Thermodynamics of small nickel clusters

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Abstract. The thermal stabilities and dynamics of small nickel clusters consisting of 7 to 23 atoms have been studied extensively by a molecular dynamics method based on a tight-binding many-body potential. Physical properties such as the caloric curve, melting temperature, and bond-length fluctuations are computed. The simulation indicates that the clusters undergo solid–liquid phase change with the increase in internal energy. The melting temperature is found to be a non-monotonic function of cluster size with some clusters exhibiting pre-melting behaviour. Considerable depression in the melting point of small clusters has been observed—the highest melting temperature for small clusters is found to be almost half the value for the bulk nickel. The results are discussed in the light of recent nanocalorimetric experiments on small finite particles.

1. Introduction

The study of phase transition in finite-size systems remains one of the most interesting topics, both theoretically [1] and experimentally [2, 3]. While second-order phase transitions are well described by size-scaling theory and critical exponents [4], the situation is not clear for first-order phase transition. In the later case, most of the interpretations have been based on experimental evidence and/or numerical simulations [5]. Of particular interest is solid–liquid transition and particle size-dependent melting point depression in small clusters. Experimental observations include structural isomerization [6], lowered melting points [2, 7], and dynamical coexistence between solid-like and liquid-like states. Early experiments [8, 9] using the transmission electron microscope (TEM) have given indications of thermal instability of small clusters at low temperatures. This observation was based on the changes in the diffraction pattern associated with the disordered nature of the particle. However, as particle size decreases, diffraction measurement becomes increasingly inaccurate due to line broadening. With the development of nanocalorimetric measurement, Lai *et al* [2] have shown recently that it is possible to measure accurately not only the melting points of small clusters but also other physical properties such as the enthalpy and heat capacity associated with the melting. Their experiment shows that small clusters melt at temperatures considerably lower than the bulk melting temperature.

The lowering of the melting point of small particles can be accounted for in terms of Pawlow's thermodynamic argument [10]. However, the absence of any universal scaling laws has left the study of melting in finite systems quite problematic. While early molecular dynamics simulations have indicated a smooth transition of equilibrium properties [11], Berry and Wales [12] have argued for a fluctuating behaviour of melting temperatures as a function of cluster size. In addition, the system-specific behaviour of the thermal stability of small clusters has not been explained yet. For example, Jellinek and co-workers [13]

have studied melting in Au and Ni clusters and have found that while small Au clusters undergo melting at considerably lower temperatures, Ni clusters, on the other hand, melt at temperatures close to the bulk melting temperature. This has triggered the question of whether clusters of different elements can exhibit different kinds of thermal behaviour. There are other questions that remain unsolved as well: Is the transition in a finite system well defined, as it is for the bulk? What is the shape of the caloric curve near the transition temperature? What are the properties that change dramatically near the melting point? While considerable progress has been made in studying the detailed dynamics of small rare-gas clusters [14], relatively few investigations of the dynamics of transition metal clusters have been reported [13, 15].

In this paper, we have studied the thermodynamic stabilities and dynamics of small Ni clusters ($7 \leqslant n \leqslant 23$) using a molecular dynamics (MD) method [16] and a tight-binding many-body potential. The potential has been shown to describe the structural, electronic, and magnetic properties of small Ni clusters quite well, and the reader is referred to our earlier papers for details [17]. Here we show that small Ni clusters melt at quite low temperatures, in contrast to the findings of our earlier study [13]. The highest melting temperature of the clusters in this size range is for Ni_{13}, and this is almost half the value of the bulk melting temperature. Some clusters are also seen to exhibit surface melting as a precursor to the bulk melting in the clusters. Physical properties such as the caloric curve (a plot of the kinetic energy versus the total energy) and bond-length fluctuations are seen to exhibit characteristic features when the clusters go from a solid-like state to a liquid-like state. The melting temperatures show a non-monotonic evolution as a function of cluster size.

The paper is organized as follows. In the next section, we describe the potential used in the simulation and the details of the numerical procedure. In section 3, we present and discuss our results. Section 4 presents a brief summary of our study.

