

phys. stat. sol. (b) **164**, 395 (1991)

Subject classification: 63.50; 61.40; S1.2

*Department of Solid State Physics, Lomonosov State University, Moscow¹⁾ (a) and
Laboratory of Surface and Interface Physics, Eötvös University, Budapest²⁾ (b)*

Molecular Dynamics of the Frozen-In Glassy State of $\text{Ni}_{80}\text{P}_{20}$

By

V. S. STEPANYUK (a), A. A. KATSNELSON (a), A. SZASZ (b),

O. S. TRUSHIN (a), and P. NAYAK (a)

A molecular dynamics approach is used for the dynamic structure simulation of the $\text{Ni}_{80}\text{P}_{20}$ glassy-like system. Calculations are made considering the rapid cooling from melt and the effect of glass transition temperature. Comparison with the experimental data is given with a reasonable correspondence.

Ein Molekulardynamikverfahren wird benutzt für eine dynamische Struktursimulation des glas-ähnlichen $\text{Ni}_{80}\text{P}_{20}$ -Systems. Die Berechnungen werden unter Berücksichtigung der schnellen Abkühlung aus der Schmelze und des Effekts der Glasübergangstemperatur durchgeführt. Ein Vergleich mit den experimentellen Werten wird mit vernünftiger Übereinstimmung durchgeführt.

1. Introduction

In the last few years computer simulation of molecular dynamics (MD) has emerged as one of the powerful tools for investigating various properties of condensed matter. In this method the properties of structures of particles (usually of about a few hundred in number) interacting via pair potentials are investigated by numerical integration of the classical equations of motion. Extensive work has already been done either using standard potentials [1] or considering packing of hard spheres [2]. These methods have already been extended also to several metallic systems. The calculations, however, were carried out using modified pair potentials, reproducing better the experimental data. Some excellent reviews have been published on this topic [3 to 5].

Recently due to the wide-range technical applications, there has been great interest in investigating the various properties of amorphous materials. The subject of our present paper is an amorphous model system: the $\text{Ni}_{80}\text{P}_{20}$ alloy. Considering the packing of hard spheres a successful model for this system was proposed [6] before. This model well explains the characteristic static structure of the alloy, but fails to give any information about the dynamics of the structural changes in the process of amorphization [6]. Since a MD computer simulation study involves numerical information of the motion of atoms interacting through pair potentials, we expect to obtain the dynamical behaviour of amorphization at the microscopic level. To study the Ni-P system the MD method was used before [7] as well. MD calculations were made, simulating a new quenching procedure known as 'mass weighted steepest descent method' for finding out the potential minimum for a stable structure. In this way the relevant features of the Ni-P alloy compared with the experimental X-ray data [8] have been successfully reproduced. This approach is successful to predict

¹⁾ Lenin Hills, SU-117234 Moscow, USSR.

²⁾ Muzeum krt. 6-8, H-1088 Budapest, Hungary.

the static properties of the amorphous Ni-P alloy, but it fails to provide any information on the dynamics of the phase transformation from liquid to amorphous state. The evolution process of a metastable phase, such as the amorphous one, is in the center of many scientific studies [9, 10].

Recently new pair potentials have been proposed for the Ni-P system [11] calculated on the basis of experimental data for electro-deposited amorphous Ni-P alloys. Bennet's model [6] was improved by using a potential which allows the relaxation of atoms to get more realistic structural characteristics of this system. It would also be interesting to use such potentials in the MD simulations of the Ni-P alloy.

In this paper, we explore the properties of the phase transition from liquid to amorphous state through simulated rapid quenching, based on MD results. The truncated Morse potential has been used for modeling the interaction between atoms of the $\text{Ni}_{80}\text{P}_{20}$ system. For a better fitting to the experimental data the values of parameters involved in this potential have been taken from [11].

