the Na_2 dimer. We have also checked these results against those obtained by the projected augmented wave (PAW) method,²⁰ taking only the $1s^2$ electrons in the core and with an energy cutoff of about 51 Ry. The Na_2 binding energy and bond length according to the present DFT method differ by less than 3% from those given by the PAW method (the PAW method yielding smaller energies and bond lengths). The DFT method employed for our thermodynamic simulations can therefore be considered to be of comparable accuracy to the (nearly) all-electron method. The lengths of the simulation cells for Na_{55} , Na_{92} , and Na_{142} are 24, 28, and 31 Å, respectively.

We have also performed certain tests on the Na_8 cluster to check the convergence of the total energy and forces at high temperatures. In Fig. 2, we plot the histograms of potential energy for the Na_8 cluster at 180, 220, 300, and 450 K with a minimum of 3, 4, and 5 iterations²¹ for obtaining the self-consistent-field (SCF) solution of the KS equations. Clearly, all the plots overlap, indicating that about four to six SCF iterations are sufficient to obtain a good convergence of the potential energy. The force convergence test has been performed on the Na_8 cluster at 400 K. The forces are converged up to about 0.0001 eV/Å in just four SCF iterations. Hence, in all our calculations, we have used a minimum of four, and in some cases up to five or six iterations for self-consistency.

The resulting trajectory data have been used to compute the ionic specific heat, via a multihistogram fit, as well as other thermodynamic indicators. Details can be found in Ref. 15.

III. RESULTS AND DISCUSSION

We have carried out a substantial search for the lowest-energy ionic structures. A basin-hopping algorithm²² with

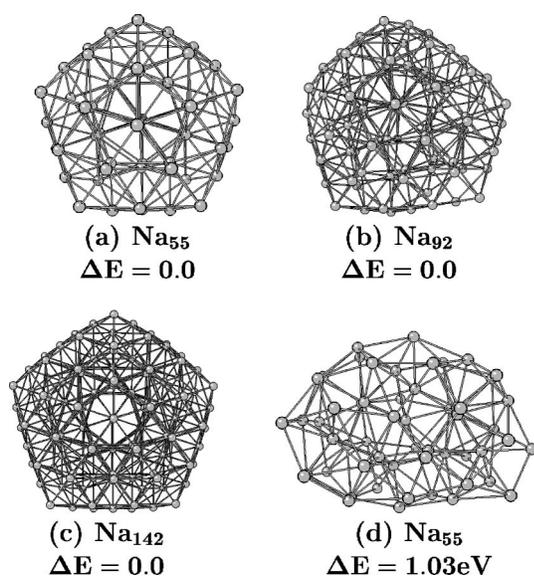


FIG. 3. Ground state geometries of (a) Na_{55} , (b) Na_{92} , and (c) Na_{142} . Structure (d) is a representative deformed excited-state structure of Na_{55} .

around 10^5 basin hops was employed to generate several hundred structures using the second-moment approximation (SMA) parametrized interatomic potential of Li *et al.*²³ About 25 of the lowest of these structures were then used as input for relaxation within the KS approach. In addition, several quenches were carried out for structures selected from a long high-temperature *ab initio* MD run, typically taken at a temperature well above the melting point (say, for $T > 400$ K). In this way, we have obtained about 20–25 distinct geometries for each size. Most of these structures should be close to the true ground state, although even this method may not yield the correct absolute ground-state structure. The resulting lowest-energy structures found for the three sizes are shown in Figs. 3(a)–3(c). The lowest-energy geometry of Na_{55} is found to be a two-shell Mackay icosahedron (with a very slight distortion from perfect regularity), in conformity with previous theory^{8,24} and experimental evidence.²⁵ Na_{142} is also found to be icosahedral, with five atoms missing from the outermost shell. (A three-shell Mackay icosahedron has 147 atoms.) As to Na_{92} , the structure consists of surface growth over a slightly distorted icosahedral Na_{55} core. The additional 37 surface atoms are accommodated so as to maintain a roughly spherical shape. Note that for Na_{92} , the SMA basin-hopping process has an unclear convergence with respect to the exact configuration of these surface atoms, and so even for the SMA potential we are unlikely to have found the true global ground-state structure. However, since our lowest-energy SMA structure turns out to be quite spherical, and since Na_{92} has a closed-shell configuration of valence electrons, we believe that the overall shape of our lowest-energy KS structure is likely to be correct.