2. Computational methods

The interaction between the atoms in a Ni cluster is modelled by a many-body potential as described by Finnis and Sinclair [18] and Sutton and Chen [19]. The potential has the form

$$V = \epsilon \sum_i \left[\frac{1}{2} \sum_{j \neq i} \left(\frac{a}{r_{ij}} \right)^n - c\rho_i^{1/2} \right] \qquad (2.1)$$

where

$$\rho_i = \sum_{j \neq i} \left(\frac{a}{r_{ij}} \right)^n. \qquad (2.2)$$

r_{ij} is the distance between the atoms i and j, a is the lattice constant, c is a dimensionless parameter, ϵ is a parameter with the dimension of energy, and m and n are integers. The parameters are obtained by fitting the data to both bulk and surface properties, and have the following values for Ni: $a = 3.52$ Å, $c = 39.432$, $\epsilon = 1.5707 \times 10^{-2}$ eV, $m = 6$, $n = 9$ [19]. This potential has been shown to reproduce bulk (e.g. the bulk melting temperature) and surface properties (e.g. the surface relaxation) quite accurately [20]. The energetics of clusters with complete geometric shells in the size range 13–309 atoms has also been studied [21] using the above form of the potential. The use of such potentials in the simulation of clusters always raises some concern. Recently, we have shown [17] that the potential not only reproduces the equilibrium geometries but also gives quantitative agreement of the
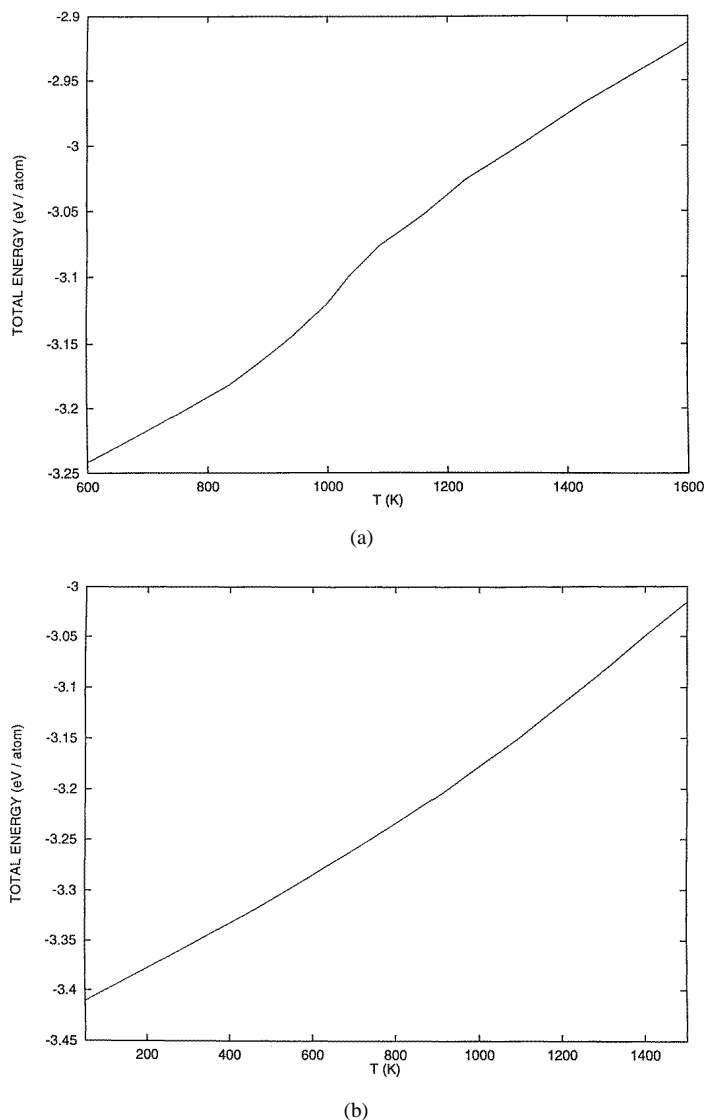
(a)

(b)

Figure 1. (a) A plot of the total energy versus temperature (caloric curve) for Ni_{13}. (b) A plot of the total energy versus temperature (caloric curve) for Ni_{16}.

energetics and bond lengths of small clusters with the first-principles results. This gives us confidence in applying the potential to study the thermal stability of small clusters.