2. The Model and the Simulation Process

Our molecular dynamical calculations have been performed in a microcanonical ensemble, where the number of particles (N), the volume (V), and the energy of the system (E) are fixed. The motion of 205 Ni atoms and 51 P atoms has been considered. The main question to be answered is whether the small particle number, using well fitted potentials [11], can characterize the basic properties of the electronic structure and the amorphous-crystalline phase transition of the Ni-P system, which can be regarded as a model? To solve this our considerations are centered on the reality of the radial distribution function (RDF) and the coordination number in the model system, investigating the second-peak behavior in RDF at the phase transition [12]. The atoms were confined in a box and interacting via pair potentials. A periodic boundary condition is imposed on the system. The volume of the box is calculated from the experimental mass density (7.82 g/cm^3) [8] for the amorphous $\text{Ni}_{80}\text{P}_{20}$ system.

The set of pair potential functions of interactions is modeled by the Morse potential with parameters [13] given as follows:

$$U(r) = \varepsilon [\exp(-2a\{(r/r_0) - 1\}) - 2 \exp(-a\{(r/r_0) - 1\})] f(r/r_0),$$

where

$$f(y) = \begin{cases} 1 & \text{for } y \leq 1(1), \\ 3z^4 - 8z^3 + 6z^2 & \text{for } 1 < y_c < (r_0/r), \\ 0 & \text{for } y_c \geq (r_0/r), \end{cases}$$

where

$$z = (y - r_c/r_0)/(1 - r_c/r_0), \quad a = 3.76 \quad \text{and} \quad r_c/r_0 = 1.4.$$

The parameters ε and r_0 used for Ni-Ni, Ni-P, and P-P are given in Table 1.

The integration of the equations of motion has been performed using the so-called 'leap-frog' algorithm [14] with a time step of $dt = 10^{-15} \text{ s}$. To start the simulation, the atoms of Ni and P were allowed to occupy the f.c.c. lattice sites within the box randomly. In this state a velocity was assigned to each particle in accordance with a Maxwell distribution

information
the evolution
ny scientific

calculated on
net's model
to get more
to use such

amorphous
ated Morse
 $\text{Ni}_{80}\text{P}_{20}$ system.
olved in this

cal ensemble,
system (E) are
main question
als [11], can
s-crystalline
olve this our
RDF) and the
avior in RDF
cting via pair
olume of the
e amorphous

orse potential

le 1.

g the so-called
simulation, the
box randomly.
ell distribution

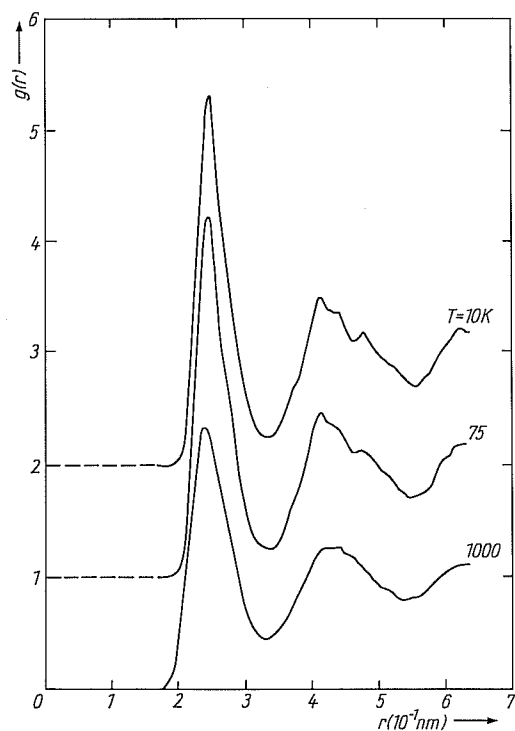
Table 1

The values of the parameters ϵ and r_0 in the Morse potential obtained from the experiment [11] for Ni-Ni, Ni-P, and P-P

pair potential	ϵ (eV)	r_0 (nm)
$U_{\text{Ni-Ni}}$	+0.19	0.253
$U_{\text{Ni-P}}$	+0.32	0.224
$U_{\text{P-P}}$	+0.06	0.210

at the given initial temperature of 2000 K. The system was stabilized to reach the liquid state at the given temperature in 3000 time steps. Starting with this temperature, the system was then cooled in the next 20000 steps (with average rate of cooling of 10^{14} K/s) to 10 K by rescaling the velocities of all particles through multiplying by a constant factor after every ten steps. The whole process consists of a sequence of cooling, stabilizing, averaging at some intermediate temperature ranging from 2000 to 10 K while bringing the system from the molten to the amorphous state.

