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Influence of Energy and Entropy on the Melting of Sodium Clusters

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Energetic and entropic influences on the melting temperatures of size selected sodium clusters are experimentally separated. It is shown that the energetic difference between solid and liquid is the leading influence for the still puzzling features in the size dependence of sodium melting points. Additionally, this energy difference decreases towards smaller cluster sizes and causes steplike melting phase transitions to vanish. The entropy difference between solid and liquid has been found to be strongly correlated with the energy and causes a pronounced damping of the energetic influences.

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Melting points in sodium clusters are not only reduced compared to the bulk [1]. They furthermore show a complex size dependence [2–5]. This is not surprising, in general, since sodium clusters are influenced by two different shell closings. On one hand, the free electrons of the sodium atoms are caged by the surface of the cluster. This leads to the electronic shells and shell closings and therefore to specific stable clusters. Additionally, there are geometric shell closings for which the atoms in the cluster are particularly closely packed. Unfortunately, the observed features, especially for clusters with more than 150 atoms, do not correlate with any known shell closing, neither electronic nor geometric.

On one hand, this could be due to unknown, perhaps deformed, geometrical structures or to unexpected jumps between different classes of known structures [6–8] which the sodium clusters choose in order to optimize the energy of both the atoms *and* free electrons. Alternatively the entropy could be responsible. It is known to contribute strongly to the melting transition [9]. This could lead to additional features in the melting points. Their maxima therefore do not necessarily coincide with energetically preferred shell closings. In order to answer these questions, this Letter will separate the entropic and energetic influences on the melting of sodium clusters.

The experiment [3,10–12] deduces the relation between the temperature and energy of mass selected clusters. The result is the caloric curve $E(T)$, which provides a deep insight into the thermodynamics of the system. Figure 1 shows experimental caloric curves of positively charged sodium clusters with 147, 128, 70, and 41 atoms. All curves are plotted in direct comparison to Na_{139}^{+}. The absolute energies relative to the ground state at $T = 0$ can be estimated by using the bulk caloric curve for extrapolation [2–4]. The specific heat c per atom is the reciprocal slope of the curves. The steps in the caloric curves for $n = 128, 139$, and 147 indicate the melting. The melting temperatures T_m vary with cluster size [2,3]. By contrast, the specific heat, apart in the transition region, is not influenced by the cluster size. Its value corresponds well to bulk sodium both below and above the melting transition. Averaged over many clusters sized, we found $c = 3.3 \pm 0.05 k_B$ per atom for the solid phase at 230 K and $4.08 \pm 0.05 k_B$ for the liquid (measured 30 K above the melting point).

Figure 2 shows the caloric curve and the entropy of Na_{139}^{+}. The entropy $S(E)$ has been calculated by putting the experimental caloric curve into the temperature definition $1/T(E) = dS(E)/dE$ and integrating it over the energy E. As with the caloric curve, the entropy provides general thermodynamic information about the cluster. By the Boltzmann relation $S(E) = k_B \ln[\Omega(E)]$, it is coupled to the thermodynamic probability $\Omega(E)$ and therefore to the total density of states.

In principle, there is one problem in doing such a calculation. The relation is for a *microcanonical* system with a given energy E. Our clusters have been thermalized in a heat bath at given T. The cluster ensemble therefore has a *canonical* energy distribution. In a temperature range very close to the phase transition, this has to be taken into account and leads to significant differences between canonical and microcanonical quantities [13]. In the ranges away from the transition, which is the focus of this Letter, the caloric curve can be taken to be linear within the width of the canonical energy distribution. Here the differences between the canonical and the microcanonical ensemble are therefore negligible within the experimental accuracy as in the bulk.

As mentioned previously, the specific heats per atom before and after the transition do not depend on cluster size. Consequently, the entropy curves can be separated into two general parts for solid and for liquid sodium clusters, which are valid for all the different cluster sizes as shown in Fig. 2(b). The only thing that changes with cluster size and causes the melting points to vary is the relative position of the two entropy curves. The higher the

