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A LIQUID DROP MODEL FOR EMBEDDED ATOM METHOD CLUSTER ENERGIES

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Abstract

Minimum energy configurations for homonuclear clusters containing from two to twenty-two atoms of six metals, Ag, Au, Cu, Ni, Pd, and Pt have been calculated using the Embedded Atom Method (EAM). The average energy per atom as a function of cluster size has been fit to a liquid drop model, giving estimates of the surface and curvature energies. The liquid drop model gives a good representation of the relationship between average energy and cluster size. As a test the resulting surface energies are compared to EAM surface energy calculations for various low-index crystal faces with reasonable agreement.

I. Introduction

The energy and equilibrium geometry of microclusters is important in understanding the reactivity of metal catalysts for example (1). There have been few first-principles in-

vestigations of their properties other than the jellium model (2) which treats the ions as a uniform positive background charge. In part this is due to the difficulty in determining the geometry of many atom clusters using ab-initio approaches (3). Recently, the embedded atom method (EAM) (4) has been used as a technique to determine the equilibrium configuration of aluminum grain boundaries as a starting point for ab-initio calculations (5) of the grain boundary energies. It was found from self-consistent calculations that the EAM results correctly gave the equilibrium geometries albeit with underestimated energies. This suggests that semi-empirical methods such as EAM, equivalent crystal theory (ECT) (6) or Finnis-Sinclair (7) could be used as a starting point for determining geometries for ab-initio calculations. It is also of interest to examine the energy per particle for trends, giving a prediction of the energy for larger clusters approaching the bulk.

In the present paper we employ EAM in order to examine the equilibrium clusters containing from two to $N=22$ atoms for six metals, Ag, Au, Cu, Ni, Pd, and Pt. EAM has been shown to accurately represent a number of properties of bulk metals (4). Although one would not expect a priori that EAM would work for small clusters since the method was designed for bulk solids, it is of interest to examine the EAM predictions for possible future use to determine starting structures for ab-initio calculations.

Section II of this paper is a brief description of the embedded atom method, as coded by one of the authors, and of the energy minimization method for determining cluster geometry. Section III compares the mean atom energy versus cluster size with a model function whose form was first reported by R. C. Tolman (8,9) to explain droplet surface tension dependence

on droplet size. Finally, we discuss the results and present concluding remarks.

II. METHOD OF CALCULATION

The embedded atom method of Foiles, Daw, and Baskes (4) is a semi-empirical method developed to examine the properties of several fcc metals. EAM views the energy of an atom in a material as the sum of two terms. One term, the embedding energy, is the energy gained when a free atom is embedded in the free electron density of a material. The second term is an effective pair-wise Coulombic repulsion between the positive charges on the atoms.

The embedding energy for a given type of atom is a function solely of the sum of valence electron densities. The wave functions used to describe the valence electrons are the spherically averaged free-atom wave functions of Clementi and Roetti (10), and McLean and McLean (11). The total charge density at a crystal lattice site i due to atoms at other sites j , excluding the charge at site i is given by

$$\rho(r_i) = \sum_j [n_{sj} \rho_s(r_{ij}) + n_{dj} \rho_d(r_{ij})], \quad (1)$$

where the distance between sites i and j is r_{ij} and $\rho_s(r_{ij})$ is the s valence electron density due to site j at a distance of r_{ij} and n_{sj} is the number of s valence electrons at a site j . Then $\sum_j n_{sj} \rho_s(r_{ij})$ is the total s electron density at i summing over all sites j with a corresponding term for the d valence electrons. The total number of valence s and d electrons on an atom, $n_{sj} + n_{dj} = Z_0$, is fixed. Z_0 is 10 for Ni, Pd, and Pt, and is 11 for Cu, Ag, and Au.

