SOLIDS

Dynamic Properties of Ni, Cu, and Fe in the Condensed State: The Molecular Dynamics Method

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Abstract—The distribution function for the density of vibrational states and the velocity distribution function in the crystalline, liquid, and amorphous states of Ni, Cu, and Fe are studied by the molecular dynamics method. In the crystalline and amorphous states, the dynamic properties are qualitatively the same, while in the liquid state, additional low-energy excitations appear. These excitations may be treated as low-frequency resonant modes that arise because of the significant contribution of nonlinearity to the interaction potentials. In all the three states, the velocity distribution functions are found to be Maxwellian; that is, the systems are ergodic, although nonlinearity-related contributions to the interaction potentials are high and the liquid and amorphous states are disordered. © 2004 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Elucidation of amorphization mechanisms on the atomic level is a topical problem today. Amorphization is known to be associated with the formation and evolution of defects (vacancies, dendrites, or clusters) even in the liquid state, i.e., with the liquid state dynamics. Therefore, studying the liquid state of a system that is amorphous in the solid state is of crucial importance for understanding the process of amorphization. Dynamic properties of condensed media define their fundamental characteristics, such as diffusion, heat capacity, heat conduction, entropy, defect formation kinetics, scattering of quasi-particles by each other and by defects, etc. In the thermodynamic limit, these characteristics are completely described by the distribution function for the density of atomic vibrational states (DAVS) and the atomic velocity (or energy) distribution function (AVDF). In our opinion, it is appropriate to study the problem of amorphization in terms of nonlinear system dynamics, since the above processes are related to phase transitions, which are nonlinear effects. The liquid state is possible only when the elastic constant is equal to zero in the presence of nonlinearity: \( \frac{d^2F}{dV^2} = \frac{dp}{dV} = 0 \) (where \( F \) is the free energy, \( V \) is the volume, and \( p \) is the pressure). This means (with no regard for the entropy contribution) that the interaction potential of an atom with all other atoms in the medium (on-side potential) has a flat or two-well bottom; that is, the atom does not have a fixed position. Media with harmonic interaction cannot be in the liquid state, because \( \frac{d^2F}{dV^2} = k \) (elastic constant). In this case, atoms sublime from the free surface [1]. It has been shown [2, 3] that excitations of two types may arise in nonlinear systems, high-frequency local excitations (at a frequency above the cutoff frequency of a crystal) and low-frequency resonant excitations, depending on the type of nonlinearity (hard or soft). The former excitations are today called discrete breathers, which have been the subject of extensive research. They can be visualized as storages of the kinetic energy of a system’s particles or “hot” areas with an elevated concentration of the kinetic energy. It is anticipated that such “defects” appear in amorphous materials and are responsible for long-term relaxation properties [4]. By using the molecular dynamics method, it was shown [5, 6] that such excitations may be present in high-temperature superconductors. As for low-frequency resonant modes, it was suggested [7] that they may diffuse, giving rise to the linear term in the expression for heat capacity at low temperatures in glasses. In other words, it is assumed that nonlinear excitations in nonlinear disordered systems may cover different frequency ranges and be responsible for the fundamental properties of these systems.

EXPERIMENTAL

Simulation was performed with a program package [8] in which emphasis is on the optimization of the time characteristics of the algorithm. A grain (crystallite) contains from 1000 to 2000 atoms, and cyclic boundary conditions are imposed. The system is brought to equilibrium at \( T = 0 \) K. The temperature is set by assigning velocities equal in magnitude but random in direction to the atoms. Then, the system is brought to equilibrium in a real time of \( \sim 10^{-11} \) s. Within this time, the equilibrium DAVS and AVDF set in. The DAVS was calculated through the autocorrelation function [9].

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\[ G(\omega) = \int_{0}^{\infty} \gamma(\tau) \exp(-i\omega\tau) d\tau, \]  \hspace{0.5cm} (1)\]

where

\[ \gamma(\tau) = \sum_{i} \langle v_i(\tau) v_i(0) \rangle / v_i^2(0) \]

is the autocorrelation function, \( v_i(\tau) \) is the velocity vector magnitude of an \( i \)th atom at a time \( \tau \), and \( \langle \ldots \rangle \) means averaging over different time intervals.

Now the system is heated stepwise to the liquid state, further heated to a desired temperature, and then cooled stepwise to \( T = 300 \) K at a rate of \( \sim 10^{-12} \) K/s, thus becoming amorphous.

The pair potential technique makes it possible to calculate the static and dynamic properties. At present, the molecular dynamics method employs model pair potentials adjusted to particular experimental data. We used pair potentials obtained in terms of the Heine–Aborenkov–Animalu pseudopotential approach [10]. In our opinion, they describe the entire set of structural and kinetic properties most adequately. As adjustable parameters, X-ray terms, electron density, and Show screening function were applied. In this case, the calculated basic characteristics of \( s, p, \) and \( d \) metals (lattice constants, elastic constants, phonon spectra, phase transition temperatures, energies of formation and migration of defects, etc.) differ from those found experimentally by \( 10–20\% \).

RESULTS AND DISCUSSION

Figure 1 shows the calculated DAVS for the crystalline, amorphous, and liquid states of Ni, Cu, and Fe. The drastic difference between the three DAVS curves is noteworthy. In the liquid state, the diffusion coefficient for Cu and Ni equals \( 5 \times 10^{-5} \) cm\(^2\)/s; for Fe, \( 10^{-5} \) cm\(^2\)/s. The melting points calculated are \( T_m = 1250 \) K for Ni and 1500 K for Cu. The temperature at which the bcc phase of Fe becomes unstable is 1050 K. At the melting point, the low-energy part of the DAVS curve starts increasing with temperature; that is, additional low-frequency states appear in the system. Such a pattern is typical of all the metals. The occurrence of low-frequency states as low-frequency resonant modes was predicted within the framework of the anharmonic approach (see above). Their identification in our case is a challenge. It appears that, as the temperature grows, the conditions of high nonlinearity are established in the system and, once a critical point (the melting point) is reached, nonlinear excitations, i.e., nonlinear resonant modes, arise. In a homogeneous medium, these modes are not localized and dynamically appear at any

![Fig. 1. Density of atomic vibrational states: (1) \( T = T_m \); (2) \( T = T_m + 100 \) K, and (3) \( T = 300 \) K (crystalline state); (4) \( T = 300 \) K (quenched state). (a) Ni, (b) Cu, and (c) Fe.](image_url)