Thermal Expansion in Small Metal Clusters and its Impact on the Electric Polarizability

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The thermal expansion coefficients of Na_N clusters with $8 \leq N \leq 40$, and Al_7, Al_{13}^-, and Al_{14}^- clusters are obtained from *ab initio* Born-Oppenheimer local-density-approximation molecular dynamics. Thermal expansion of small metal clusters is considerably larger than that in the bulk and is size dependent. We demonstrate that the average static electric dipole polarizability of Na clusters depends linearly on the mean interatomic distance and only to a minor extent on the detailed ionic configuration when the overall shape of the electron density is enforced by electronic shell effects. Taking thermal expansion into account brings theoretical and experimental polarizabilities into quantitative agreement.

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Since electronic shell effects were put into evidence in small metallic systems [1–4], metal clusters have continuously attracted great interest both experimentally and theoretically [5–10]. Besides technological prospects, one of the driving forces for this research has been the fundamental question of how matter develops from the atom to systems of increasing size, and how properties change in the course of this growing process. In some cases it has been possible to extract detailed information from experiments done at low temperatures [11] and the related theories [12]. In many cases, however, a deeper understanding is complicated by the finite temperature which is present in most experiments due to the cluster production process, see, e.g., the discussion in [13]. Whereas a lot of theoretical information about finite-temperature effects in nonmetallic systems has been gained in the past years [14], only little is known about it in metallic clusters. Here, sodium is a particularly interesting reference system because of its textbook metallic properties and the fact that it has been extensively studied within the jellium model, see, e.g., Ref. [15] for an overview. Aluminum, on the other hand, is of considerable technological interest. Some advances to study temperature effects in metal clusters including the ionic degrees of freedom were made using phenomenological molecular dynamics [16], a tight-binding Hamiltonian [17], the Thomas-Fermi approximation [18], or the Car-Parrinello method [19]. Recently, it has also become possible to study sodium clusters of considerable size [20] using *ab initio* Born-Oppenheimer, local spin density molecular dynamics (BO-LSD-MD) [21].

In this paper we report on the size dependence of a thermal property which is well known for bulk systems, namely, the linear thermal expansion coefficient

$$\beta = \frac{1}{l}\frac{\partial l}{\partial T}. \qquad (1)$$

For crystalline sodium at room temperature, it takes [22] the value $71 \times 10^{-6}\ \mathrm{K}^{-1}$, for Al $23.6 \times 10^{-6}\ \mathrm{K}^{-1}$. To date, however, it has not been known how small systems are affected by thermal expansion. At first sight, it is not even obvious how thermal expansion can be defined in small clusters. Whereas in the bulk it is no problem to define the length l appearing in Eq. (1), e.g., the lattice constant, it is less straightforward to choose a meaningful l in the case where many different ionic geometries must be compared to one another. For small metal clusters, the latter situation arises because of the many different isomers which appear at elevated temperatures.

We have calculated the thermal expansion coefficients for Na_8, Na_{10}, Na_{12}, Na_{14}, Na_{20}, and Na_{40} in BO-LSD-MD simulations. Results concerning isomerization processes in these simulations have been presented in [23], and the BO-LSD-MD method is described in detail in Ref. [21]. A meaningful length to be used in Eq. (1) if it is applied to finite systems with similar overall deformation is the mean interatomic distance

$$l_{\mathrm{miad}} = \frac{1}{N(N-1)} \sum_{i,j=1}^{N} |\mathbf{R}_i - \mathbf{R}_j|, \qquad (2)$$

where $\mathbf{R}_i$ are the positions of the N atoms in the cluster. Obviously, l_{miad} measures the average "extension" of a clusters ionic structure, and we calculated it for all configurations obtained in a BO-LSD-MD run. Two different methods were used to calculate β. First, we discuss the heating runs, in which the clusters were thermalized to a starting temperature and then heated linearly with a heating rate of 5 K/ps and a time step of 5.2 fms. l_{miad} was recorded after each time step. In this way, for Na_8 the temperature range from about 50 to 670 K was covered, corresponding to 24 140 configurations, for Na_{10} from about 150 to 390 K (9260 configurations), for Na_{14} from about 50 to 490 K (17 020 configurations), for Na_{20} from about 170 to 380 K (8000 configurations), and for Na_{40} from about 200 to 400 K (7770 configurations).