The effective charge of an atom as a function of distance, r , is given by

$$Z(r) = Z_0 (1 + \beta r^\nu) e^{-\alpha r} \quad (2)$$

α , β , and ν are parameters as taken from Table I of reference 12. The embedding function, $F(\rho)$, for each of the metals is determined by using the universal binding energy relation (UBER) of Rose, Smith, Guinea, and Ferrante (13). This relation is used to calculate the energy of an atom at a bulk site in the crystal for the case of an isotropic expansion or contraction of the crystal, parameterized by the lattice spacing, a . The UBER is

$$E(a^*) = -E_c (1 + a^*) e^{-a^*}, \quad (3)$$

where E_c is the cohesive energy of an atom in the crystal, and

$$a^* = \left(\frac{E_c}{9B_0\Omega} \right)^{-\frac{1}{2}} \left(\frac{a}{a_0} - 1 \right). \quad (4)$$

a_0 is the equilibrium lattice constant of the crystal, B_0 is the equilibrium bulk modulus of the crystal, and Ω is the equilibrium volume per atom. The pair-wise interaction between the atom at site i and an atom at site j in the crystal is simply given by

$$\Phi_{ij}(r_{ij}) = \frac{Z_i(r_{ij}) Z_j(r_{ij})}{r_{ij}} \quad (5)$$

The embedding function is then determined

$$F(\rho_i) = E(a) - \frac{1}{2} \sum_j \Phi_{ij}(r_{ij}) \quad (6)$$

Once the embedding energy is determined the energy at a site is given by

$$E(r_i) = F(\rho_i) + \frac{1}{2} \sum_j \Phi_{ij}(r_{ij}) \quad (7)$$

To build an embedding function a set of coordinates of an fcc metal is generated for an arbitrary crystal lattice parameter, a . The embedding function is then built as a function of ρ by summing the total charge density, ρ_i , at site i at contracted and expanded lattice parameters, generating a large look-up table of $F(\rho)$ values via equation 6 for computational efficiency.

The minimum energy configurations for the metal microclusters were determined by repeatedly simulating the following "melt/quench" cycle. From a given starting atom configuration, the total cluster energy was calculated. Each atom was then visited in random order, having its position slightly perturbed in search of a lower total cluster energy. The amount of atom motion per visit was kept relatively small, to allow the entire cluster to "cool" simultaneously (uniformly). Examining the cluster total energy, when the program detected a specified small energy difference (typically 10^{-6} eV) from one trip through all the atoms to the next trip, the resulting atomic configuration was saved as a "local minimum energy" cluster. To start the next cluster, atoms were randomly located within a volume which was roughly twice the unit cell size per atom multiplied by the number of atoms. The random placement of atoms within that initial volume corresponds to a "melt". The energy minimization algorithm was then applied to the new configuration to start the next "quench" cycle. Though a global minimum energy is not guaranteed, this "melt/quench" cycle was repeated sufficiently to build confidence that the lowest energy found was at least close to the global minimum.

III. DISCUSSION

In this paper we examine whether some general analytic representations of the mean energy per particle can be obtained as a function of cluster size. We will discuss the geometry for these structures in another publication. An obvious choice to examine for an analytic representation is the liquid drop model which has been used in nuclear physics (14) and has been successfully applied to cluster energies obtained from jellium calculations both quantum mechanical (15) and extended Thomas-Fermi (16). Accordingly, we examine how well this model applies to the present EAM results.

We express the energy, therefore, in the general form (16):

$$E_T(N) = E_b N + \sigma_s N^{\frac{2}{3}} + l_c N^{\frac{1}{3}} \quad (8)$$

where N is the number of particles, E_b is the mean bulk energy, σ_s is the surface energy, and l_c is the curvature energy. For the purposes of the present calculation we represent this as

$$E_T(N) = E_c (N - 1) + \sigma_s (N - 1)^{\frac{2}{3}} + l_c (N - 1)^{\frac{1}{3}} \quad (9)$$

and finally

$$E_{avg}(N) = \frac{E_T(N)}{N} = (E_c (N - 1) + \sigma_s (N - 1)^{\frac{2}{3}} + l_c (N - 1)^{\frac{1}{3}})/N \quad (10)$$