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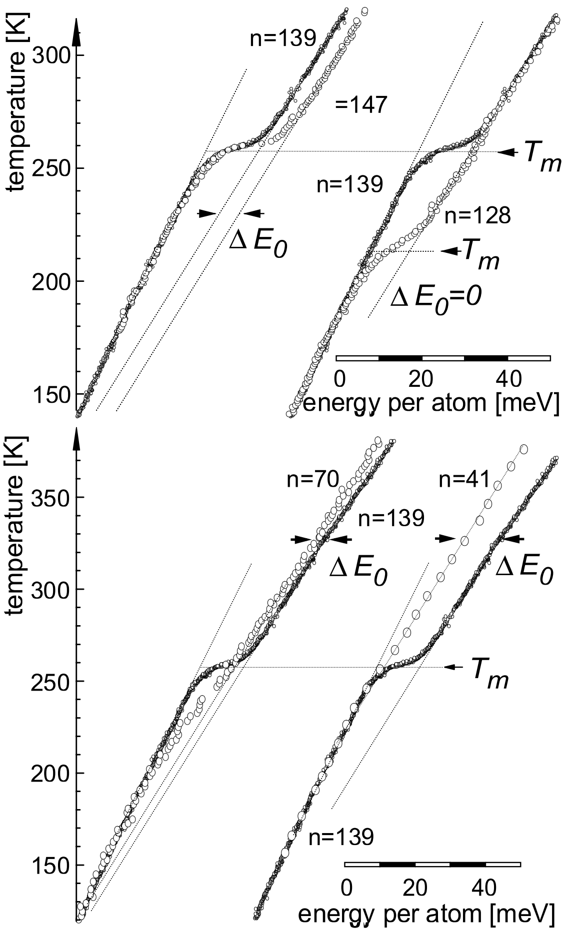

FIG. 1. Experimental caloric curves of positively charged sodium clusters with 147, 128, 70, and 41 atoms. The energy is normalized to the number of atoms and plotted in comparison to the curve of Na_{139}^+. While the melting points T_m strongly depend on cluster size, the specific heats for solid and liquid are general and size independent. Na_{70}^+ and Na_{41}^+ represent relatively small clusters that do not show a pronounced melting point but still show the characteristic change in the specific heats on going from solid to liquid. The energy offsets ΔE_0 quantify the energetic influence on the melting.

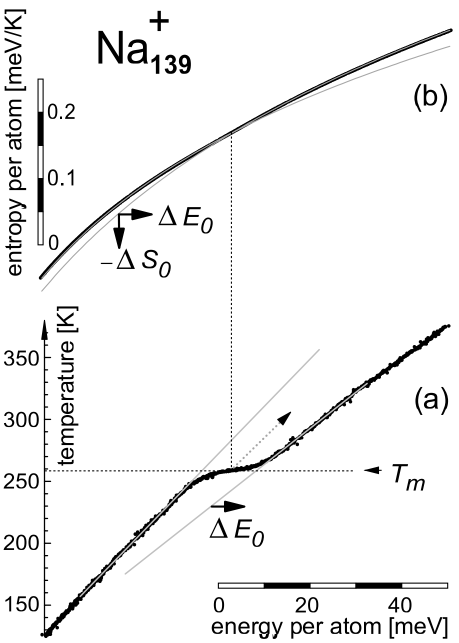

FIG. 2. The caloric curves $E(T)$ of a positively charged sodium clusters with 139 atoms. The energy is normalized to the number of atoms. The related entropy of the cluster is shown in (b). The caloric curve and entropy can be separated into two general and size independent parts, one for the liquid and one for solid. The entropic crossover point is linked to the melting point (dotted lines). Between the two parts of the entropy, there is a certain offset in energy and entropy (E_0, S_0). Energetic and entropic shifts in direction of the arrows (ΔE_0, $-\Delta S_0$) increase the melting temperature (dotted arrow) but only ΔE_0 affects the offset between the caloric curves for solid and liquid. This difference allows us to separate the two effects as described in the text.

energy of their crossover point the higher the melting temperature. The offset between solid and liquid has two components, the energy E_0 and the entropy S_0. The cluster size dependent fluctuations of the melting point are therefore due to two different influences which can be experimentally separated as indicated in Fig. 2.

(1) One possibility to increase T_m is to shift the entropy curves *entropically* by $-\Delta S_0$. Reducing the entropic offset S_0 between solid and liquid increases the melting point. The caloric curves in the solid and the liquid phase on the other hand are *not* affected, as the absolute value of the entropy does not enter the calculation of the caloric curve.

(2) The second possibility to increase T_m, shown in Fig. 2(b), is to increase the *energetic* offset E_0 between the two entropy curves for solid and liquid by ΔE_0. An increase of E_0 also increases the melting point. But in contrast to the entropic shift, which does not change the relative positions of the solid and liquid caloric curves, the energetic shift ΔE_0 leads to an equivalent energy shift of the caloric curves. It can therefore be directly deduced from the experimental data by comparing the caloric curves of different cluster sizes as indicated in Fig. 1.

