PHASE CHANGES IN NICKEL CLUSTERS FROM AN EMBEDDED-ATOM POTENTIAL

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ABSTRACT. The meltinglike behavior of Ni_n , $n=12,13,14,19$ clusters is studied using molecular dynamics simulations. The cohesion in clusters is modelled by an embedded-atom potential incorporating many-body effects. The features of the phase change transition derived are compared to those obtained earlier from pairwise interactions and a different many-body (Gupta-like) potential.

1. Introduction

Structural, phase and phase change properties of atomic clusters have been and remain in the focus of theoretical studies of these systems [1]. The question of how the molecularlike rigidity and floppiness of clusters evolves into bulk phases and phase transitions, as the clusters grow in size, is one of the many intriguing questions yet to be answered. It appears that the structural and phase properties of clusters are intimately related to and often play a decisive role in determining the other features of these systems, for example, their chemical reactivity [2].

In the framework of cluster studies, the phenomena of phases and phase changes, traditionally viewed as thermodynamic in nature, can be described and understood, especially for smaller clusters, in purely dynamical terms. A meltinglike transition in a cluster can be viewed as a transition from a highly restricted and correlated motion of the constituent particles, characteristic of a solid, to their uncorrelated large-amplitude or even diffusive motion, characteristic of a liquid. Since the type of the motion of the particles at a given total energy is defined by the forces acting on them, the details of a phase change transition in a cluster depend, in general, on the nature of its cohesion. Van der Waals (in particular, Lennard-Jones) clusters have been studied extensively, and the melting properties of ionic and covalent clusters have also been examined [1]. Only very recently, however, have the studies been extended to metallic clusters [3,4]. One of the reasons for this is that mimicking the metallic cohesion, where the many-body effects play an important role, is a nontrivial task. This is particularly true for transition metal clusters, in which the d-electrons may be involved in bonding.

In this communication, we give a brief account of the results of our studies of the melting behavior of Ni_n , $n=12,13,14,19$, clusters based on an embedded-atom potential. The theoretical background is given in the next section. In section 3 the results are presented and discussed. A summary of the findings is given in Section 4.

2. Theoretical Background

We extracted the structural and dynamical properties of clusters from microcanonical

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molecular dynamics simulations. Hamilton's equations of motion were solved for all the atoms in a cluster on a grid of total energies using Hamming's modified predictor-corrector propagator with a step size of 10^{-15} s. The clusters were prepared with zero initial total linear and angular momenta. The lengths of the runs ranged from 2.1 to $3.0 \cdot 10^6$ steps. The total energy was conserved within 0.03%. The forces experienced by the atoms were calculated from an embedded-atom potential [5] fitted to reproduce simultaneously the measured equilibrium lattice constant, the equilibrium cohesive energy, the bulk modulus, the three cubic elastic constants and the vacancy formation energy of the bulk nickel, as well as the equilibrium bond length and bond energy of the nickel dimer. The general form of the potential is

$$V = \sum_{i < j}^n \phi(r_{ij}) + \sum_i^n F(\bar{\rho}_i), \quad (1)$$

where ϕ is a pairwise (Morse) interaction, F is the so-called embedding energy, r_{ij} is the distance between atoms i and j , and $\bar{\rho}_i$ is the local electron density experienced by atom i . This density is supplied by all the atoms j surrounding atom i :

$$\bar{\rho}_i = \sum_{j \neq i}^n \rho_j(r_{ij}), \quad (2)$$

where ρ_j is the electron density created by atom j at the position of atom i . For details of the parameterization and fitting of the potential see Ref. 5.

To characterize the phases and phase changes in the clusters, a number of time-dependent and equilibrium quantities has been calculated and monitored as a function of the total energy (per atom). Of these we present here results for the following:

1) "Instantaneous temperature" T_i of the cluster as a function of time,

$$T_i = \frac{2 \langle E_k \rangle_s}{(3n-6)k}, \quad (3)$$

where E_k is the kinetic energy of the cluster, k is the Boltzmann constant, and $\langle \rangle_s$ stands for a short-time average. This average was calculated over time intervals of $5 \cdot 10^{-13}$ s to attenuate the fluctuations in the kinetic energy due to the vibrational motions in the cluster;

2) Relative root-mean-square (rms) bond length fluctuation δ as a function of the temperature T of the cluster, where

$$\delta = \frac{2}{n(n-1)} \sum_{i < j} \frac{(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2)^{1/2}}{\langle r_{ij} \rangle}, \quad (4)$$