Figure 1 shows how l_{miad} changes with temperature for Na_8 and Na_{10}. Both curves show large fluctuations, as is to be expected for such small systems. However, one clearly sees a linear rise as the general trend. We therefore

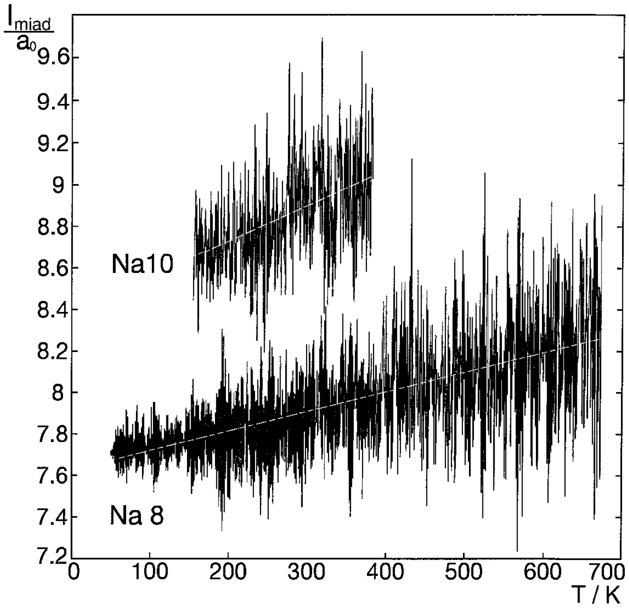

FIG. 1. Mean interatomic distance in a_0 versus temperature in K for Na_8 and Na_{10}. The dashed lines indicate linear fits to the complete set of data (see text for discussion). Note the different slopes for the two clusters.

made linear fits to the data for each cluster in two ways. The first column in the left half of Table I gives the linear thermal expansion coefficients which we obtained from fitting the data in the temperature interval between 200 and 350 K, i.e., at about room temperature, where bulk sodium is usually studied. In order to allow for an estimate of the statistical quality of the fits in view of the fluctuations, the second and third column in the left half of Table I list the ratio of the fit parameters, i.e., the axis interception a and the slope b, to their standard deviations. It becomes clear from these results that thermal expansion in the small clusters is considerably larger than that in the bulk. This can be understood as an effect of the increased surface-to-volume ratio in the finite systems. However, the expansion coefficient also strongly depends on the cluster size. This can even be seen directly from the different slopes in Fig. 1. As we will show below, this size dependence has far reaching consequences for the interpretation of experimental data which is usually measured on hot clusters, as, e.g., the static electric polarizability.

In addition to the values given in Table I, we calculated the expansion coefficient of Na_{12} with a different method. In two separate runs, the cluster was thermalized to temperatures of about 200 and 350 K, and then BO-LSD-MD was performed for 5 ps at each temperature, i.e., without heating. From the average l_{miad} found in the two simulations, $\beta_{Na_{12}} = 2.5\beta_{bulk}$ was calculated. Thus, also the second method leads to a β that is larger than that of the bulk; i.e., it confirms the results of the heating runs.

The average thermal expansion coefficient for the full temperature range covered in each simulation is obtained from a fit to the complete set of data, shown as dashed lines in Fig. 1 for Na_8 and Na_{10}. This average is of interest because it covers several hundred K for each cluster in the range of temperatures which are to be expected for clusters coming from the usual supersonic expansion sources [24]. The right half of Table I lists these average expansion coefficients and their statistical deviations in the same way as before. As expected, the values differ from the previous ones for the small clusters, because the expansion coefficient is influenced by which isomers are or become accessible at a particular temperature, i.e., especially at low temperatures it is temperature dependent. In Fig. 1 one sees, e.g., from comparison with the average dashed line that, for temperatures between 50 and 100 K, the thermal expansion is smaller than that seen for higher temperatures. However, once the cluster has reached a temperature where it easily changes from one isomer to another, the thermal expansion coefficient becomes nearly independent of the temperature. In the case of Na_8, e.g., β changes only by about 5% in the interval between 300 and 670 K.

Detailed previous investigations [20,23] have shown that small clusters do not show a distinct melting transition. However, the largest cluster studied here, Na_{40}, shows a phase transition above 300 K [20]. At the melting point, the octupole and hexadecupole deformation of the electronic density sharply increase. If l_{miad} is a relevant indicator for structural changes, then melting should also be detectable from it. Indeed, we find a noticeable increase in l_{miad} at 300 K and similar fluctuation patterns as in the

TABLE I. Left half, first column: linear thermal expansion coefficient of small Na clusters in the temperature interval between 200 and 350 K, given in terms of the bulk value 71×10^{-6} K^{-1}. Columns two and three give the ratio of the axis interception a and the slope b to their standard deviations as obtained from the fits. Right half: expansion coefficient averaged over 50–670 K for Na_8, 150–390 K for Na_{10}, 50–490 K for Na_{14}, 150–460 K for Na_{20}, and 200–300 K for Na_{40}. See text for discussion.

