Crystallization of nickel nanoclusters by molecular dynamics

H Chamati and K Gaminchev
Institute of Solid State Physics, Bulgarian Academy of Sciences,
72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
E-mail: chamati@issp.bas.bg

Abstract. We investigated the melting properties of bulk nickel and the crystallization of nickel nanocrystals via molecular dynamics using a potential in the framework of the second moment approximation of tight-binding theory. The melting behavior was simulated with the hysteresis approach by subsequently heating and cooling gradually the system over a wide range of temperatures. The crystallization of nickel nanoclusters consisting of 55, 147 and 309 atoms was achieved after repeatedly annealing and quenching the corresponding quasicrystals several times to avoid being trapped in a local energy minimum. The time over which the global minimum was reached was found to increase with the cluster size.

1. Introduction
Metallic clusters, with sizes ranging from 1 to 100 nm, has received considerable attention during the last three decades [1, 2]. These materials are arranged in structures that are completely different from their bulk parents. It has been found both experimentally and theoretically that they may exist in many different structures: icosahedral, decahedral, Marks polyhedra, etc. The change in the behavior of nanosized particles can be traced back to their large surface to volume ratio. Thus the major contributions to the physical and chemical properties emanates from their surfaces [3, 4].

Nickel, a transition metal with many technological and industrial applications especially when combined with other chemical elements to form alloys, has always attracted the attention of materials researchers, experimentally and theoretically. On the theoretical side various potentials have been proposed to model the interaction among the atoms that are able to reproduce the experimental measurements known so far and to explore unknown physicochemical properties that might lead to important technological applications.

Applying quantum mechanical methods, e.g. ab initio, to get insights into the physical properties of materials is computationally expensive, restricting the simulations to very small samples on short time scales. For systems with large number of particles over large time scales it is more appropriate to utilise semiempirical potentials, that incorporate the main features of the quantum mechanical properties of the system under study. There exist several efficient semiempirical potential formalisms depending on the way their corresponding expressions are derived from quantum mechanics. These potentials take into account the local density profiles of materials. They include the embedded atom method [5], Finnis-Sinclair potentials [6], second-moment approximation of tight-binding theory [7, 8], to name a few. In particular in the second moment approximation, the expression of the total energy is based on a small set...
of adjustable parameters, which are usually determined by matching the relevant experimental data [8] or first-principles results [9].

In a recent work [10] one of the present authors has proposed an improved version of the interatomic potential of reference [11] for the paramagnetic nickel, within the framework of the second moment approximation of the tight-binding theory. While the original potential [11] was obtained by fitting the relevant adjustable parameters to augmented plane wave results of the total energies of nickel and the stable alloys it forms with Aluminum, the potential of reference [10] was adapted solely for nickel. It was modified in such a way to improve on the results obtained with its original counterpart. The named potential was fitted only to the experimental values of the lattice parameter and the cohesive energy of Ni. This potential was used to estimate several properties, such as the bulk modulus, elastic constants, vacancy and surface formation energies. Its predictions for the elastic constants showed a satisfactorily good agreement with experimental data, except for $C_{12}$. The calculated surface energies were in good agreement with the experimental results and showed the correct anisotropies. Furthermore molecular dynamics simulations were carried to compute the temperature dependence of the thermal lattice expansion and the mean–square displacements, the phonon-dispersion curves along the high symmetry axes and the radial distribution function above the theoretical melting temperature. In general it was found that this potential was superior to its original counterpart in predicting the physical properties of nickel.

In this paper we continue to test the ability of the potential of reference [10] to reproduce known experimental results and to check its transferability to different atomic environments. In addition we use it to find the equilibrium shapes of quasi-crystals with free surfaces containing a well defined number of atoms by minimizing the total energy. Here the number of atoms is chosen to correspond to magic numbers identifying two well defined atomic structures: icosahedra and decahedra [12]. It is worth mentioning that nickel should crystallize in an icosahedral structure [3].

The plan of this paper is as follows. In Section 2 we give details of the computational procedure. Our results and their comparison to experimental, along with relevant discussions are presented in Section 3. Our conclusions are drawn in Section 4.

