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Molecular dynamics simulations of the melting curves and nucleation of nickel under pressure

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ABSTRACT

Three embedded atom method potentials have been applied to investigate the melting properties of nickel under compression. In these three potentials, Mendelev's potential can reproduce a satisfying melting curve, which accords well with the experiments and first-principles calculations. Thus, we recommend that the Mendelev's potential should be a reliable potential for simulating melting properties of nickel. Using Mendelev's potential, we calculated the melting of Ni with two approaches, i.e., hysteresis approach and two-phase method. Both approaches produce results in very close proximity, with the disagreement less than 4.35% at the applied pressures. Fitting the well-known Simon equation to our melting data yields the melting curves for Ni: $1651(1+P/35.172)^{0.607}$ (hysteresis approach) and $1725(1+P/39.812)^{0.617}$ (two-phase approach). Based on the hysteresis method, we investigated in detail the melting nucleation of nickel at high pressure, and found that with pressure increasing, the critical nucleus size r^* increases fast first and then decreases, and again rises. When taking account of the Gibbs free energy barrier ΔG^*, it found that the ΔG^* increase monotonically with pressure up to 300 GPa, and can be described as a third-order polynomial relation.

1. Introduction

The melting of metals under compression is of great interest in condensed-matter physics, geophysical and planetary sciences, high-pressure physics, etc. Over the past decade, extensive experimental [1–8] and theoretical [9–16] studies have been performed on the melting properties of a number of metals. However, the accurate determination of melting curves under compression is still challenging both for experimentalists and theorists. The enormous discrepancies between diamond-anvil cell (DAC) measurements [1,2,17,18] and shock-wave (SW) data [19,20] have not yet been fully resolved. In the case of Ni, almost a thousand degrees of discrepancies exist in extrapolating from DAC pressures of about 60 GPa to SW pressure of 100 GPa [7,12,21], so the high-pressure melting curve of Ni also remains inconclusive up to now.

On the theoretical side, several attempts at calculating the melting properties of Ni have been proposed [12,22–25]. Most of these studies have been performed using empirical interatomic potentials [22–24]. Only Pozzo and Alfè [12] adopted ab initio calculations to calculate the melting curve of Ni from 0 to 100 GPa. Ab initio prediction is expected to be reliable, because it has no any adjustable parameters and was firmly established more than two decades ago. However, it failed to give a consensus with the recent DAC measurements [7] at high pressure, as well as other simulations based on empirical potentials [24]. This motivates us to further investigate the high-pressure melting of Ni.

To date, several techniques have been used to determine the melting curves of materials: one-phase or hysteresis method [26], two-phase or solid–liquid coexistence method [27], free energy method [28–31], and Z method [32–34]. In the present work, we adopted one- and two-phase approaches to investigate the melting of Ni. In the one-phase method, a solid at a given pressure is heated until melt (HUM), and then the obtained liquid is cooled until freezing. The melting temperature is estimated from the temperatures of the maximum overheating and overcooling states. In the two-phase method, MD simulations are performed on supercells containing a solid–liquid interface, and the overheating can be overcome in the traditional HUM approach. The melting temperature is obtained from the solid–liquid coexistence, where the free energies of solid and liquid states are equal. In both approaches, the melting curves are strongly dependent on the selected empirical potential parameters. Different potential parameters can reproduce different melting curves. Most potential parameters were only fitted to the properties of solid phase. However, if they were fitted to those of both solid and liquid

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phases, one could correctly reproduce the melting curves of materials. In this work, we investigated in detail the melting curves of nickel using MD simulations with three EAM potentials. We hope we can find a reliable potential to simulate melting properties of nickel, and then it can be further used to simulate other properties such as thermoelastic and thermodynamic properties, etc.

The rest of the paper is organized as follows: in Section 2, we briefly described the used model and the simulation details. In Section 3, we presented the detailed simulation results and the discussions; the general conclusions were drawn in Section 4.

2. Theoretical methods and calculation details

2.1. Potential functions

For molecular dynamics simulations of melting of nickel, we have adopted three EAM potentials (EAM-1 [35]; EAM-2 [36]; EAM-3 [37]) to compare which one is appropriate to simulate the melting properties of nickel at high pressures and high temperatures. There are some fitted parameters' differences among the three EAM potentials. In the EAM, the total energy of an atomic system is represented by

$$U=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\varphi(r_{ij})+\sum_{i=1}^{N}\Phi(\rho_i) \tag{1}$$

where the subscripts i and j label distinct atoms, N is the number of atoms in the system, φ is a pair-interaction potential as functions of distance r_{ij} between atoms i and j and Φ is the embedding energy as functions of the host electron density ρ_i on atom i. The host electron density,

$$\rho_i=\sum_j \psi(r_{ij}) \tag{2}$$

is the sum of atomic electron densities created at site i by all other atoms of the system. The tabular forms of these potentials can be found in Refs. [38,39].

