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Equations of state for amorphous and crystalline nickel by means of molecular dynamics method

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Abstract

There are few theoretical studies on the equation of state (EOS) for amorphous materials while much work has been carried out for crystalline systems. In this study, the EOSs for both crystal- and amorphous-structured nickel are obtained by using an anisotropic molecular dynamics method based on the Voter-Chen formalism of embedded atom method. In order to achieve the EOSs, polynomial curve fitting method has been applied to the data obtained from molecular dynamics simulations carried assuming isothermal and isobaric conditions. Isothermal bulk modulus and their pressure derivatives for both amorphous and crystal structures have also been calculated. The results are compared with the values obtained from well-known Vinet and Davydov EOSs.

Key Words: Equation of state, molecular dynamics simulation, amorphous structures, embedded atom method

1. Introduction

An equation of state is an expression describing the relationship between some thermodynamic properties of a system. The EOS is important to investigate the thermodynamic properties of materials, especially in case of materials under high pressure and/or at high temperature. Isothermal bulk modulus and its pressure derivatives, as well as elastic constants and thermal expansion coefficients, all of which can be calculated from EOSs of materials, are of interest to material scientists. The properties of materials under extreme thermodynamic conditions are also of interest to geophysicists, metallurgists and many other workers [1–3].

Material scientists are continuously producing new and relevant materials, for which calculated EOSs would further their thermodynamic characterizations. In the case of amorphous materials prepared by rapid cooling or any other processes, although they have excellent electrical, magnetic, and optical properties in general, they also often have unstable structures under variable thermodynamic conditions and thus tend to transform from amorphous to crystal structures [4–7]. However, studies of EOSs for amorphous materials are inadequate.

There are several experimental and theoretical approaches to determine EOS for solids [7–12]. Some of them use the results and techniques of Vinet, Davydov, Birch-Murnaghan, and Rose-Vinet [13–16].

One is the Molecular dynamics (MD) method, which aims to determine phase space trajectory of a physical system via numerical integration of classical Newton’s equations of motion defined for the model system [17, 18]. The forces exerted on the atoms in a model system are derived from a model potential energy function representing the physical interactions of atoms with each others. By solving the equations of motion using the methods and algorithms of numerical integration one can reach the minimum energy position in phase space in which the model system takes place. The general idea is to identify a point in the phase space during integration for which there is a state of minimum energy, as a reflection of the real physical system.

In the present study, the physical interactions between atoms in a nickel system have been modeled with the Voter-Chen version of the embedded atom method (EAM) based on many-body interactions. In isothermal and isobaric conditions, several anisotropic molecular dynamics simulations were carried out for both crystal (c-Ni) and amorphous (a-Ni) model nickel structures. The EOSs for c-Ni and a-Ni structures were determined from obtained thermodynamic data. Also, The EOSs obtained from MD simulations here were compared with those of Vinet and Davydov.

2. Method

The EOS for a given thermodynamic system is generally expressed in the mathematical form $P = f(VT)$. In order to obtain isothermal bulk modulus K_T and thermal expansion coefficient α for a physical system under constant pressure, it is enough to know the P-V-T relationship [12]:

$$K_T = -V \left(\frac{\partial P}{\partial V} \right)_T \quad (1)$$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (2)$$

Two methods used often to determine the P-V-T relationship at high pressures and high temperatures are known as the Vinet and Davydov equations of state [13]. Other EOSs used for solids are the Birch-Murnaghan, Stacey, and Rose-Vinet, etc. [3, 8, 15, 16].

In the present study, results from MD simulations are compared with the only two known EOSs from Vinet and Davydov; the comparisons are elaborated in the following two subsections.

2.1. Vinet EOS

The Vinet EOS is based on the interatomic potential description and its parameters are derived from experimental data, and is given by [13, 14]

$$P = 3K_0x^{-2}(1-x) \times \exp[\eta(1-x)]. \quad (3)$$

Here, $x = (V/V_0)^{1/3}$, $\eta = \frac{3}{2}(K'_0 - 1)$, V_0 is the volume at zero pressure, K_0 is the bulk modulus at zero pressure and the derivative of the bulk modulus is K'_0 . Also, isothermal bulk modulus is obtained as follows using the Equation (1):