Next we examine the specific heat for the three clusters investigated, which are plotted in Figs. 4(a)–4(c). These curves feature a single dominant peak with a width varying from about 40 K for Na_{55} to about 20 K for Na_{142} , in general

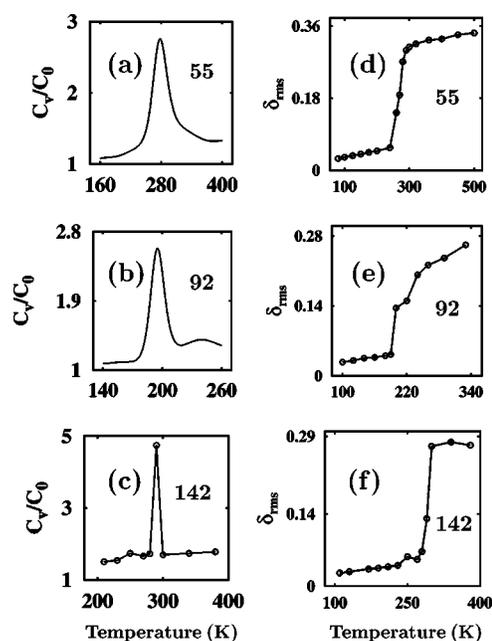


FIG. 4. Left panel, normalized canonical specific heat for (a) Na_{55} , (b) Na_{92} , and (c) Na_{142} . $C_0 = (3N - 9/2)k_B$ is the zero-temperature classical limit of the rotational plus vibrational canonical specific heat. Right panel, root-mean-square bond-length fluctuation δ_{rms} (Ref. 19) for (d) Na_{55} , (e) Na_{92} , and (f) Na_{142} .

agreement with the experimental observation. A detailed investigation of the ionic dynamics shows this peak to correspond to a “meltinglike” transition, from a low-temperature solidlike state, in which ions vibrate about fixed points (and the cluster as a whole may rotate), to a higher-temperature liquidlike state with diffusive ionic dynamics. As one illustration of this, we show in Figs. 4(d)–4(f) the root-mean-square bond-length fluctuation δ_{rms} .¹⁹ For each size there is a sharp step in δ_{rms} that correlates closely with the peak in the specific heat. The “melting” phenomenology found is qualitatively similar to that found in earlier studies with simpler potentials.^{10,11,13}

The KS melting temperatures T_m are given along with the approximate “latent heats” L in Table I. Following the convention in the experimental works,^{1,3} we define T_m here as the maximum of the peak in the specific heat. We have also calculated a quantity δE defined as the average potential energy of the just melted cluster with respect to the ground-state structure at $T = 0$ K. Schmidt *et al.*²⁶ have inferred from the experimental caloric curve that the melting temperature is strongly influenced by such an energy contribution. They showed further that T_m follows closely the variation in δE as a function of the cluster size. In Table I, we have also given T_m and L calculated by the SMA parametrized potential.^{9,10} The striking feature of the results summarized in this table is that only the first principles KS-based calculations reproduce, qualitatively as well as quantitatively, the experimentally observed variation in the melting temperatures and the latent heat for the three clusters investigated.²⁷

A noteworthy feature of the data in Table I is that Na_{92} melts at a significantly lower temperature than Na_{142} . This is true both for the KS data, which include electronic shell

TABLE I. Melting temperatures, latent heat, and δE (see text) for Na_N given by the present Kohn-Sham (KS) approach, the second-moment approximation (SMA) potential, and a density-based (DB) approach. The statistical error in the KS melting temperatures is about 8%.