2. Computational methodology

In the second moment approximation of the tight-binding theory the total energy of the system reads

$$E = \sum_i \left[ A \sum_{j \neq i} e^{-p \left( \frac{r_{ij}}{r_0} - 1 \right)} - \xi \sqrt{\sum_{j \neq i} e^{-2q \left( \frac{r_{ij}}{r_0} - 1 \right)}} \right] \quad (2.1)$$

The first term is a of the Born–Mayer type pairwise potential describing repulsive contributions, while the second term represents the band–structure term. To make contact with the embedded atom formalism we identify the sum under the root square as the density function and the root square itself as the embedding function. In expression (2.1) $r_{ij}$ is the distance between a pair of atoms $i$ and $j$. Here interactions up to fifth neighbors were taken into account. The adjustable parameters $A$, $\xi$, $p$, $q$, and $r_0$ were part of a large set of parameters that have been determined in reference [11] through fitting to the total energy of the system as computed by first–principles augmented plane wave calculations and taking into account the experimental values of the cohesive energy, the lattice constant and the structural stability of the ground state of Al, paramagnetic Ni (both fcc and bcc structures) and their alloys NiAl$_3$, Ni$_3$Al (L1$_3$ structure), as well as NiAl (B2 structure). It is worth noticing that the constructed potential for Aluminum was found to be accurate in predicting a number of thermodynamic and structural properties [13]. The corresponding values of the first four parameters in equation (2.1) are taken from reference [11] and are given by $A = 0.07415$ eV, $\xi = 1.4175$ eV, $p = 13.8297$ and $q = 2.2448$, while the fifth parameter, instead of $r_0 = 2.4307$ Å of [11], we have proposed in reference [10] the value $r_0 = 2.502$ Å. This value was chosen to give better fit to the equilibrium lattice constant $a_0$ and the cohesive energy $E_0$ of
fcc nickel. For the sake of comparison we report here some results obtained with both potentials. These are $E_0 = 4.435$ eV/atom and $a_0 = 3.421$ Å [11], against $E_0 = 4.43$ eV/atom and $a_0 = 3.52$ Å [10]. The later values are in accord with the experimental result [14].

Notice that despite the relatively simple form (2.1) and the small number of parameters used to fit the total energy, this potential has proven its ability to reproduce quite well some experimental data in comparison to the embedded atom method potential of reference [15], whose total energy was fitted to 17 experimental values and \textit{ab initio} results.

The above interatomic potential is used in conjunction with molecular dynamics simulations in the canonical isothermal (NVT) and isobaric (NPT) ensembles. The used simulation box was made up of 4000 atoms arranged on a fcc lattice with 40 layers with 100 atoms each. Simulations were carried out using periodic boundary conditions on the three space directions in order to neglect the emergence of possible surface effects. The equations of motion were integrated by means of the Verlet algorithm and a time step $\delta t = 5 \times 10^{-15}$ s. This value ensures energy conservation of the trajectories during the simulation process. In the NVT ensemble, the system was equilibrated at a target temperature during 1000 time steps, which were sufficient to obtain stationary values for the kinetic and the potential energies. The thermodynamic averages were computed satisfactorily over trajectories lasting 50 ps. In the NPT ensemble used to explore the hysteresis by gradually heating and cooling the sample at intervals of 10 K, the simulation box was equilibrated at a given temperature for over 6000 time steps and averages were computed over the next 1000 steps. Here we have monitored the change in the simulation box volume and the energy per atom.

During the simulation, the value of the lattice constant at each temperature was chosen so as to result in zero pressure in the system. The mean–square displacements at each temperature were computed in order to get insights into the melting behavior of nickel within the framework of the present model.

The structural properties are identified via the computation of the radial distribution function expressed via

$$g(r) = \frac{1}{4\pi N} \left\langle \frac{1}{r^2} \rho \Delta r \sum_{i=1}^{N} n_i(r) \right\rangle,$$  \hspace{1cm} (2.2)

where $n_i(r)$ stands for the number of particles in a spherical shell of thickness $\Delta r$ and at a distance $r$ from the $i$–th atom, $\rho$ is the number density of the studied material and $N$ – the number of molecular dynamics steps. The brackets $\langle \cdot \cdot \cdot \rangle$ in equation (2.2) indicate the thermodynamic average. The system was first equilibrated at a higher temperature than the targeted one for 2000 times steps and then cooled and equilibrated at the named temperature for another 2000 steps. Statistical averages for the calculation of the structural properties were obtained from the data of the next 4000 steps.