$$K_T = K_0x^{-2} [1 + \{\eta x + 1\} (1-x)] \times \exp[\eta(1-x)]. \quad (4)$$

2.2. Davydov EOS

Via a similar approach, the Davydov equation of state is given as follows [13, 14]:

$$P = \frac{3K_0}{(f+2)} \left[x^{-4/3} + fx^{-1} - (f+1)x^{-2/3} \right] \times \exp \left[f(1 - x^{1/3}) \right] \quad (5)$$

$$K_T = \frac{K_0}{(f+2)} \left\{ 4x^{-2/3} + 4fx^{-1} + (f^2 - 2f - 2)x^{-2/3} - f(f+1)x^{-1/3} \right\} \\ \times \exp \left[f(1 - x^{1/3}) \right], \quad (6)$$

where f is given by

$$f = \frac{3}{4} \left\{ (K'_0 - 3) + \left[(K'_0 + 1) \left(K'_0 - \frac{5}{3} \right) \right]^{1/2} \right\} \quad (7)$$

The parameters in these equations can be taken from experimental data.

2.3. Molecular dynamics method

In this study, the MD method developed by Parrinello and Rahman [19], which allows anisotropic volume change, has been used for determining the changes of thermodynamic parameters of nickel along isothermal and isobaric curves. In the MD method, the conserved quantity is the enthalpy, ($H = E + P \cdot V$). For a statistical ensemble with constant number of particles N , constant pressure P and constant enthalpy H , the MD cell axes are defined by three vectors depending on time. So, the MD cell axes become the dynamical variables involving in the Lagrangian given by

$$L = KE_p + KE_H - PE_P - P \cdot V. \quad (8)$$

Here KE_p is the total kinetic energy of particles, KE_H is the kinetic energy of the MD cell, PE_P is the total potential energy of particles, and PV is the thermodynamic potential of the MD cell. The equations of the motions for the system can be derived from the Equation (8), following the instructions of classical mechanics. The equations of motions are second order differential equations. Hence, one can transform the equations to the initial value problem and solve them by using numerical methods. Consequently, the phase space trajectory of the system is achieved. However, in order to reach proper results it must be chosen appropriate functions that represent the physical interactions between particles in the modeled system.

In our simulations, interatomic interactions were modeled by Voter-Chen formalism of EAM. In the EAM approach, the potential energy of an atom in a crystal is given by the sum of total electrostatic energy and the energy required for embedding the atom into its location in the crystal [20, 21]. So, total potential energy of the system with N particles, which is used in Equation (8), is written as

$$PE_P = \frac{1}{2} \sum_{i,j}^N \varphi(r_{ij}) + \sum_i^N F_i \left[\sum_j \rho_j(r_{ij}) \right], \quad (9)$$

where r_{ij} is the distance between atoms i and j , φ is a pairwise interaction potential depending only on nuclear separates, F is the embedding functional, and ρ_j is the electrostatic charge contribution on the location i from

atom j . These functions and their parameters can be found in literature [21]. Rather than the run-time calculations of these functions, their tables of values with respect to distance between atoms can be used with together numerical interpolation, i.e. tabulated EAM formalism. In this study, the MD simulations have been performed in this way and the tables of the functions were received from literature [22].

2.4. MD Simulations

The equations of motions of the modeled systems were solved using the Verlet algorithm. Size of the time step for integration was adopted to be 1.5×10^{-15} s. The beginning structures of the MD cell for all of the model systems were constructed by placing 1372 Ni atoms on fcc lattice points and periodic boundary conditions were applied on the cell axes. The pressure on the system was kept at zero and the temperature was increased from 100 K to 1500 K with 100 K steps. The same simulation study was made separately for 1, 2, 4, 10, 15 and 20 GPa pressure values in order to obtain the curve families of isotherms and isobars for the crystal model (c-Ni). Fast cooling technique was applied on the melted model nickel, equilibrated for a period of 50k integration steps (50 ps) at 2000 K temperature, to acquire the amorphous structure of nickel model (a-Ni), using the cooling rate of 3.84×10^{12} K/s. The obtained model a-Ni under zero pressure was heated from 200 K to 400 K in 25 K increments. After that, the calculations for 1, 2, 4, 10 and 20 GPa pressure values were reiterated for model a-Ni. Then, P-V curves obtained from simulations were compared with the curves calculated from both Vinet and Davydov EOSs using experimental data. In the calculations of Vinet and Davydov EOSs, the values of equation parameters V_0 , K_0 and K'_0 were taken as 10.95 \AA^3 (43.8/4), 181 GPa and 5.2 GPa respectively, from the literature [23].