N	KS	Melting temperature (K)			
		Expt. ^a	SMA ^b	SMA ^c	DB ^d
55	280	290	175	162	190
92	195	210	(170) ^e	(133) ^e	240
142	290	270	240	186	270

N	KS	Latent heat (meV/atom)			δE (meV/atom)
		Expt. ^a	SMA ^b	SMA ^c	KS
55	13.8	13.0	20.1	8.3	53.2
92	6.4	6.0	(16.9) ^e	(4.2) ^e	32.3
142	14.9	14.0	(23.0) ^f , (23.6) ^g	10.5	58.0

^aSchmidt and Haberland, Ref. 3.

^bCalvo and Spiegelmann, Ref. 10.

^cManninen *et al.*, Ref. 9.

^dAguado *et al.*, Ref. 13.

^e $N=93$.

^f $N=139$.

^g $N=147$.

effects explicitly, and for the SMA, DB, and ETF¹¹ data, which do not. We are thus led to conclude that geometry plays a significant role in the melting-point depression of Na_{92} : Na_{55} and Na_{142} are complete, or close to complete, Mackay icosahedra, while Na_{92} has surface growth on a two-shell icosahedral core and is less stable. However, as we shall see, the electronic structure does play a subtle role in the behavior of the melting temperatures of these clusters.

As mentioned earlier, previous simulations gave a melting temperature for Na_{55} significantly lower than the experimental one. Moreover, for each of the SMA,^{9,10} ETF,¹¹ and DB¹³ models, $T_m(55)$ is found to be significantly less than $T_m(142)$ calculated within the same model, while in the experiment $T_m(55)$ is very slightly greater than $T_m(142)$.²⁸ This discrepancy is largely removed within the present KS model: we find that $T_m(55) \approx T_m(142)$, within statistical error, and that both melting temperatures agree with experiment. This suggests quite strongly that the high melting point of Na_{55} relative to Na_{142} is due to electronic shell effects, since these are the main new element in our KS approach not included in previous simulations. This is particularly clear in the case of the DB and ETF methods. In these approaches, quantum shell effects are effectively averaged out as a function of size by the use of a density-dependent electron kinetic-energy functional, and the total cluster energy follows quite closely a smooth dependence on cluster size given by a liquid-drop-type formula.¹¹ In all other respects, however, such as the use of pseudopotentials and density-dependent exchange-correlation functionals, the DB and ETF methods are similar to the present KS method.²⁹ We note that both Na_{55} and Na_{142} are close to “magic” systems (Na_{58} and Na_{138} , respectively), but shell effects are relatively more important for smaller systems,³⁰ which could lead to a relative enhancement in stability for Na_{55} and thus a relatively higher melting temperature.

Further evidence for the role of quantum shell effects in melting may be obtained by examining the *shape* of the cluster before and after melting. In Fig. 5 we plot the deformation parameter ϵ_{def} for Na_{55} , defined as $\epsilon_{\text{def}} = 2Q_1 / (Q_2 + Q_3)$, where $Q_1 \geq Q_2 \geq Q_3$ are the eigenvalues, in descending order, of the quadrupole tensor $Q_{ij} = \sum_I R_{iI} R_{jI}$. Here i and j run from 1 to 3, I runs over the number of ions, and R_{iI} is the i th coordinate of ion I relative to the cluster center of mass. A spherical system ($Q_1 = Q_2 = Q_3$) has $\epsilon_{\text{def}} = 1$; a value $\epsilon_{\text{def}} > 1$ indicates a quadrupole deformation of some type. From Fig. 5 we see that at low temperatures $\epsilon_{\text{def}} \approx 1$, corresponding to the compact icosahedral ground state, but as the cluster melts, the system acquires a quadrupole deformation with $\epsilon_{\text{def}} \approx 1.6$. A more detailed investigation of this deformation with two-dimensional deformation parameters such as the Hill-Wheeler parameters³⁰ (not shown) indicates the cluster to be undergoing shape fluctuations around a net prolate deformation. A typical deformed liquidlike structure is shown in Fig. 3(d). A related phenomenon was observed earlier by Rytkönen *et al.*³¹ for Na_{40} , except that the magic Na_{40} cluster underwent only an *octupole* deformation rather than a quad-