$\langle \rangle$ stands for the long-time (over the entire trajectory) average, and T is calculated in accordance with Eq. (3) with $\langle \rangle_s$ replaced by $\langle \rangle$;

(3) power spectra $I(\omega)$,

$$I(\omega) = 2 \int_0^\infty C(t) \cos \omega t dt, \quad (5)$$

calculated from the velocity autocorrelation function $C(t)$,

$$C(t) = \frac{\sum_{j=1}^{n_t} \sum_{i=1}^n \vec{v}_i(t_{0j} + t) \cdot \vec{v}_i(t_{0j})}{\sum_{j=1}^{n_t} \sum_{i=1}^n \vec{v}_i^2(t_{0j})}, \quad (6)$$

where $\vec{v}_i$ is the velocity of atom i and n_t is the number of the different time origins t_{0j} . Up to 8000 time origins along a trajectory were used to suppress the effect of the initial conditions and to assure convergence of $C(t)$.

3. Results and Discussion

The time dependence of the instantaneous temperature of a cluster, which is a measure of its short-time averaged kinetic energy, is an informative characteristic of the state of this cluster at a given total energy. At low energies the cluster oscillates around its most stable structure. An averaging over a few oscillations along the trajectory yields the short-time averaged kinetic and potential energies as functions of time; these remain almost constant, and their sum is, of course, the fixed total energy of the cluster. As its total energy increases, the cluster begins to sample its other isomeric forms as well. These latter have, in general, different potential energies and therefore the short-time averages of the potential, and thus of its complement - the kinetic energy, begin to substantially deviate from a constant. The instantaneous temperature T_i of a cluster considered as a function of time is, thus, a sensitive indicator of its structural rearrangements, i.e., of its phase changes. (The possible exceptions are the transitions between permutational isomers or isomers with accidental degeneracy. But even in these cases, the passage over a barrier is reflected in a very short time decrease of the value of T_i . The situation is more complicated in the case of rotating clusters [6], where even nondegenerate isomers may have both equal, or at least similar, and different T_i 's).

In Fig. 1, the patterns of the time dependence of T_i at different total energies are shown for each of the Ni_n , $n = 12, 13, 14, 19$, clusters. One notices that indeed, as the total energy increases, the instantaneous temperature evolves from being essentially constant to fluctuating, first around a single value and then around two or more values, which form distinguishable branches. Eventually, at high energies, the fluctuations become so large that no separate branches can be resolved. This general evolution of the patterns of T_i with the total energy is similar to what has been found earlier for nonmetallic clusters [1]. Quenching thermally the trajectories from points corresponding to different branches of T_i , we have confirmed that these branches correspond to different isomers of a cluster; a detailed characterization of these isomers will be given elsewhere. Thus, as in the case of nonmetallic clusters, the nickel clusters considered here pass, when energized, through a stage of spontaneous isomerizations with the different isomers surviving long enough on the time scale of their characteristic vibrational periods. And, as found earlier, the isomerization stage persists over a finite range of total energies.

A careful examination of the panel of Fig. 1 corresponding to Ni_{14} reveals also some differences. As the energy increases, the pattern of T_i changes from being essentially constant, to two-branched, to moderately fluctuating with no branches resolvable, then back to fluctuations around distinct branches, and eventually to large fluctuations with no distinguishable branches. Such behavior has not been observed in nonmetallic clusters.

Figure 1. Instantaneous temperatures T_i as functions of time. The graphs correspond to the following total energies per atom: Ni_{12} : (a) -2.98 eV, (b) -2.88 eV, (c) -2.83 eV, (d) -2.67 eV, (e) -2.52 eV; Ni_{13} : (a) -3.05 eV, (b) -2.82 eV, (c) -2.73 eV, (d) -2.40 eV; Ni_{14} : (a) -3.11 eV, (b) -3.06 eV, (c) -3.05 eV, (d) -2.93 eV, (e) -2.73 eV, (f) -2.47 eV; Ni_{19} : (a) -3.25 eV, (b) -3.12 eV, (c) -3.02 eV, (d) -2.91 eV, (e) -2.66 eV.