We have used constant-energy MD simulation. The classical equations of motion are integrated using the fifth-order Gear predictor–corrector and the velocity-Verlet algorithms [16]. The accuracy of MD simulations is determined by the degree to which energy and angular and linear momenta are conserved. The Gear and Verlet algorithms give the same accuracy: the total energy deviated at worst by 0.01% for 2×10^5 steps. The clusters are initially 'prepared' with zero total linear and angular momenta starting from their ground-state geometries. Prior to computation of the ensemble averages, the clusters are equilibrated for 2×10^5 steps at each temperature. Each trajectory is then followed for 3×10^5 MD steps
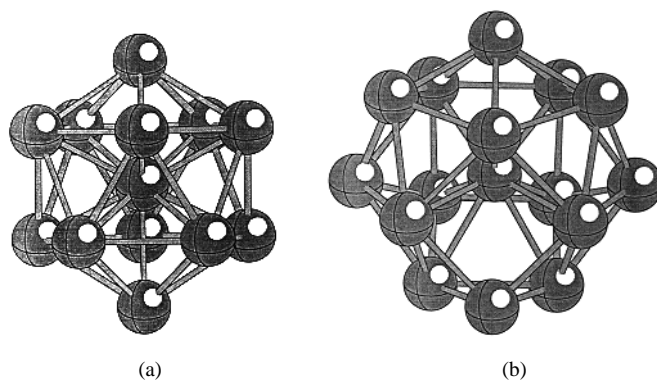
Figure 2. (a) The equilibrium geometry of the Ni_{13} cluster. Note that all of the surface atoms are equidistant from the central atom, giving Ni_{13} a closed-shell structure. (b) The equilibrium geometry of the Ni_{16} cluster. Note that *not* all of the surface atoms are equidistant from the central atom, giving Ni_{16} an open-shell structure. There are three kinds of surface atom: one is fourfold coordinated; seven atoms are fivefold coordinated; and seven more are sixfold coordinated.
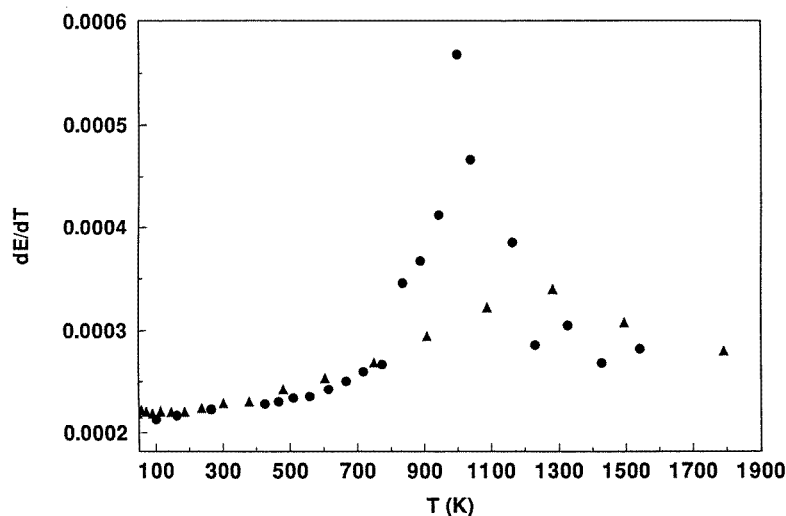

Figure 3. A plot of the first derivative of the internal energy with respect to temperature. The triangles correspond to Ni_{16} and solid circles correspond to Ni_{13}.

to compute the physical quantities. The clusters are heated or cooled by an adiabatic process, by slowly rescaling the velocity of each atom in the cluster. This is in accordance with the procedure for the proper heating of microclusters suggested by Briant and Burton [22].

The solid–liquid transition is generally probed by monitoring the caloric curve and the root mean squared (rms) bond-length fluctuation (δ). The later is defined as

$$\delta = \frac{2}{N(N-1)} \sum_{i<j} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle} \tag{2.3}$$

where r_{ij} is the distance between the atoms i and j. The symbol $\langle \ \rangle$ implies averaging over the entire run. According to the Lindemann index, melting starts in the system when δ is 0.1.

The internal temperature T is related to the kinetic energy via the equipartition theorem, and is given by

$$T = \frac{2\langle E_{kin}\rangle}{(3N - 6)k_B} \tag{2.4}$$

where E_{kin} is the kinetic energy, N is the number of atoms in the cluster, and k_B is the Boltzmann constant.