This form is chosen to fit the reference energy in the embedded atom method, where E_c is the cohesive energy per particle and is an input parameter which EAM imposes as the bulk value, and the $(N-1)$ substitution for N reflects the reference energy of the atomic state having zero embedding energy. We then fit this expression for σ_s and l_c , examine the quality

of the fit, and compare the resulting surface energy values to EAM surface energies (4,12) for the most densely packed planes of the solids. To calculate surface tension, σ , we use the Wigner-Seitz radius, r_{WS} , in the relation (17):

$$\sigma = \frac{\sigma_s}{4\pi r_{WS}^2} \quad (11)$$

In figures 1 a,b we show the results for clusters ranging from two to twenty-two atoms. We see that this expression is excellent for nickel, copper, and silver, and seems to not do well for the dimers of gold, platinum, and palladium. We then show in figure 2 the same fit for these three materials omitting the dimer and find that the quality of the fit improves substantially. The reasons for this result will be discussed in a forthcoming publication. Interestingly, this model gives a good representation of the mean energy per particle to very small cluster sizes as was found by Perdew in his jellium calculations (18).

In Table I we give the fitting parameters and the rms deviations for two cases, including and omitting the dimer contributions. In Table II we show the comparisons to the surface energies. As can be seen omitting the dimers substantially improves the quality of the fit for gold, palladium and platinum as would be expected from figures 1 and 2. We also found that removing other lower size clusters did not substantially change the quality of the fit consequently, these results are not included. The reasons for the poorer quality of the dimer results will be discussed in a forthcoming publication. We compare to the EAM surface energies (4,12) for the three highest density planes, and note that one would expect the large clusters to have densely packed surfaces. As can be seen the agreement with the EAM surface energies is good, indicating the functional form produces physically reasonable results. We

also include the experimental values for surface energy for comparison. As is known, EAM tends to underestimate the surface energy (19).

IV. CONCLUDING REMARKS

We have performed EAM calculations for clusters ranging in size from two to twenty-two atoms. The results have been compared to a liquid drop model for describing the average binding energy versus cluster size. The model is a good representation for clusters of copper, nickel, and silver ranging from two to twenty-two atoms, and for palladium, platinum, and gold for three to twenty-two atoms. The surface energies obtained from fits to the liquid drop model are in reasonable agreement with EAM values for densely packed fcc surface planes.

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Cluster Size 2 to 22

	σ_s	l_c	E_c	RMS Dev.
Ag	-1.648893 eV	1.446568 eV	2.85 eV	0.0062 eV
Au	-2.546917	3.124959	3.93	0.033
Cu	-2.229823	1.178453	3.539	0.0073
Ni	-2.724332	2.11155	4.45	0.0060
Pd	-2.799042	1.638896	3.91	0.028
Pt	-3.044819	5.288845	5.77	0.014

Cluster Size 3 to 22

Ag	-1.64146	1.43108	0.0063
Au	-1.994469	1.973783	0.0046
Cu	-2.235914	1.191224	0.0075
Ni	-2.719677	2.10185	0.0061
Pd	-2.509354	1.035254	0.0078
Pt	-2.665766	4.498986	0.0033

Table 1: Fitting parameters (Eq. 10) for each element including and omitting dimers. Input values for the cohesive energy were obtained from ref. 20

	r_{ws}	Present Results	EAM			Expt.(avg)
			(100)	(110)	(111)	
Ag	1.597 Å	821 ergs/cm ²	705	770	620	1240
Au	1.593	1002	918	980	790	1500
Cu	1.411	1432	1280	1400	1170	1790
Ni	1.377	1829	1580	1730	1450	2380
Pd	1.522	1381	1370	1490	1220	2000
Pt	1.533	1446	1650	1750	1440	2490

Table 2: Present values for the surface energies for the 3 to 22 atom fits as determined from Eq. 11 compared to EAM value for the densest packed planes of the solid elements and experimental values (EAM and experimental values are obtained from refs. 4 and 12 and the Wigner-Seitz radius is taken from ref. (20).)

