

Thermodynamics of small platinum clusters

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Abstract

Using the Voter and Chen version of an embedded atom model, derived by fitting simultaneously to experimental data of both the diatomic molecule and bulk platinum, we have studied the melting behavior of free, small platinum clusters in the size range of $N = 15$ – 19 in the molecular dynamics simulation technique. We present an atom-resolved analysis method that includes physical quantities such as the root-mean-square bond-length fluctuation and coordination number for individual atoms as functions of temperature. The results show that as the Pt₁₅–Pt₁₈ clusters exhibit multistage melting, melting in Pt₁₉ cluster takes place in a single but interesting stage. None of these melting stages occurs at a specific temperature, rather, melting processes take place over a finite temperature range. This range is larger for less symmetric clusters. An ensemble of clusters in the melting region is a mixture of different isomeric forms of the clusters. The multistage melting and the occurrence of a single melting stage over a temperature range are two different phenomena.

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1. Introduction

The thermodynamic properties of small clusters, especially metal clusters and their atomic structures remain having a significant importance in nanoscale materials investigations. In the last two decades many theoretical [1–10] and experimental [11–15] studies have been carried out on this particular area. Because of the presence of large numbers of surface atoms rather than bulk atoms, thermodynamic and structural properties of small clusters are different from those of the corresponding bulk materials. We have reported the structural

properties of small Pt clusters described by the Voter–Chen [16] version of the embedded atom method (EAM) [17] potential in our previous studies [18]. Platinum, rhodium, and palladium have been used very extensively in heterogeneous catalysis, especially for the reactions involving CO and H₂.

The melting behavior of small clusters are strongly related to their sizes (N) and to the potential used to model the interatomic interactions. The differences between the solid–liquid phase transitions of the clusters and the bulk melting can be listed as follows: (i) the phase transition in a cluster does not occur at a specific temperature, rather, it takes place over a finite temperature range [19], (ii) an ensemble of clusters in the phase-change region is a mixture of solid-like and liquid-like clusters in the most of the small clusters [1], (iii) although the phase-change range generally decrease as

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the cluster size increases, coalescing to the bulk transition temperature as N approaches infinity, both the range and the melting temperature show much variation as a function of N [5], and (iv) there can be a range of energy for which a cluster has a negative heat capacity [20].

The object of our present work is to present an atom-resolved analysis [21] of temperature-dependent behavior of Pt_N clusters ($N = 15\text{--}19$) modelled by the Voter–Chen version [16] of the EAM potential by employing molecular dynamics (MD) simulations. We have reported the melting behavior of the first and second shell icosahedral Pt clusters somewhere else [22]. Here, we should address the question of whether a standard MD simulation will generate an ergodic trajectory for the clusters studied in this work. Quasiergodicity problems are known to be more severe when the system is in the solid–liquid coexistence regime and has a multi funnel potential energy surface (PES) [10]. A generally successful method for overcoming quasiergodicity problems is the parallel tempering approach [5,7,23]. Since the sizes studied here do not possess multi funnel energy landscapes such as the PES of a 38-atom cluster, the quasiergodicity problems will be relatively limited and can be overcome by ensuring long runs in the cluster coexistence region. Nevertheless, we want to examine the results reported here by using parallel tempering algorithms in a future work.

2. Computational details

In any N -scaling energy expression, the total energy, E_{tot} of a system of N atoms can be written as a sum

$$E_{\text{tot}} = \sum_i^N E_i. \quad (1)$$

In the EAM, the configuration energy E_i of each atom i is represented as

$$E_i = \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}) + F_i(\bar{\rho}_i), \quad (2)$$

where F_i is the embedding term, ϕ_{ij} is the pairwise-addition part of the interaction between atoms i and j , r_{ij} is the distance between atoms i and j , and $\bar{\rho}_i$ is the total “host” electron density at the position of atom i :

$$\bar{\rho}_i = \sum_{j \neq i} \rho_j(r_{ij}). \quad (3)$$

The sums over neighboring atoms j are limited by the range of the cutoff (r_{cut}) for ϕ and ρ , which is 5.5758 Å for Pt. The pairwise interaction is taken to be a Morse potential,

$$\phi_r = D_M [1 - \exp(\alpha_M(r - R_M))]^2 - D_M, \quad (4)$$

where the three parameters, D_M , R_M , and α_M define the depth, position of the minimum, and a measure of the curvature at the minimum, respectively. The density function is taken as the density of a hydrogenic 4s orbital

$$\rho(r) = r^6 [\exp(-\beta r) + 2^9 \exp(-2\beta r)], \quad (5)$$

where β is an adjustable parameter. Key to the EAM is the nonlinearity of the function $F(\bar{\rho})$ which provides a many-body contribution to the energy. If F were purely linear, the two terms in Eq. (2) could be collapsed to give a simple pair potential. Thus, a nonlinear $F(\bar{\rho})$ provides a many-body contribution to the energy. Because $\bar{\rho}_i$ depends only on scalar distances to neighboring atoms, the many-body term has no angular dependence. Nonetheless, this spherically symmetric, many-body interaction is quite important. All of the five parameters (D_M , R_M , α_M , β , and r_{cut}) defining $\phi(r)$ and $\rho(r)$ in the Voter–Chen model were determined by minimizing the root-mean-square deviation (χ_{rms}) between the calculated and experimental values of three elastic constants (C_{11} , C_{12} , and C_{44}), the unrelaxed vacancy formation energy (E_{vac}^f) of the bulk Pt, and of the bond-length (R_e) and bond strength (D_e) of the diatomic molecule. These parameters can be found in Table 1.

The use of molecular data in the fitting procedure leads one to expect the Voter–Chen’s model to be more suitable for the small clusters. The experimental melting temperature of bulk platinum is 2041 K. We are going to test the theoretical melting temperature of bulk platinum described by the Voter–Chen potential in a future study. In order to study the temperature-dependent behavior of the Pt_N clusters ($N = 15\text{--}19$) reported here, we have calculated the time averaged root-mean-square (RMS) bond-length fluctuations and that of the coordination number (CN) of the individual atoms over a time interval of 5 ns at different temperatures (5 ns correspond to 5 million MD steps in the phase space of the clusters since a single time step is of 10^{-15} s). Before starting to calculate the time average of these physical quantities, the clusters are equilibrated first (for 5 million time steps) in the MD at each total energy. Starting from very low temperatures (less than 10 K), we have increased the total energies of the clusters by 0.1% of the total energy in a stepwise manner and recorded the time averages of the physical quantities at 201 different temperatures (up to 3000 K). The set of coordinates obtained at the end of an MD trajectory is used to seed the next trajectory at each total energy. The heat capacity per atom for each cluster has also been calculated.

Table 1
Optimized potential parameters of Pt

D_M (eV)	R_M (Å)	α_M (Å ⁻¹)	β (Å ⁻¹)	r_{cut} (Å)
0.76551	2.5446	2.0035	3.84120	5.5758

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