3. Results and discussion

We first discuss the variation of the total energy of clusters containing 7 to 23 atoms as a function of temperature. There are two main types of caloric curve observed for clusters in this size range, as shown in figures 1(a) and 1(b). While for all clusters, the total energy increases monotonically with temperature, for clusters with closed atomic shells such as Ni_{13} (see figure 2(a)) the change in slope at a characteristic temperature is much more abrupt than that in the open-shell clusters such as Ni_{16} (see figure 2(b)). This can be seen more clearly in figure 3 where we have plotted the first derivative of the total energy with respect to temperature. The triangles correspond to Ni_{16} while the solid circles correspond to Ni_{13}. Although in both the cases the change in slope occurs over a broad range of temperature, the change is more abrupt in the case of Ni_{13}. The temperature range where the slope changes significantly is the transition region in which the clusters transform from a near-rigid structure to a non-rigid form but remain bound for thousands of vibrational periods. The decline in the slope of the total energy near T_m indicates an increase in the heat capacity in the transition region. This behaviour is expected for a first-order-like phase transition. However, there is no evidence of a discontinuity in either the energy or its slope near T_m, which would have indicated a true singularity, as is the case for bulk melting. The absence of a sharp change in the slope is an indication of a finite-size effect, and arises because of the inability of the cluster to contain both of the phases at the same temperature. This behaviour is manifested over a range of temperatures, where, unlike in the bulk, solid and liquid clusters may coexist. Within this band of temperatures, the equilibrium ratio of solid-like and liquid-like forms changes smoothly. Indeed, for some clusters the change in slope is rather smooth (see those for Ni_{16} in figure 1(b) and in figure 3). However, the transition region can be effectively probed by computing the Lindemann index.

In figures 4 and 5 we present the rms bond-length fluctuation (δ) versus temperature for two typical clusters ($N = 13, 16$). From the view point of melting behaviour, it is convenient to classify the clusters into two categories.

(i) In the first category, the δ versus T plots show three distinct regions. As an example, we show the variation of δ with temperature for Ni_{13} in figure 4. In the first region which corresponds to solid phase, δ varies slowly with temperature until it shows a sharp change. In the second region, δ varies rapidly with temperature and melting starts in the system. The third region corresponds to the liquid state where again δ varies slowly with temperature. The liquid character is further confirmed by calculating the diffusion coefficient as well as obtaining it by graphical visualization. This phenomenon of a phase change in nickel clusters is quite similar to that for rare-gas clusters [1]. However, the melting behaviours of some nickel clusters are quite distinct from that of a rare-gas system as discussed below.
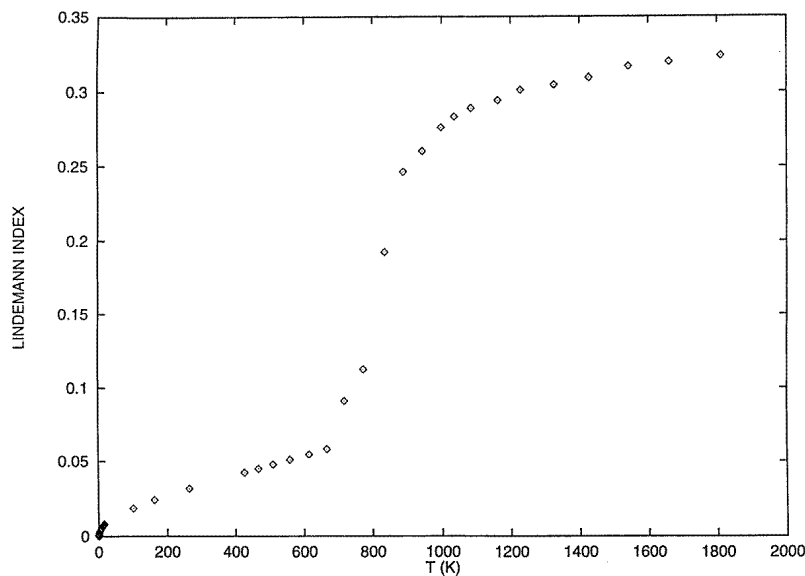
Figure 4. A plot of the Lindemann index, δ (see the text for the definition), for Ni_{13}.

(ii) The variation of δ with temperature for the second category of clusters (e.g. with $N = 16$) suggests that these clusters melt in two stages. Figure 5 shows the plot of δ versus temperature for Ni_{16}. In the first stage, δ shows an abrupt change at a rather low temperature (of about 60 K for $N = 16$; see inset (a)). In the second stage, at a higher temperature (of about 1000 K for $N = 16$; see inset (b)), δ again shows a jump in its value over a relatively broad range of temperatures.