The caloric curves shown in Fig. 1 are examples for the two different cases. There is no ΔE_0 between Na_{139}^+ and Na_{128}^+ but a change in melting points, while Na_{139}^+ and Na_{147}^+ have similar melting points but a pronounced ΔE_0. In both cases, the influence of the entropic shift ΔS_0 is obvious. From $n = 128$ to 139 it is negative, the entropy difference decreases, and therefore the melting point increases. From $n = 139$ to 147, an increase of ΔS_0 compensates the increase of ΔE_0 so that T_m is kept almost constant.

Note that the latent heat, which is the energy width of the step at the melting point, typically increases together with T_m due to the differences in the heat capacity of the solid and the liquid phase. This holds even in a case without any change in the energy offset between the phases, as for Na_{139}^+ and Na_{128}^+. The correlation between latent heat and melting point in an anharmonic system is therefore not necessarily coupled to an energy influence on the melting points.

Na_{70}^+ and Na_{41}^+ in Fig. 1 represent relatively small clusters that do not have a pronounced melting point but still show the characteristic change in the specific heat on going from solid to liquid. The changes in energy offsets E_0 can therefore still be deduced even without knowing the melting point. The energy difference between solid and liquid for Na_{70}^+ is smaller than in the case of Na_{139}^+ but the difference is not big. This indicates that the phase transition with its step in the caloric curve is still existent and only smoothed over a broad temperature range. The heat capacity of this cluster still shows a broad peak between 200 and 250 K. This is different for Na_{41}^+. Here the heat capacity continuously increases from solid to liquid with no peak in between, not even a smoothed one. This is related to a big energy offset ΔE_0 from Na_{139}^+. The energy difference between solid and liquid is much smaller than in the case of 139, obviously too small for something such as a first order phase transition with a step in the caloric curve.

Figure 3 shows the energy differences ΔE_0 between numerous different cluster sizes. The energies are deduced as shown in Fig. 1. In general, the energy offsets correlate with the melting points. High melting points are typically found when the energy differences between the solid and the liquid phase are big. Is the energy therefore responsible for the behavior of the melting points? To answer this question, the influence of the entropy has to be analyzed first.

Knowing the energy offset, the entropy offset is obtained by a fit of the two general entropy branches for solid and liquid (Fig. 2) to the experimental entropy $S(E)$. A correlation between the two offsets has been found that is even stronger than for T_m and E_0. This is shown by the relation of S_0 and E_0 in Fig. 4. Note that the influence of the entropy on the melting point is opposite to that of the energy. A high energy offset causes a high melting point while a high entropy difference between solid and liquid reduces T_m (Fig. 2). This shows that the energy difference between solid and liquid is the deciding origin for the features found in the size dependence of melting points. The entropy, on the other hand, strongly compensates the influence of the energy. Calculating T_m based on the measured E_0 but without this entropy compensation leads to fluctuation in the melting points which are a factor of 3 to 4 bigger than experimentally found. Focusing back on the entropy curves $S(E)$ shown in Fig. 2, this result means the two general entropy branches for solid and liquid typically shift tangentially to $S(E)$ when cluster size and melting point are changing.

