



Cluster size dependence of surface energy of Ni nanoclusters: A molecular dynamics study

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ABSTRACT

In this Letter we have presented a method for applying pressure on nanoparticles in the computer simulations, using an ideal gas as the pressure medium. Simulations have been performed under different isothermal conditions (200–400 K) and for pressures up to 60 GPa for different sizes of Ni nanoclusters ($N = 336, 484, 736, 1004, 1956$ Ni atoms). We have noticed that the surface energy depends on temperature, pressure, and cluster size and its dependence on the cluster size is significant. At constant temperature and pressure, surface energy decreases with cluster size. Also, at constant temperature and N , surface energy increases with pressure.

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1. Introduction

In recent decades, consolidated solids composed of nanometer size clusters (nanophase materials) have drawn a great deal of attention because of their unique thermomechanical, electrical, and magnetic properties [1,2]. In contrast to conventional polycrystalline solids, nanophase materials have a large fraction of atoms in the interfacial regions, which have a dramatic effect on the structure and physical properties of these materials [3–7].

One of the most commonly used parameters for the description of the energetic situation on the surface of a solid is the surface energy. The surface energy is analogous to the surface tension of a liquid. Surface energy describes the interaction between cohesive and adhesive forces which, in turn, is dictated if wetting occurs. The surface energy may be defined as the excess energy of the surface of a material compared to its bulk [8,9]. Although the surface tension of liquids has been understood and measured since the time of Young and Laplace, the surface energy of solids has eluded understanding and evaded measurement, despite its postulated importance to catalysis, crystal growth, colloidal behavior, sintering and fracture [10].

Its surface energy must depend on its structure. Information about low-energy structures of Ni nanoparticles can be found in [11,12]. In non-crystalline structures the difference from the bulk energy is due not only to surface contributions but also to internal strain.

Grunwald and Dellago [13] used an ideal gas flow through a surface to apply pressure on CdSe nanoparticles for their computer simulations.

We have recently presented an approach for applying pressure on the nanosystems with molecular dynamics simulation [14]. This method is especially appropriate for finite systems for which no periodic boundary condition is applicable.

The purpose of the present work is to calculate the surface energy for Ni nanoclusters, relative to the solid. Molecular dynamics, MD, simulation technique was employed to perform the relevant calculation. Simulations have been performed under different isothermal conditions (200–400 K) and pressures up to 600 kbar for different Ni nanoclusters sizes.

2. Molecular dynamics simulation

We have used molecular dynamics simulation to calculate the surface energy of Ni nanoclusters. In this Letter, the procedure used is similar to that introduced in Ref. [14]. We will briefly explain this method. At the beginning of the simulation, we consider spherical clusters. In our simulations, the pressure medium consists of particles that do not interact with each other (ideal gas), but do interact with the particles of the crystal via a soft sphere potential of the form

$$U(r) = \varepsilon \left(\frac{\sigma}{r} \right)^{12} \quad (1)$$

where r denotes the distance between two particles, σ is the interaction range and ε is the interaction strength. We have used argon gas as pressure medium in these simulations. In our simulations of the Ni nanocrystals, however, if one takes merely the interaction potential of Eq. (1) among each Ar atom and the atoms of nanocluster, the pressure never converges. To overcome this problem, we may assume that a small fraction of argon atoms interact with the atoms of the nanocluster as follows, instead of Eq. (1),

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$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

The Lennard–Jones potential parameters for a nickel–argon pair are: $\epsilon = 8.642$ kJ/mol, $\sigma = 2.84$ Å [15,16]. The fraction of Ar atoms that interact through Eq. (2) may be found by try and error, in such a way that it leads to pressure convergence. We have used the quantum Sutton–Chen potential for the Ni–Ni interactions [17,18]. The MD simulations are carried out in a NpT ensemble with the periodic boundary conditions, for the system including the nanocluster and argon gas. Temperature is controlled by a Nose–Hoover thermostat [19] and the equations of motion are integrated using the Verlet Leapfrog algorithm [15] with a time step of 0.001 ps. The system was equilibrated for 500 ps (500000 time steps), the averages were computed over the following 1 ns (1000000 time steps). We have used the DL-POLY-2.20 program [20]. The results for the bulk Ni were obtained from specific MD simulations for different isotherms and isobars. Simulations have been performed under different isothermal conditions (200–400 K) and for pressures up to 60 GPa for different sizes of Ni nanoclusters ($N = 336, 484, 736, 1004, 1956$ Ni atoms). The bulk calculations were done with the NPT ensemble at ambient pressure and with the periodic boundary conditions, applying a Nose–Hoover thermostat–barostat with the relaxation times for the temperature and pressure of 0.1 and 1.0 fs, respectively. The Verlet leapfrog scheme was used to integrate the equations of motion. In these calculations for bulk system, a time step of 1 fs was used and trajectories were carried out for a total of 800 ps, with the first 500 ps used to equilibrate the system.