This feature of two-stage melting (i.e. pre-melting followed by bulk melting) is seen to be characteristic of all open-shell nickel clusters (i.e. clusters with geometries where the outer shells are not fully decorated with atoms) such as $N = 16$–22. The pre-melting behaviour is strongly influenced by vacancies and anharmonicities, which are distinctly larger in open-shell clusters than in closed-shell clusters. The surface atoms which do not belong to the complete shell (in this case an icosahedron) are, in general, more weakly bound than the other atoms in the cluster, and, therefore, the mean squared amplitudes of these atoms are significantly larger than those in closed-shell clusters. This gives rise to enhanced harmonicities, and provides fluidity in the system at lower temperatures, a fact that leads to pre-melting behaviour in these systems. The pre-melting behaviour is very similar to the surface melting phenomena observed in bulk crystals [23] and arises due to the difference in coordination numbers between the atoms on the surface and the atoms in the bulk. A similar mechanism should also prevail in those clusters for which, at a certain temperature, the surface atoms show a diffusive behaviour while atoms belonging to the internal shell are still fixed in their positions. Although pre-melting has been observed experimentally in bulk systems [23], similar experiments on small clusters are still lacking. This is because of the difficulty in measuring the minuscule amount of heat involved in small systems. However, it seems likely that clean calorimetric experiments on size-selected clusters will soon be achieved using appropriate thermometers and calorimeters [2, 3] and one will then be able to probe pre-melting in small clusters experimentally.

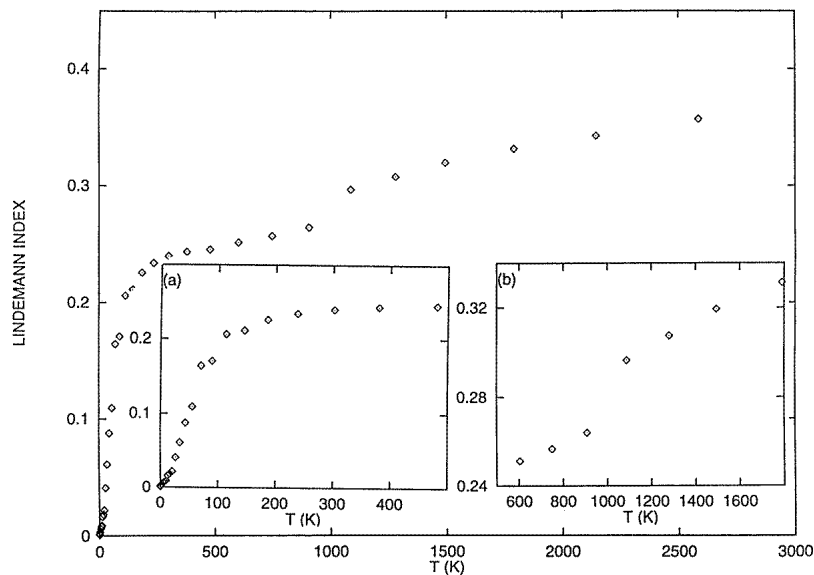We would also like to add here that for a number of clusters, caloric curves were

Figure 5. A graph showing the variation of the Lindemann index, δ, for Ni_{16}. The sharp changes in δ at two stages are amplified in the insets (a) and (b). See the text for details.
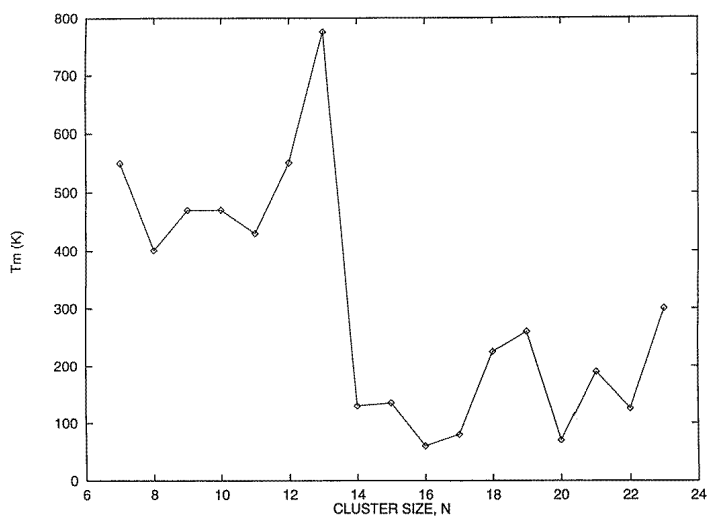

Figure 6. The variation of the melting temperature (the first temperature at which the melting starts in the system) as a function of cluster size. Melting is defined via the Lindemann index as discussed in the text.