The results of the calculations of the pair correlation function $g(r)$, the diffusion coefficient D , and the partial pair correlation functions $g_{ij}(r)$ are presented in the following. The plots of these functions at different temperatures reflect various significant features of the $\text{Ni}_{80}\text{P}_{20}$ alloy, when going from the molten to the glass-like state in the simulated process of rapid cooling.



The pair correlation function $g(r)$ for three different temperatures, i.e. 1000, 75, and 10 K, has been plotted in Fig. 1. There is a splitting in the second peak, which is one of the important properties of glass-like states. However, the calculation of the self-diffusion coefficient for Ni at this temperature was found to be too high ($D = 4.8 \times 10^{-6} \text{ cm}^2/\text{s}$), which means that the splitting of the second peak could occur even if the system is existing in the supercooled liquid state. The diffusion coefficient near $T = 10$ K suddenly decreases by a factor of 100 ($D = 0.098 \times 10^{-6} \text{ cm}^2/\text{s}$ for Ni).

Fig. 1. Pair correlation function of the $\text{Ni}_{80}\text{P}_{20}$ system, cooled down from 2000 K to three different temperatures: 10, 75, and 1000 K

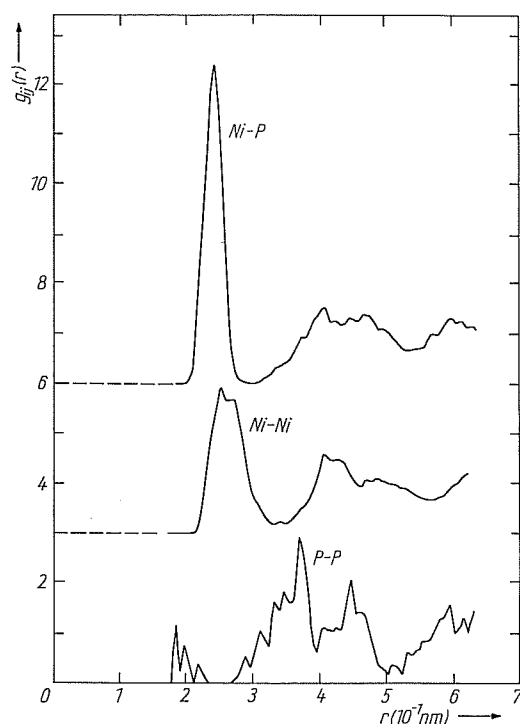


Fig. 2. Plot of the partial pair correlation function at $T = 10$ K for Ni-P, Ni-Ni, and P-P

This is an indication of the onset of a phase transition (glass transition, T_g) to the amorphous state. A plot of the partial pair correlation function $g_{ij}(r)$ at $T = 10$ K is given in Fig. 2. A strong interaction between the Ni and P atoms leads indirectly to a considerable correlation between the positions of these atoms. This creates a trend of compound formation in the system Ni-P. Our calculated values of the coordination number for both Ni-Ni and Ni-P have been compared with the experimental results [15] in Table 2. It is found that the agreement with the experimental data for Ni-Ni and Ni-P pairs is reasonably good. However, there is a discrepancy in the coordination number for the P-P pair. Probably this discrepancy is created by the low number

of P atoms when the cluster formation becomes difficult and the averaging of pair correlation functions is less reliable. It is obvious that the discrepancies in the comparison with experiment in this small model system appear first of all in the partial quantities of the small-concentration component. The positions of the maxima r_1, r_2 and the first minima r_{\min} of the radial distribution function and the average coordination number have been collected in Table 3. A good agreement with experimental data [8] can be seen. There is hardly any shift in the positions of the maxima and only a slight shift is connected with change of temperature, in agreement with experiments [8]. There still exist a few minor discrepancies with experimental observations which are assigned to the improper values of the parameters of the potential.