	β/β_{bulk}	$\sigma(a)/a$	$\sigma(b)/b$	β/β_{bulk}	$\sigma(a)/a$	$\sigma(b)/b$
Na_8	2.4	0.001	0.04	1.7	<0.001	0.01
Na_{10}	3.6	0.002	0.03	2.8	0.001	0.02
Na_{14}	1.2	0.002	0.07	1.7	<0.001	0.01
Na_{20}	1.9	0.001	0.03	1.9	0.001	0.01
Na_{40}	–	–	–	1.2	0.001	0.04

multipole moments. In our simulation, we could determine only the expansion coefficient for the solid phase, and it is given in the right half of Table I.

As seen in Fig. 1, Na_8 shows thermal expansion already at 50 K. This raises the question which asks at which temperature the expansion actually starts, i.e., where anharmonic effects in the ionic oscillations will start to become important. In this context we note that one can compare the l_{miad} at $T = 0$ K found by extrapolation from the heating data to the l_{miad} which is actually found for the ground state structure at $T = 0$ K. We have done this for Na_8, Na_{10}, and Na_{14}, where the ground state structures are well established. In all cases, the differences between the two values were less than 1%. This indicates that the anharmonic effects for Na clusters are important down to very low temperatures. Furthermore, the anharmonicities should also be observable in the heat capacities [20], where they will lead to deviations from Dulong-Petit's law. We have checked this and indeed found deviations between 8% (Na_{20}) and 19% (Na_8) from the Dulong-Petit value.

As an example of the considerable influence of thermal expansion on measurable physical properties, we discuss the average static electric dipole polarizability α, which is defined as one-third of the trace of the polarizability tensor. It was one of the first observables from which the existence of electronic shell effects in metal clusters was deduced [1], and it has been measured for clusters of various sizes and materials [10]. For Na clusters with up to eight atoms, the polarizability was also calculated in different approaches [5–7,9,10]. These calculations qualitatively reproduce the experimentally observed trends, but they all underestimate the measured value. We show that this discrepancy is to a large part due to the fact that the calculations were done for $T = 0$, whereas the measurement is done on clusters having temperatures of about 400–600 K [24].

For various, different isomers obtained in our heating runs for Na_8 and Na_{10}, we have calculated the polarizability from the derivative of the induced dipole moment with respect to the electric field (finite field method). Since highly unsymmetric isomers from the high-temperature part of the simulations were taken into account, the full tensor was computed by numerically applying the dipole field in the different directions in separate calculations. We have checked that the used field strength of $5 \times 10^{-5} e/a_0^2$ is large enough to give a numerically stable signal and small enough to be in the regime of linear response. In Fig. 2 we have plotted the thus obtained polarizabilities versus l_{miad}, and show three instances of ionic geometries for each cluster which demonstrate how different the structures actually are. Nevertheless, within a few percent, the polarizabilities are on a straight line. This shows that the average polarizability depends mainly and strongly on the mean interatomic distance, and only to a minor extent on details in the ionic configurations. Of course, the situation might be more complicated for clusters where the overall shape, i.e., the lowest terms in the multipole expansion of the valence electron density, is not stabilized by electronic shell effects. For the present clusters, however, the deformation induced by the electronic shell effects persists even at elevated temperatures. That α is less sensitive to the detailed ionic configuration than, e.g., the photoabsorption spectrum, is understandable because it is an average quantity.