In order to protect structural stability and to prevent any solid-solid phase transition, the amorphous model a-Ni has been heated up to 400 K. Furthermore, a-Ni model has been forced up to 20 GPa pressure. Nevertheless, it has been observed that the a-Ni model remains in its stable structure under these thermodynamic conditions.

3. Results and discussions

The results of the simulations can be examined in two groups: firstly, the calculation of isobar curves obtained by changing the temperature of the model system under constant pressure and, secondly, the calculation of isotherm curves for the system under different pressures, and constant temperature. The plethora of data makes it impracticable to present all of it in tables. Therefore, data is restricted to c-Ni and a-Ni model systems under different pressures and at 300 K constant temperature, with the atomic volumes, the potential energies per atom, molar enthalpy and isothermal bulk modulus calculated from equation (1) and given in Table 1. Since the a-Ni model is not stable at the temperatures higher than 400 K, for only the c-Ni model under zero pressure the changes of the same variables with temperature are given in Table 2.

By using the data in Table 1, P-V graphics have been plotted for c-Ni and a-Ni models and is shown in Figure 1. Also, P-V curves obtained from Vinet and Davydov EOSs given by the equations (3) and (5) are shown in Figure 1.

When the isotherms are analyzed, one can see that the curves for c-Ni and a-Ni models are in qualitative agreement with the curves obtained from Vinet's and Davydov's EOSs; and that, especially for the c-Ni model, the curve from 10 GPa to 20 GPa is in good agreement with the reference EOSs curves. However, it has been observed that the a-Ni model has a larger atomic volume and that the change of this quantity with pressure,

Table 1. Atomic volumes, potential energies per atom, molar enthalpy and calculated isothermal bulk modulus values changing with pressure for c-Ni and a-Ni models at a constant temperature of 300 K.

P (GPa)	E_p (eV)		H (kJ/mol)		V (\AA^3)		K (GPa)	
	c-Ni	a-Ni	c-Ni	a-Ni	c-Ni	a-Ni	c-Ni	a-Ni
0	-4.433	-4.313	-423.8	-412.3	11.0828	11.5788	168.9	152.6
0.5	-4.432	-4.314	-420.4	-408.9	11.0501	11.5409	171.6	153.1
1.0	-4.432	-4.315	-417.1	-405.5	11.0178	11.5032	174.8	161.5
2.0	-4.432	-4.315	-410.6	-398.7	10.9548	11.4319	181.8	164.3
4.0	-4.432	-4.315	-397.6	-385.2	10.8343	11.2928	200.4	175.5
10	-4.423	-4.304	-359.6	-345.6	10.5099	11.1641	221.7	186.1
20	-4.388	-4.265	-298.4	-282.2	10.0583	10.4155	–	–

Table 2. Atomic volume, V , potential energy per atom, E_p , and molar enthalpy, H , values changing with temperature for only c-Ni model under zero pressure.

T (K)	E_p (eV)	H (kJ/mol)	V (\AA^3)
100	-4.460	-428.9	10.97
300	-4.433	-423.8	11.08
500	-4.404	-418.5	11.20
700	-4.374	-413.1	11.33
900	-4.342	-407.5	11.46
1100	-4.308	-401.7	11.62
1300	-4.271	-395.7	11.78
1500	-4.232	-389.4	11.96

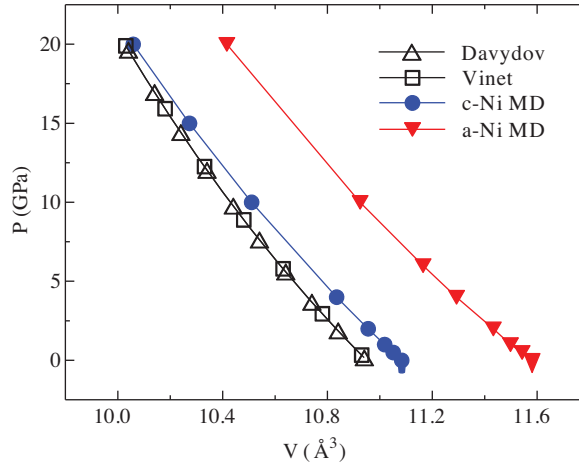


Figure 1. Isotherms for c-Ni and a-Ni models at 300 K with Vinet and Davydov EOSs.