Energy minimization leading to the most stable shape of nanoclusters was achieved, with the aid of the Wulff construction, by starting from fcc structures having free surfaces, with a well defined number of atoms corresponding to the one of the magic numbers according to the formula [12]

$$\varsigma(k) = \frac{10}{3} k^3 - 5k^2 + \frac{11}{3} k - 1,$$  \hspace{1cm} (2.3)

identifying nanoparticles with five–fold symmetry structured in $k$ shells. So for $k$ a natural number the series of magic numbers is 13, 55, 147, .... The free surfaces were produced by fixing the dimensions of the computational box at a length large enough to avoid interactions between the periodic slabs in all directions. The initial fcc quasicrystals were annealed at high temperatures about the melting one and then were the subject of successive molecular dynamics quenching procedures (similar to the quasidynamic minimization procedure) that led to the final configurations.

3. Results and Discussion

In reference [10] results computed with the potential (2.1) for various structural and thermal properties were presented. In particular the melting temperature extracted from the behavior of the mean-square displacement extracted from the atomic density profile and based on the Lindemann criterion
[16] was established at 1880 K. For the purpose of this paper we have calculated anew the mean-square displacement at various temperatures using an approach taking the atomic positions. A linear extrapolation of our atomic mean-square displacement results yields a melting temperature of about 1930 K, showing that the present potential overestimates the melting temperature of nickel, compared to the experimental result of 1728 K [14], but comparable to the theoretical results of reference [8]. To check the validity of this value having in mind that the potential is transferable to different atomic environments, such as the liquid phase, we computed the pair distribution functions (see Section 2 for details) at 1900 K and 2000 K. The results are shown in figure 1. This clearly shows that at 1900 K the potential still describes a crystalline phase, while nickel should be liquid at this temperature. At 2000 K, however we have a behavior characteristic of a liquid phase. These findings are a clear confirmation that the melting temperature is most likely to be at 1930 K. On the other hand it is possible that the relaxation time at 2000 K is much longer than the simulation length.

![Figure 1](image)

**Figure 1.** Radial distribution functions of nickel at $T = 1900$ K and $T = 2000$ K, obtained using molecular dynamics simulation.

Another way to find the equilibrium melting temperature from molecular dynamics is the use of the hysteresis approach. In this approach the simulation box is heated gradually beyond melting and then cooled in a similar way until crystallization in the NPT ensemble at zero pressure. The temperature dependence the lattice constant are depicted in figure 2. During the process of heating we observe an abrupt increase in both the energy (not shown here) and the volume upon melting. The inverse process (cooling) leads to a sudden drop at a lower temperature i.e. where nickel solidifies. Following reference [17] we deduce the equilibrium melting point $T_m$ from the expression $T_m = T_+ + T_- - \sqrt{T_+ T_-}$, where $T_+$ and $T_-$ are the temperatures for the maximum degree of superheating and supercooling, respectively. According to this expression and using $T_- = 1210$ K and $T_+ = 2180$ K, we obtain $T_m = 1766$ K, which slightly above the temperature reported in reference [17] obtained with a quantum corrected Sutton-Chen potential.

A final test of our model consists in the crystallization of nanoparticles with numbers of atoms corresponding to magic numbers. We have started our simulations with 55, 147 and 309 atoms arranged in fcc structures with free surfaces as described above. The lowest energy configuration nanoclusters was obtained by employing a simulated annealing and quenched molecular dynamics technique. This procedure is commonly used to find the global and local minima in complicated situations. The results were tested by varying cooling rates and melted configurations. In general this approach does not guarantee that the energy minimum found is mandatory the global one. Usually the procedure stops at the first local minimum reached. Consequently, various different verifications are necessary to make
Figure 2. Dependence of the lattice constant of bulk fcc nickel on the temperature in the isobaric canonical ensemble via molecular dynamics simulation. The statistical errors are smaller than the symbols size.

Figure 3. Icosahedral structure composed of 55 atoms of nickel obtained using molecular dynamics simulation.

sure that after a series of annealed and quenched molecular dynamics runs the minimum found is likely to correspond to the global one. In addition, icosahedral clusters have five-fold symmetry and therefore they are metastable structures. Nevertheless, it is found in several cases that icosahedral metallic clusters have the lowest energy compared to other structures. We started with fcc clusters consisting of a number of atoms corresponding to a magic number [given by equation (2.3)] of the icosahedral structure. We heated the initially constructed clusters up to temperatures that are higher than the melting point. The resulting liquid is subsequently quenched with different cooling rates in order to minimize the energy. The procedure is repeated several times and the coordinates of the quenched cluster were saved. A comparison of the energies of the saved configurations showed that indeed those with the lowest energy have an icosahedral-like structure. In figure 3 we show the shape of the lowest energy nanocluster with 55 atoms. To show its degree of symmetry we present three different projections on two dimensional planes. We have also noticed that changing the cooling rates during simulations leads to polycrystalline structures. It was found the time needed to reach the global minimum increases with the particle size. This is in agreement with the conclusions of references [18, 19], where the influence of the cooling rates
in the crystallization of nanoclusters was investigated.