Fig. 2, which displays the relative rms bond length fluctuations δ as functions of the temperature T , clearly indicates that the change in the state of the clusters is a meltinglike transition. The signature of this transition is a sharp increase in the value of δ ; cf. the Lindemann criterion for bulk melting [7]. The most resistant to melting is Ni_{13} with the transition occurring close to the bulk melting temperature (1726 K). This can be rationalized in terms of the high stability of the 13-atom icosahedral equilibrium structure. The reference to the structure explains, however, only the relative stability of this cluster. The meltinglike transition in an initially icosahedral Ar_{13} , described by a Lennard-Jones potential, takes place far below the triple point of argon. It is the difference in the nature of bonding in Ni_{13} and Ar_{13} that is ultimately responsible for the large difference in the degree of reduction in the melting temperature of these clusters. The resistivity to melting decreases in the order Ni_{19} , Ni_{12} and Ni_{14} . The most stable equilibrium structures of these clusters are: Ni_{19} - double icosahedron, Ni_{12} and Ni_{14} - relaxed structures obtained from an icosahedral Ni_{13} by removing a surface atom and adding an atom over a threefold face, respectively. The T -dependence of δ clearly displays the peculiarities of the melting behavior of Ni_{14} : it exhibits more stages in its meltinglike transition than the other clusters. The first sharp increase in δ at $T < 500$ K corresponds to intermittent isomerizations between two topologically similar structures, one with the 14th atom over a threefold face and the other over an edge. The graphs (b) and (c) for Ni_{14} in Fig. 1 correspond to this "premelting" [4b] stage. The next, almost horizontal, part of the δ curve represents the stage in which groups of atoms of the 12-atom surface of the underlying 13-atom cluster "rock" around the icosahedral geometry in a fairly symmetrical fashion. The 14th atom occasionally inserts itself into the surface of the 13-atom cluster, and another atom is subsequently

Figure 2. Relative rms bond length fluctuations δ as functions of the temperature T . The points indicated by the arrows correspond to the total energies represented in Fig. 1.

expelled onto the surface. A representative pattern of the T_i 's for this stage is given by the graph (d) of the corresponding panel in Fig. 1. The second sharp rise of δ in the vicinity of $T = 1500$ K signifies initiation of isomerization transitions and eventually melting of the cluster; cf. the graphs (e) and (f), respectively, for Ni_{14} in Fig. 1. Comparison of the δ curves for the Ni_{13} and Ni_{14} clusters indicates that the major effect of the 14th atom is adding the premelting stage. The meltinglike transition proper takes place in the two clusters over essentially the same temperature range and is described by very similar values of δ .

Figure 3. Power spectra of the Ni_{14} cluster at different total energies per atom. $I(\omega)$ is in units of 10^{-15} s .

The distributions of the vibrational frequencies for Ni_{14} at energies corresponding to the cases (a)-(f) of Fig. 1 are shown in Fig. 3. These also confirm the meltinglike nature of the transition taking place in the cluster. At low energies the motion of atoms is characterized by oscillations with well-resolvable individual frequencies. No diffusive motion ($\omega = 0$), characteristic of a liquid, is present. As the energy increases, a continuum of frequencies, including $\omega = 0$, sets in.

Finally, we note that all the features described above, including the premelting phenomenon, are in agreement with what has been found for the melting behavior of transition metal clusters using a size-dependent Gupta-like potential [4b]. The common feature of the embedded-atom and the Gupta-like potentials is that both incorporate many-body effects. It is these effects which are probably responsible for the specific phase change features of nickel (or even more generally, metal) clusters above.

4. Summary

A brief report on the meltinglike behavior of small nickel clusters derived from an embedded-atom potential has been presented. The meltinglike transition in Ni_n , $n=12,13,14,19$ is characterized by a finite-size (in terms of the total energy) isomerization range similar to that found earlier in studies of nonmetallic clusters. The premelting phenomenon in Ni_{14} and the only very moderate reduction in the melting temperature of Ni_{13} are, however, novel features. It is reassuring that all our findings agree, even in detail, with the melting properties derived for transition metal clusters using a different, so-called Gupta-like potential. Both potentials incorporate many-body effects, which seem to have a substantial effect on the mechanism of the meltinglike transition in clusters of at least some sizes.

Acknowledgments

Work at ANL is performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under contract number W-31-109-ENG-38. Work at LANL was supported by the Energy Conversion and Utilization Technologies (ECUT) Program of the U. S. Department of Energy.

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