regenerated by cooling high-energy liquid-like clusters extremely slowly. This was accomplished more easily for highly symmetric clusters like that with $N = 13$, and was problematic for other relatively less stable clusters, because of the difference in energy between the ground-state structure and the next-higher-energy structure. This difference is large for stable clusters like Ni_{13}, while for others a large number of geometrical isomers have
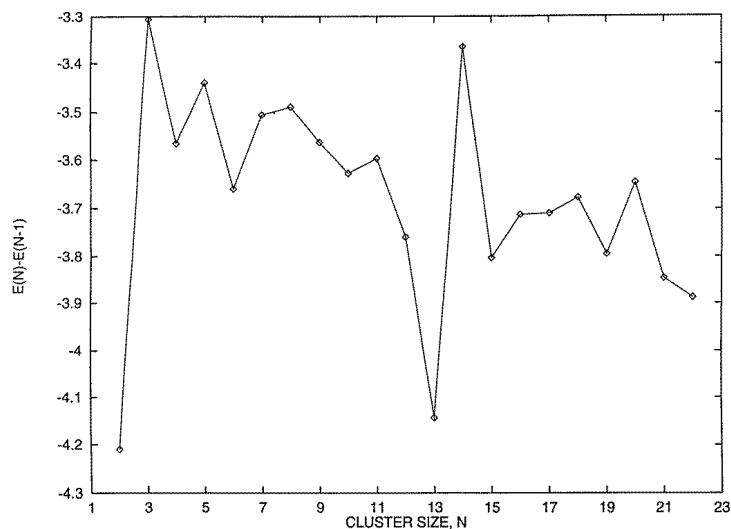
Figure 7. A plot of the 'cohesive energy', $\Delta E(N)$, as a function of cluster size.

similar energies.

The size dependence of the melting temperature of small Ni clusters is presented in figure 6. Since the melting starts at the pre-melting temperature, for clusters showing pre-melting, we have taken pre-melting temperature as a measure of the melting point. The melting temperatures have been estimated by monitoring the caloric curve, the Lindemann index, and the diffusion coefficient. Similar criteria for melting in small clusters have been also been used previously. We note that the melting temperatures are a non-monotonic function of cluster size, with Ni_{13} showing the maximum thermal stability. Clusters of less than 13 atoms in general have higher melting points than those consisting of more than 13 atoms. It is interesting to note that for clusters with $N < 13$, all of the atoms are surface atoms, while in clusters with $N \geqslant 13$, there is at least one atom that can be identified as a bulk atom. As pointed out earlier, most of the clusters with $N > 13$ have open-shell structures (i.e. not all of the surface atoms are equidistant from the bulk atom), and show pre-melting behaviour. In these cases, while it is relatively easy to determine the temperature at which the melting starts in the clusters in the first stage, the second stage of melting proceeds over a relatively wider range of temperature, thereby making the determination of a second set of melting temperatures quite difficult. It would be very useful if calorimetric experiments on Ni clusters could be carried out and compared with our simulation. A good agreement would bear further testimony to the effectiveness of the current many-body potential in simulating thermal properties of small clusters.

In order to see whether the thermal stability of clusters is related to their energetic stability at 0 K, we have calculated the energy difference between an N-atom and an $(N-1)$-atom cluster ($\Delta E = E(N) - E(N-1)$). A negative value for ΔE would imply that the N-atom cluster is energetically more stable than the preceding one. We plot these values in figure 7 and compare the results with the thermodynamic stability in figure 6. We note that energetically more stable clusters are, in general, also thermodynamically more stable. This is in contrast to what has been observed earlier for alkali [24] and alkaline-earth clusters [25], where little correlation was found between the ground-state stability and the thermal stability.

4. Conclusion

In summary, we have systematically studied the thermal stability of small nickel clusters ($N = 7$–23) using a molecular dynamics method based on a tight-binding potential. Melting is probed in small clusters using the caloric curve and the Lindemann index. It is shown that small clusters undergo a transition from a solid-like state to a liquid-like state with an increase in the internal energy. The caloric curves indicate the transition to be of the first-order kind, although the discontinuity in temperature and its slope are different to those for the bulk. It is shown that small clusters melt at temperatures well below the bulk melting temperature, a result which can be easily verified by experiment. Melting temperatures are found to be a non-monotonic function of cluster size, with some clusters exhibiting 'pre-melting' behaviour in analogy with surface melting in bulk crystals. While it was possible to trace back the caloric curves for some clusters starting from a high-temperature liquid-like state, reproducing the exact ground-state structure was quite difficult for a number of cases. This effect of hysteresis has a profound effect on the nucleation, a topic that needs further attention.

Acknowledgment

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