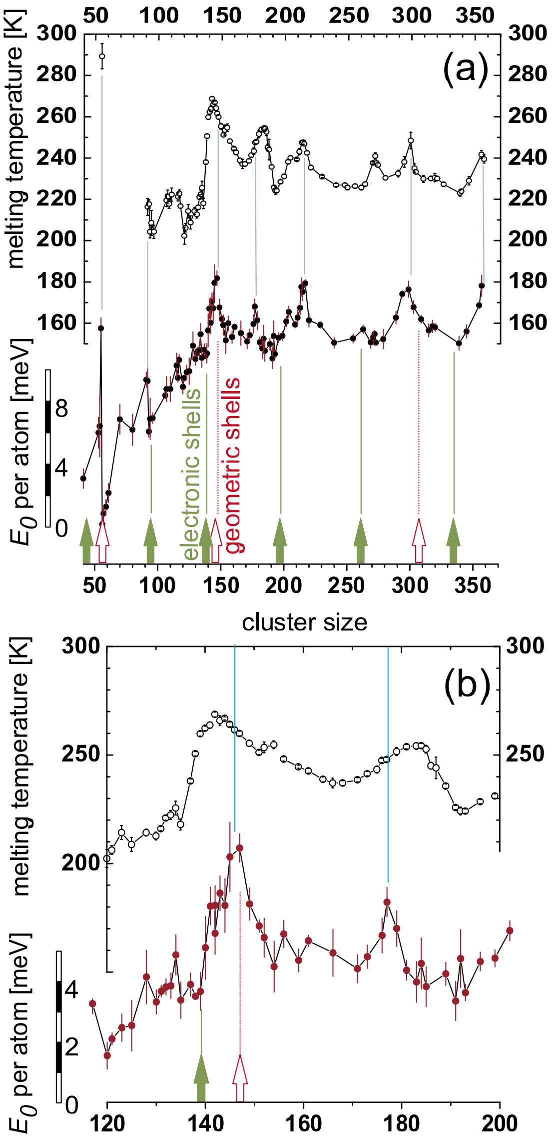

FIG. 3 (color online). Energy differences E_0 between solid and liquid as a function of cluster size. The zero point of the energy scale is missing since it cannot be deduced from this experiment. The changes ΔE_0 between the cluster sizes can be extracted by using the relative scale on the left. The lower figure is an expansion of (a). In general, the energy differences between solid and liquid correlate with the melting points which are plotted in comparison as the upper curves. The slight deviations, especially in the position of the maxima, are shown in (b). The arrows mark the electronic and geometric shell closings which cannot sufficiently explain the observed features in the melting point.

Nevertheless, Fig. 1 shows some exceptions to this coupling of the energy and entropy, as has already been noted. Furthermore a close examination of Fig. 3 around $n = 147$ shows that the peak maximum for E_0 and the melting points are slightly shifted. A similar shift, but in the opposite direction, can be found at 175–190 atoms. The data belonging to these size ranges are marked as

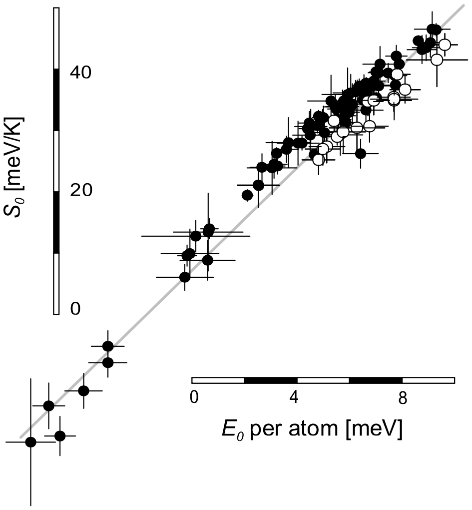

FIG. 4. Entropy and energy offsets show a strong positive correlation. A large energy difference between solid and liquid increases the melting point, while a large entropy difference reduces it. The main entropic effect is therefore damping of the energetic influences. Without it the measured energy differences would cause 3–4 times stronger fluctuations in the size depending melting points than observed by the experiment.

open dots in Fig. 4 and can be found at slightly, but systematically, lower entropies.

Several calculations have been published on the melting properties of sodium [7,8,14–16]. The main problem is that today's computing power is not sufficient to take both, electronic and geometric, shell closings into account for sizes above 55 atoms. A perfect quantitative agreement with the experiment can therefore not be expected. But nevertheless, applying the analysis proposed in this Letter to those calculations shows the same systematic tendency of decreasing energy offsets toward smaller cluster sizes, which is related to a entropy-energy compensation as shown in Fig. 4.

Most clearly, this effect can be observed in Lennard-Jones clusters [17]. Because of the simple potential precise data sets over widespread size ranges can be deduced. Here the step in the caloric curve connected to melting vanishes for clusters with less than 39 atoms. Apart from a small surface transition in the mass range 31–38 atoms, clusters with less than 39 atoms melt at relatively high temperatures. Here melting occurs without a pronounced step in the caloric curves, but there is still a clear change of the heat capacities from solid to liquid and a simultaneous vanishing of the geometric magic numbers. This qualitative change in the melting is here due to a structural change which causes smaller energetic and entropic differences between solid and liquid clusters. It has been shown that this structural transition for Morse clusters is shifted to bigger cluster sizes when the Morse parameter is tuned to cause softer potentials as the one of sodium [18].

Apart from the very specific features in the experimental melting points of sodium clusters, some more general, cluster specific trends have been discovered in this Letter: The energetic difference between solid and liquid is the major influence on the melting points. This energy difference decreases towards smaller cluster sizes and finally causes steplike melting phase transitions to vanish. The entropy difference between solid and liquid also strongly affects the melting but it is correlated with the energy. The main entropic effect is therefore a simple damping of the energetic influences.

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