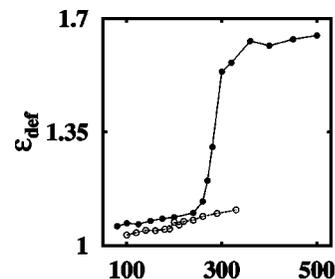


FIG. 5. Time-averaged coefficient ϵ_{def} (see text) describing the degree of quadrupole deformation of Na_{55} (continuous line) and Na_{92} (dotted line).

rupole deformation as observed here for the nonmagic Na₅₅. We do not observe statistically significant quadrupole deformations for Na₉₂ or Na₁₄₂, for which $\epsilon_{\text{def}} \approx 1$ at all temperatures.

Interestingly, simulations of Na₅₅ carried out by us within the SMA model do not show a deformation upon melting, but rather the cluster remains essentially spherical at all temperatures, $\epsilon_{\text{def}} \approx 1$. Since the SMA model explicitly excludes quantum shell effects, we believe that the deformation of Na₅₅ is due to the quantal Jahn-Teller distortion of the open-shell system of valence electrons. As further support for this explanation, we note that the mean prolate deformation in the liquidlike state agrees well with that found in jellium-model calculations for neutral Na₅₅ that we have carried out, which yield a uniaxial prolate deformation with a major- to minor-axis ratio of $R_{\text{maj}}/R_{\text{min}} \approx \sqrt{\epsilon_{\text{def}}} \approx 1.3$, in close agreement with the liquidlike simulations. Evidently, the compact ground-state structure is favored by the possibility of geometric packing into an icosahedron, while in the nonrigid liquidlike state the cluster can lower its free energy by undergoing a spontaneous shape deformation. On this reasoning, the magic Na₉₂ cluster would not be expected to deform upon melting, consistent with the observation. On the other hand, the Na₁₄₂ cluster *would* be expected to deform, at least slightly; presumably, the Jahn-Teller forces here are sufficiently weak that any deformation is not statistically significant.

Note that, as mentioned earlier, the melting temperature is strongly influenced by the potential-energy difference δE between liquidlike and solidlike states. Therefore, even if the ground state is quite spherical, as for Na₅₅, the melting temperature may still be influenced by important quantal de-

mation effects entering only in the liquidlike state. The KS simulations undertaken here incorporate all these various effects correctly.

IV. CONCLUSION

In conclusion, the KS approach appears to be capable of making quantitative predictions of melting temperatures and latent heats in Na clusters. Na₅₅, Na₉₂, and Na₁₄₂ are each magic or nearly magic, but only Na₅₅ and Na₁₄₂ are also close to icosahedral shell closures. The fact that Na₉₂ melts at a significantly lower temperature than the other two shows that geometric effects are very important in determining the pattern of melting temperatures observed experimentally. However, electronic shell effects can play an important role too, both in influencing overall binding energies and bond lengths as a function of size, and indirectly via shape deformation effects that may arise differently in the solidlike and liquidlike states. For an accurate treatment of the metallic bonding, and a quantitative prediction of melting temperatures and latent heats, it is essential to incorporate electronic shell effects appropriately, as is possible, for example, within the KS approach used here. This is especially true for the smaller sizes of clusters. There is a size regime up to $N \approx 150$ or so where a full KS treatment is warranted.

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