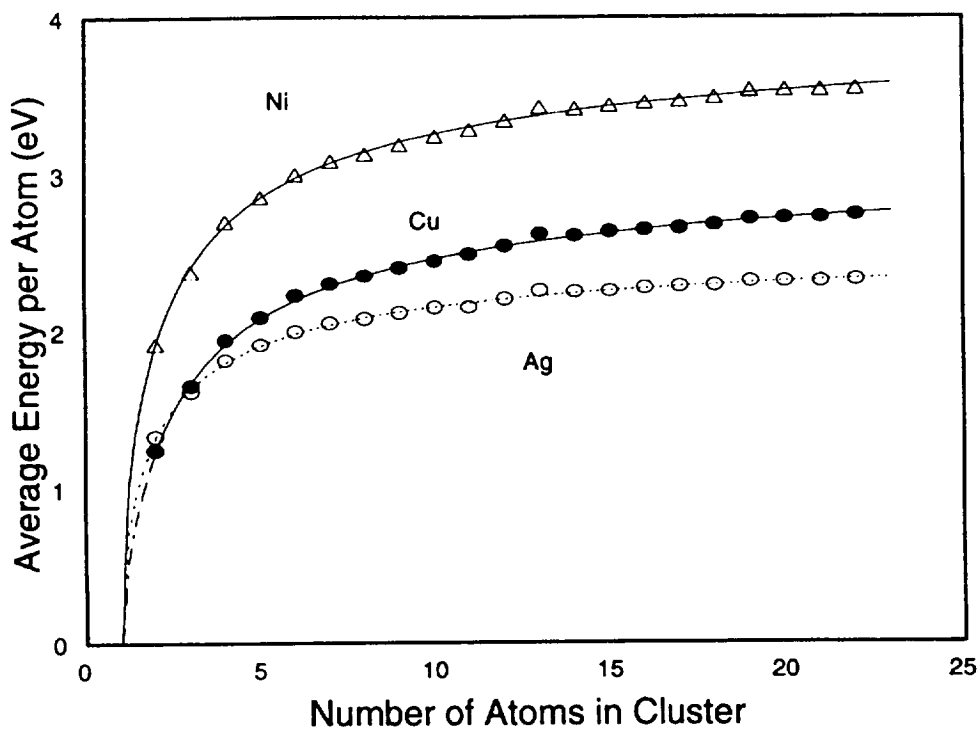


Figure 1.—(a) Comparison of average EAM energy per atom (symbols) to liquid drop model fit (curves) versus cluster size, for Copper, Nickel and silver minimum energy clusters, size $N = 2$ to 22.