Figure 4. two-dimensional projections of the icosahedral structure shown in figure 3.

4. Conclusions
We presented an extensive molecular dynamics study of the melting properties of bulk nickel and the crystallization of quasicrystals in the nanometer range. The simulations were performed with the help of an interatomic potential in analogy to the tight-binding scheme in the second moment approximations. This potential was proposed in reference [10] and has proven its ability to reproduce with a fair accuracy the experimental data of a number of thermodynamic, as well as structural properties of nickel.

To gain insight into the melting properties of nickel we computed the mean-square displacement over a wide range of temperature. According to the Lindemann criterion [16] we estimated the melting temperature at 1930 K. This result is higher than the experimental value of 1728 K [14], but in agreement with most of the potentials designed to describe to the properties of nickel. Our result was checked by exploring the behavior of the pair distribution function at 1900 K and 2000 K. We found a fcc structure at 1900 K and a liquid phase at 2000 K. Further we constructed the hysteresis of nickel by heating and cooling gradually a simulation box over a wide range of temperatures. We found a large hysteresis with two abrupt jumps of the volume of the box at two different temperatures: upon heating at \( T_+ = 2180 \) K and upon cooling at \( T_- = 1210 \) K.

The transferability of the model was checked further by investigating the crystallization of nickel quasicrystals using a series of alternating annealing and quenching molecular dynamics simulations till the lowest energy shape is reached. Our procedure was applied to quasicrystals composed of a number of atoms, corresponding to magic numbers characteristic of icosahedra and decahedra. Starting from perfect fcc structures, containing 55, 147 and 309, with free surfaces above melting and repeating the procedure several times we end up with almost perfect icosahedral structures. The global minimum of the stable configuration was attained after a certain number of cycles that depended upon the size (number of atoms) of the nanocrystal.

We conclude that despite its relative simplicity the potential of reference [10] is capable of producing the main characteristics of nickel, yet it has to take into account the magnetic nature of the real element.

Acknowledgments
We thank Professor N. Papanicolaou for a careful reading of the manuscript. This paper was partially supported by grant No BK-01/2012.

References
[1] Contescu C I and Putyera K (eds) 2009 Dekker encyclopedia of nanoscience and nanotechnology 2nd ed (Boca Raton: CRC Press)
[2] Cao G and Wang Y 2011 Nanostructures & nanomaterials: synthesis, properties, and applications (World Scientific Series in Nanoscience and Nanotechnology vol 2) (New Jersey: World Scientific)
[3] Mitin V V, Sementsov D I and Vagidov N Z 2010 Quantum Mechanics for Nanostructures (Cambridge University Press)
[4] Roduner E 2007 Nanoscopic Materials: Size-Dependent Phenomena (Cambridge: Royal Society of Chemistry)
[5] Daw M and Baskes M 1984 Phys. Rev. B 29 6443–6453
[6] Finnis M W and Sinclair J E 1984 Phil. Mag. A 50 45–55
[7] Gupta R 1981 Phys. Rev. B 23 6265–6270
[8] Cleri F and Rosato V 1993 Phys. Rev. B 48 22
[9] Chamati H and Papanicolaou N I 2004 J. Phys.: Condens. Matter 16 8399–8407
[10] Chamati H 2011 J. Mater. Sci. Tech. 19 42–51
[11] Papanicolaou N I, Chamati H, Evangelakis G A and Papaconstantopoulos D A 2003 Comput. Mater. Sci. 27 191–198
[12] Martin T P 1996 Phys. Rep. 273 199–241
[13] Chamati H, Stoycheva M S and Evangelakis G A 2004 J. Phys. Condens. Matter 16 5031–5042
[14] Kittel C 2005 Introduction to solid state physics 8th ed (Hoboken NJ: Wiley)
[15] Mishin Y, Farkas D, Mehl M J and Papaconstantopoulos D A 1999 Phys. Rev. B 59 3393
[16] Lindemann F 1910 Phys. Z. 11 609–612
[17] Luo F, Chen X R, Cai L C and Ji G F 2010 J. Chem. Eng. Data 55 5149–5155
[18] Gafner Y, Gafner S and Entel P 2004 Phys. Solid State 46 1327–1330
[19] Gafner S, Redel’ L and Gafner Y 2007 The Physics of Metals and Metallography 104 180–186