Table 2

Comparison of the partial coordination numbers (Z_{ij}) for Ni-Ni, Ni-P, P-Ni, and P-P. The calculated values are for temperatures $T = 10$ and 1000 K and the experimental values [15] for $T = 1473$ K

type of pair	experiment [15]	present calculation	
	$T = 1473$ K	$T = 10$ K	$T = 1000$ K
Ni-Ni	10.60	11.26	10.90
Ni-P	8.10	11.23	10.80
P-Ni	2.60	2.53	2.57
P-P	3.40	1.34	1.49

Table 3
Comparison of the maxima r_1 , r_2 and minima r_{\min} of the radial distribution function at $T = 75$ K

	r_1 (nm)	r_{\min} (nm)	r_2 (nm)	N
present calculation ($T = 75$ K)	0.2422	0.3277	0.4417	13.03
experiment [8]	0.2547	0.3150	0.4430	13.01

Table 4
Comparison between our present calculation and experimental results

	r_1 (nm)	r_2 (nm)	r_3 (nm)
Bennet's results [6]	1	1.73	2.0
present calculation	1	1.727	2.00

Comparing the hard-sphere packing results with those of Bennet [6] (Table 4) a complete agreement is seen.

3. Conclusion

In our present paper, a computer simulation for a system with small number of particles has been performed to see the changes at the transition from the molten to the amorphous state of the binary system Ni₈₀P₂₀ at fast cooling. A splitting of the second peak in the pair correlation function characterizing the local order is observed when the system is cooled down. The sudden fall of the diffusion coefficient with temperature also indicates the process of amorphization (glass transition) at a given cooling rate. The overall agreement of the simulation with the experimental data proves the validity of using the pair potential functions based on static structure data in the study of the dynamics of phase transformation from the liquid to the amorphous state, and the applicability of relatively small systems to describe the basic properties of such model systems.

References

[1] A. RAHMAN, Phys. Rev. **136**, A405 (1964).
L. VERLET, Phys. Rev. **159**, 98 (1967).
[2] B. J. ADLER and T. E. WAINWRIGHT, J. chem. Phys. **33**, 1439 (1960).
[3] M. R. HOARE, Ann. New York Acad. Sci. **281**, 157 (1978).
[4] Y. WASEDA, Progr. Mater. Sci. **26**, 1 (1981).
[5] J. L. FINNEY, in: Amorphous Solids and the Liquid State, Ed: N. H. MARCH, R. A. STREET, and M. TOSI, Plenum Press, New York/London 1985 (p. 31).
[6] C. H. BENNET, J. appl. Phys. **43**, 2727 (1972).
[7] T. A. WEBER and P. H. STILLINGER, Phys. Rev. B **32**, 5402 (1985); **31**, 1954 (1985).
[8] G. S. CARGILL III, Solid State Phys. **30**, 227 (1975).
[9] A. SZASZ, D. J. FABIAN, Z. PAAL, and J. KOJNOK, J. non-crystall. Solids **103**, 21 (1988).

- [10] X. D. PAN, A. SZASZ, and D. J. FABIAN, J. appl. Phys. **66**, 146 (1989).
- [11] Ji CHEN Li and N. COWLAM, Phys. Chem. Liquids **17**, 29 (1987).
- [12] J. ULLO and S. YIP, Phys. Rev. A **39**, 5877 (1989).
- [13] J. LAKKONENE and R. M. NIEMINEN, J. non-crystall. Solids **75**, 237 (1985) and references therein.
- [14] D. FINCHAM, Computer Phys. Commun. **21**, 247 (1980).
- [15] Y. WASEDA, Proc. 3rd Internat. Conf. Liquid Metals, Ed. R. EVANS and D. A. GREENWOOD, Academic Press, London 1976 (p. 156).

(Received June 26, 1990; in revised form January 7, 1991)