2.2. Molecular dynamics simulations

All MD simulations were performed by using the large-scale atomic/molecular massively parallel simulator (LAMMPS) software package [40] with period boundary conditions. A time step of 2 fs was used to perform the integration of the Newton equation of motion and the smooth particle mesh Ewald method [41] was employed with the electrostatic interaction. The Nośe–Hoover thermostat and barostat method [42] was applied to control the temperature and pressure. We typically used 60,000 time steps for the equilibration run, and another 40,000 time steps for calculating the average thermodynamic properties. To verify that 100,000 time steps were sufficient for present simulations, different time steps were used at each simulated pressure.

In the one-phase simulations, we started with the supercells consisting of 6 × 6 × 6, 8 × 8 × 8, 10 × 10 × 10 conventional unit cells corresponding to 864, 2048, and 4000 Ni atoms in the fcc structure. The supercell was subjected to incremental heating under the isothermal–isobaric (NPT) ensemble at fixed pressure until melt (T_+, Fig. 1); and then, the obtained liquid Ni was cooled by the same temperature augment until recrystallization (T_-). The equilibrium melting point T_m can be estimated from the magnitudes of superheating, T_+, and supercooling, T_-, temperatures: [26]

$$T_{\rm m}=T_+ + T_- - \sqrt{T_+T_-}. \tag{3}$$

The two-phase MD simulations started with the supercells containing 7 × 7 × 14, 8 × 8 × 16, 9 × 9 × 18 unit cells, respectively corresponding to 2744, 4096, 5832 Ni atoms in the fcc structure. We froze the half part of the z-coordinate of the supercell, and then heated another half up to 8000 K (far above the melting point) in the microcanonical ensemble (NVE). Consequently, the coexistence phase containing a solid–liquid interface was constructed. The obtained coexistence phase box was used as the initial configuration for further simulations, which is shown in Fig. 2(b). In the two-phase simulations, the solid phase is identified by periodical arrays of atoms, while in the liquid phase the atoms distribute randomly. To obtain two-phase melting points, we heated the system under the NPT ensemble. If the systemic temperature is too high, the system containing both a solid and a liquid (Fig. 2b) will melt (Fig. 2c); if the systemic temperature is too low, the system will eventually crystallize (Fig. 2a). By this means, the melting temperature can be bracketed in a desired interval by performing multiple simulations at different temperatures for any given pressure.

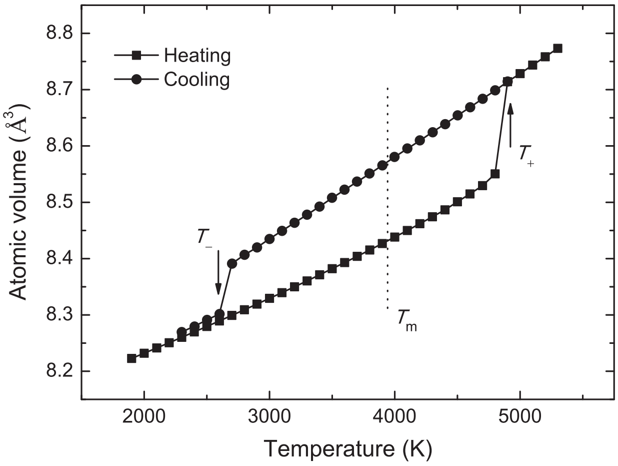

Fig. 1. Atomic volume versus temperature during incremental overheating and overcooling process of Ni at 100 GPa. The melting point T_m can be estimated from the overheating and overcooling temperatures T_+, and T_-, using Eq. (3).

2.3. Melting nucleation

Melting represents a typical first-order phase transition with two metastable states existing on both sides of the transition point. The transition point can be determined by the equality of the corresponding thermodynamic potentials. Nevertheless, the transition point is triggered by nucleation, in which the Gibbs free energy barrier (ΔG^*) to forming nuclei of the daughter phase should be overcome. Based on the one-phase method, we can investigate the issue of melting nucleation. According to the classical homogeneous nucleation theory for solidification [43], in an ideal case of a spherical critical nucleus where the strain energy duo to phase change is neglected [44], a critical size of nucleation can be expressed as

$$r^*(T)=\frac{2\gamma_{sl}T_m}{\Delta H_m(T-T_m)} \tag{4}$$

and a critical work of nucleation

$$\Delta G^*(T)=\tfrac{4}{3}\pi\gamma_{sl}r^{*2} \tag{5}$$

can be obtained for the homogeneous nucleation of melting. Here T_m, ΔH_m and γ_{sl} are melting point, enthalpy of fusion and solid–liquid interfacial energy, respectively. The γ_{sl} can be calculated as [45]

$$\gamma_{sl}=\left(\frac{3}{16\pi}\beta k_B T_m \Delta H_m^2\right)^{1/3} \tag{6}$$

where k_B is the Boltzmann's constant, ΔH_m is the change of enthalpy per unit volume between the liquid and the solid at the melting point