3. Surface energy

Surface energy is defined as the energy needed in bringing a molecule to the surface for forming and maintaining the surface

area in equilibrium, which is represented by the surface free energy per unit surface area in thermodynamics (the reversible work per unit area to form a new surface of a substance) [21,22].

In this Letter, we have calculated the surface energy of a cluster (compared to the bulk) from [23]

$$\gamma = (P_{E, \text{cluster}} - P_{E, \text{Bulk}})/(4\pi R_c^2) \quad (3)$$

where $P_{E, \text{cluster}}$ and $P_{E, \text{Bulk}}$ are the molecular potential energies of the cluster and bulk Ni, respectively, at given temperature and pressure, and R_c is the cluster radius.

Firstly, we have calculated the potential energy of the bulk nickel using molecular dynamics simulation with the QSC potential. Secondly, we have calculated the potential energy of the nickel nanoclusters with different sizes.

4. Results and discussion

Eq. (3) may be used to calculate the surface energy of a cluster, compared to its corresponding bulk solid. The calculated potential energy of cluster at different pressures and temperatures is summarized for some given cluster sizes in Table 1.

Then, the calculated $P_{E, \text{cluster}}$, along with $P_{E, \text{bulk}}$, can be used to obtain γ , via Eq. (3).

In Figure 1, we have plotted surface energy (γ) as a function of cluster size for the Ni nanoclusters for different isotherms and isobars. This figure shows a decrease in surface energy when cluster size increases. As cluster size decreases, a larger fraction of atoms are on the surface of cluster. Since surface atoms have less binding energy, compared to the bulk atoms, therefore with decrease in number of particles, magnitude of potential energy per atom of cluster is expected to decrease (less negative). Therefore, a de-

Table 1
The calculated potential energy from MD simulations for given sizes of Ni nanoclusters (in eV) at given temperatures and pressures, compared to the bulk.

N	P (kbar)	$P_{E, \text{cluster}} (T = 200)$	$P_{E, \text{cluster}} (T = 250)$	$P_{E, \text{cluster}} (T = 300)$	$P_{E, \text{cluster}} (T = 350)$	$P_{E, \text{cluster}} (T = 400)$
336	1	-3.897	-3.888	-3.881	-3.873	-3.865
336	100	-3.866	-3.858	-3.852	-3.845	-3.840
336	200	-3.820	-3.814	-3.809	-3.803	-3.799
336	300	-3.768	-3.763	-3.760	-3.756	-3.753
336	400	-3.715	-3.713	-3.711	-3.709	-3.707
336	500	-3.669	-3.669	-3.668	-3.666	-3.665
336	600	-3.636	-3.635	-3.634	-3.631	-3.629
484	1	-5.712	-5.700	-5.687	-5.675	-5.664
484	100	-5.668	-5.656	-5.646	-5.636	-5.627
484	200	-5.602	-5.592	-5.583	-5.575	-5.567
484	300	-5.525	-5.518	-5.512	-5.505	-5.501
484	400	-5.448	-5.444	-5.440	-5.437	-5.434
484	500	-5.381	-5.381	-5.377	-5.375	-5.373
484	600	-5.334	-5.332	-5.328	-5.324	-5.321
736	1	-8.834	-8.813	-8.793	-8.775	-8.754
736	100	-8.766	-8.747	-8.731	-8.715	-8.698
736	200	-8.665	-8.649	-8.635	-8.622	-8.607
736	300	-8.549	-8.537	-8.526	-8.516	-8.505
736	400	-8.430	-8.423	-8.417	-8.411	-8.404
736	500	-8.327	-8.326	-8.321	-8.317	-8.310
736	600	-8.255	-8.251	-8.245	-8.239	-8.231
1004	1	-12.189	-12.160	-12.131	-12.103	-12.076
1004	100	-12.097	-12.070	-12.046	-12.022	-12.001
1004	200	-11.959	-11.936	-11.916	-11.894	-11.876
1004	300	-11.799	-11.782	-11.766	-11.749	-11.737
1004	400	-11.636	-11.626	-11.617	-11.606	-11.597
1004	500	-11.495	-11.493	-11.485	-11.476	-11.468
1004	600	-11.397	-11.391	-11.381	-11.369	-11.360
1956	1	-24.232	-24.179	-24.125	-24.073	-24.016
1956	100	-24.056	-24.008	-23.964	-23.919	-23.873
1956	200	-23.787	-23.747	-23.710	-23.670	-23.631
1956	300	-23.475	-23.445	-23.417	-23.386	-23.358
1956	400	-23.156	-23.140	-23.124	-23.106	-23.085
1956	500	-22.880	-22.880	-22.865	-22.851	-22.833
1956	600	-22.688	-22.680	-22.663	-22.643	-22.621

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