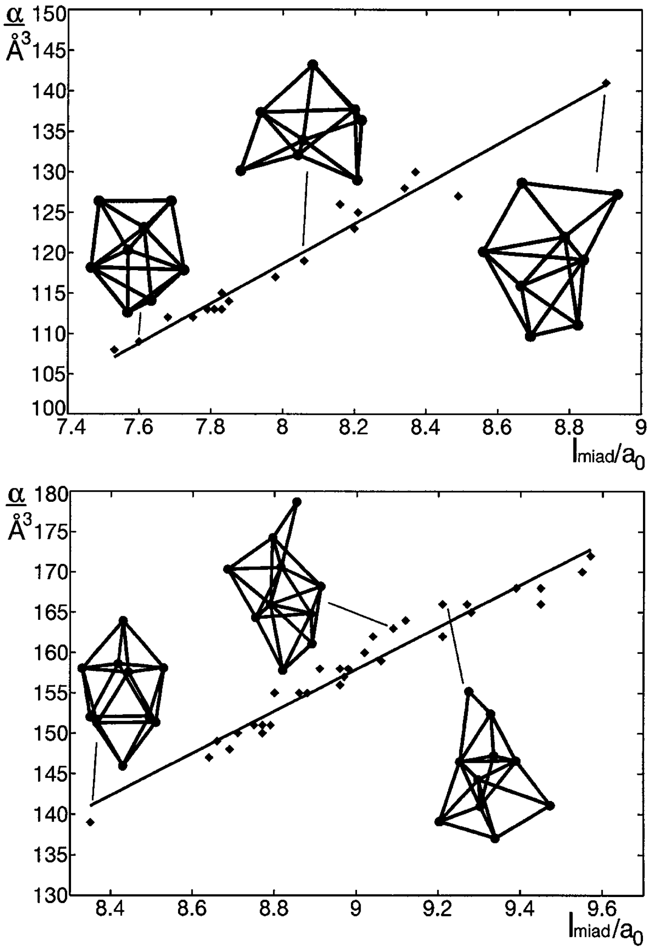

FIG. 2. Static electric dipole polarizability versus mean interatomic distance for different isomers of Na_8 (upper panel) and Na_{10} (lower panel). Three examples of different geometries are shown as insets for both sizes.

The dependence of the polarizability on the mean interatomic distance has the consequence that α also strongly depends on the temperature. From Fig. 2, one deduces that an average bond-length increase of $1a_0$ in Na_8 and Na_{10} leads to an increase in the polarizability of about 25 Å^3. Thus, neglecting the thermal expansion in $T = 0$ calculations leads to polarizabilities which are smaller than the ones measured on clusters coming from supersonic expansion sources [1,10]. Of course, also underestimations of the cluster bond lengths that are due to other reasons will directly appear in the polarizability. With the Troullier-Martins pseudopotential, e.g., the BO-LSD-MD underestimates the dimer bond length by 4.5%, and it is to be expected that the situation is similar for the bond lengths of larger clusters. Taking this into account, one can proceed to calculate the polarizability for clusters with a temperature corresponding to the experimental one of about 500 K [24]. In the experiments the clusters are spending about 10^{-4} s in the deflecting field from which the polarizability is deduced, i.e., the experimental time scale is orders of magnitude larger than the time scale of the fluctuations in the mean interatomic distance (see Fig. 1). Thus, the fluctuations will be averaged over and can be neglected. From the average expansion coefficients we obtain a bond length increase of $0.48a_0$ for Na_8 and $0.87a_0$ for Na_{10} at 500 K, which in turn leads to an increase in the polarizability of 12 Å^3 and 23 Å^3, respectively. The resulting polarizabilities of 130 Å^3 for Na_8 and 172 Å^3 for Na_{10} compare favorably with the experimental values 134 ± 16 Å^3 and 190 ± 20 Å^3 [1,10]. For all other cluster sizes, the two experiments [1,10] give different values for the polarizability. From this paper, it becomes clear that differences in the experimental temperatures might be the reason for the discrepancies. Therefore, an accurate measurement of the clusters' temperatures is necessary before further quantitative comparisons can be made. However, a detailed comparison [25] showed that the theoretical $T = 0$ polarizability of all isomers underestimates both experimental results. Thus, the increase in α that is brought about by thermal expansion will lead to better agreement between theory and experiment for all cluster sizes.

Thermal expansion is also observed in aluminum clusters. For Al_7 we performed 5 ps of BO-LSD-MD at each of the fixed temperatures 100, 300, 500, and 600 K, for Al_{13}^- at 260, 570, and 930 K, and for Al_{14}^- at 200, 570, and 900 K, in analogy to the procedure for Na_{12}. From the average l_{miad} at each temperature, we calculated the expansion coefficients $\beta_{\mathrm{Al}_7} = 1.3\beta_{\mathrm{bulk}}$, $\beta_{\mathrm{Al}_{13}^-} = 1.4\beta_{\mathrm{bulk}}$, $\beta_{\mathrm{Al}_{14}^-} = 1.4\beta_{\mathrm{bulk}}$. It should be noted that with Al_{13}^- we have chosen an electronically as well as geometrically magic cluster [26], i.e., a particularly rigid one, and the fact that it also shows a larger expansion coefficient than the bulk is further evidence for the conclusion that the increased expansion coefficient is indeed a finite size effect. A noteworthy difference between Al and Na is seen in the temperatures where the expansion sets in. Whereas for Na this temperature is below 50 K, we observe that Al_{13}^- and Al_{14}^- show no expansion below 300 K.

In summary, we have calculated thermal expansion coefficients for small metal clusters and demonstrated that thermal expansion in these systems is larger than that in the bulk. For the case of sodium, the dependence of the expansion coefficient is not monotonous according to the cluster size. We showed that the average static electric dipole polarizability of clusters, whose overall shape is fixed by electronic shell effects, depends linearly on the mean interatomic distance. Thus, thermal expansion increases the static electric polarizability, and we demonstrated that taking this effect into account brings the theoretical values in close agreement with the experimental ones.

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