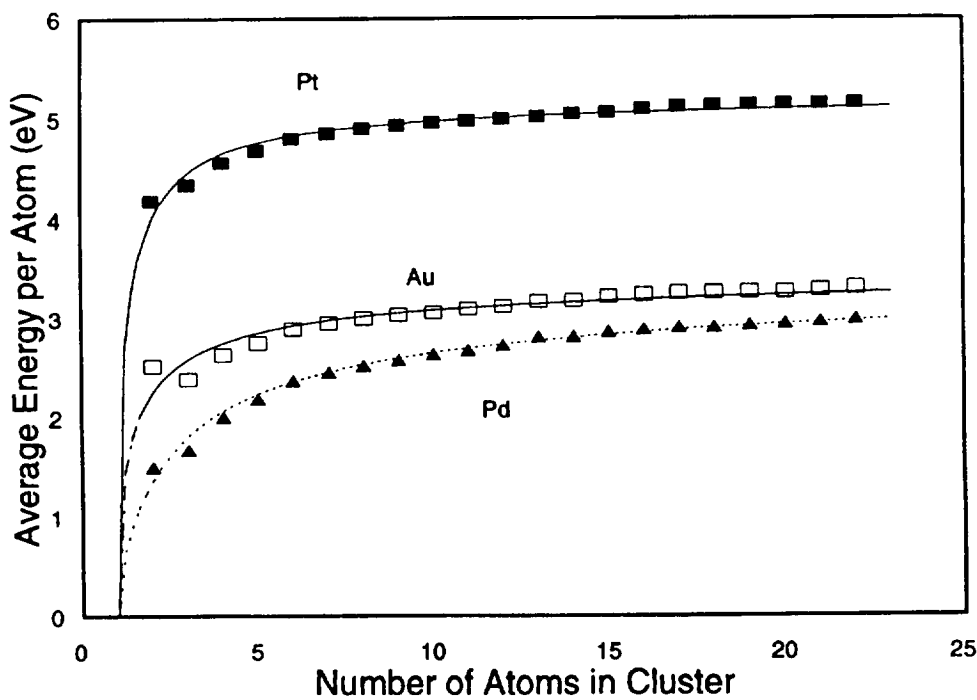


Figure 1.—(b) Comparison of average energy per atom (symbols) to liquid drop model fit (curves) versus cluster size, for gold, Platinum and Palladium minimum energy clusters, size $N = 2$ to 22.

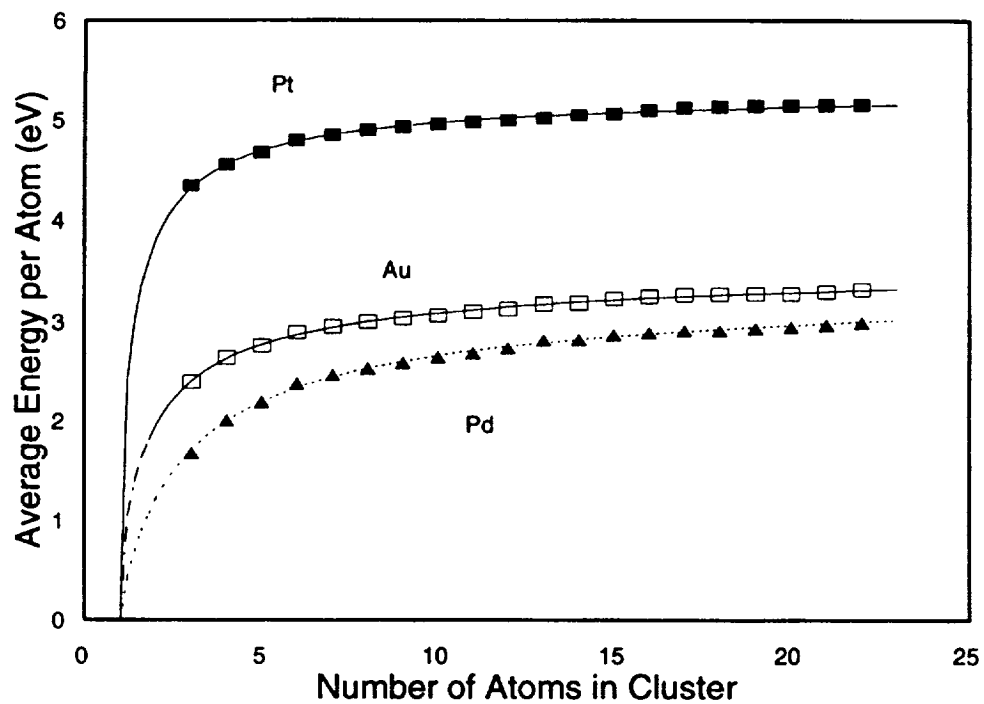


Figure 2.—Comparison of average energy per atom (symbols) to liquid drop model (curves) versus cluster size, for gold, Platinum and Palladium minimum energy clusters, size $N = 3$ to 22.

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