i.e. isothermal bulk modulus or the slope of isotherm within any pressure range is larger than that of the c-Ni model. This is an expected result, when the atomic structures and densities of the amorphous materials and the close-packed structures of crystal structures are taken into account. The isothermal bulk modulus was

calculated as 168.9 GPa for c-Ni model and 152.6 GPa for a-Ni model, using equation (1) with the data given in Table 1, within zero to 0.5 GPa range and at 300 K temperature. It has been seen that the calculated isothermal bulk modulus for c-Ni model exhibits error on the order of -6.7% compared with the experimental value of 181 GPa [23]. Changes of isothermal bulk modulus for both model systems have been plotted as a function of pressure and is shown in Figure 2. Also, its first order function, $K = f(P)$, determined from linear curve fitting can be seen in this figure, K_C for c-Ni model and K_A for a-Ni model system. If these equations were taken into account, the isothermal bulk modulus for both model systems would be 170.8 GPa and 155.8 GPa for c-Ni and a-Ni models, respectively. Also, the pressure derivatives have been determined to be 5.39 for crystal and 3.32 amorphous models. The experimental value of pressure derivative of isothermal bulk modulus is 5.2 for crystal nickel [23]. So, the error in calculation of pressure derivative for crystal model is 3.7 pct. However, its experimental value for amorphous case was not found.

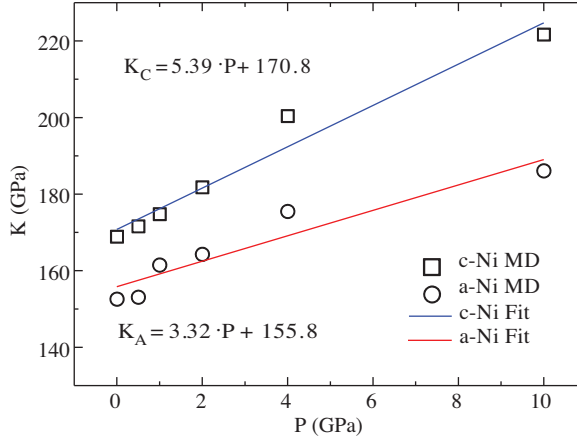


Figure 2. Changes of isothermal bulk modulus for crystal and amorphous models with pressure and its linear equations.

The EOSs for c-Ni and a-Ni models have been determined by using the polynomial curve fitting method and are given as

$$P(V)_C = -280.9 + 165.7 \cdot V - 21.7 \cdot V^2 + 0.82 \cdot V^3 \quad (10)$$

$$P(V)_A = 2687 - 653.3 \cdot V + 53.9 \cdot V^2 - 1.51 \cdot V^3. \quad (11)$$

4. Conclusion

In conclusion, by using the molecular dynamics method proposed by Parrinello and Rahman, based on the Voter-Chen embedded atom method including many-body interatomic interactions, the thermodynamic parameters such as atomic volume, molar enthalpy, potential energy and isothermal bulk modulus of the amorphous- and crystal-structured nickel were obtained. The P-V curves for amorphous and crystal model systems were plotted and the EOSs were determined via polynomial curve fitting method of obtained data. Also, changes of isothermal bulk modulus with pressure were plotted and their pressure derivatives for both model systems were calculated. The obtained data in this way were compared with the values calculated from the EOSs of Vinet and Davydov.

Although obvious discrepancies between Vinet and Davydov EOSs are not observed, it has been determined that there are an apparent difference between the values from our MD simulations and Vinet or Davydov

EOSs. The differences be attributed to the fact that the number of atoms used in the simulations may not be enough to represents the anharmonic effects that occur in real bulk nickel system under high pressure [24]. However, the calculated isothermal bulk modulus, 168.9 GPa, is in agreement with experimental value of 181 GPa with an error of -6.7% . Especially, experimental and theoretical studies made on EOS for amorphous structures are quite limited in the literature. So, the calculated isothermal bulk modulus, 152.6 GPa, and its pressure derivative of 3.32 for amorphous structures can be used in further work.

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