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Thermodynamic, dynamic and structural relaxation in supercooled liquid and glassy Ni below the critical temperature

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Abstract

The thermodynamic, dynamic and structural relaxations of supercooled liquid and glassy Ni have been investigated using molecular dynamics simulations based on the embedded atom method. The glass transition temperature T_g is estimated to be 800 K by characterizing the pair correlation function, and the critical temperature T_c is 840 K according to the calculated diffusion constant. Three temperature regions can be observed as the temperature decreases: (a) in the temperature range $840 \text{ K} \leq T \leq 1000 \text{ K}$, crystallization of supercooled liquid occurs when the characteristic relaxation time is long enough to reach the incubation time τ ; (b) a complicated region composed of partial crystal and glass will appear within the range $810 \text{ K} \leq T < 840 \text{ K}$; and (c) glass crystallization can be detected as the temperature is below 810 K. Results for dynamic and structural relaxations indicate that not only the crystallization of supercooled liquid but that of the glass derive from the nucleation and growth of crystal nuclei, which relates closely to the structural rearrangements of atoms. A temperature–time–transformation schematic plot has been constructed based on the temperature dependence of the characteristic relaxation times.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the past 20 years, the topic of glass transition has remained a long-standing issue in condensed-matter physics, although significant progress has been made in understanding the properties of glasses by experimental, theoretical and computational efforts [1–4]. So far, it is known that, in the range between high temperatures and the glass transition

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temperature T_g , structural and thermodynamic quantities show a relatively weak temperature (T)-dependence, while general dynamic properties show a pronounced T -dependence, demonstrating complicated dynamic behaviour in supercooled liquids [2]. In particular, even at temperatures below T_g , the dynamics of polymeric systems, structural glasses and other disordered systems are not purely of the vibrational type but contain a very interesting relaxation component, which is known as ‘ageing’ [5]. Therefore, structural and dynamic studies are expected to make major contributions to liquid and amorphous metal research in the future [6].

Molecular dynamics (MD) simulations are an effective tool for gaining insight into the time dependence of the structure and dynamics of supercooled liquids and glasses, and they are also a very useful extension of experimental and analytical investigations of such systems. Information on the positions and velocities of atoms is available at any given time and temperature, which allows us to determine quantities that are very difficult to measure experimentally. Many interesting dynamical phenomena occurring on a timescale between 10^{-12} and 10^{-7} s can be accessible to MD simulations. To date, much work has focused on the relaxation dynamics of supercooled liquids, as well as the nucleation kinetics for solidification, mostly in dealing with computer simulations of simple systems [7–12] to direct observations in colloidal and polymer systems [13, 14]. These experiments and computer simulations on different types of materials provide a qualitative description that is coincident with the mode coupling theory (MCT) [15], which is a theory that predicts a critical temperature T_c at which the α -relaxation time of the system diverges. The diffusion constant and shear viscosity also exhibit different T -dependences: a curved behaviour above T_c and a linear relationship below, when represented in an Arrhenius plot [16, 17]. Numerous investigations have also been made to describe the relaxation dynamics in a temperature range below T_c and find that, despite the difficulty in quantitative calculations, it can be predicted that there is a crossover from a power-law dependence above T_c to a weaker T -dependence below T_c [18, 19]. Such results provide valuable information on the understanding of relaxation dynamics of supercooled liquids. Nevertheless, in general simulations, the model system is chosen to favour the clarification of dynamical relaxations under supercooling, while the crystallization is highly suppressed. Therefore, correct descriptions of the thermodynamic, dynamic and structural relaxation of glass-forming liquids within the temperatures at which the viscosity is much higher are still not really known, and this has been the focus of our current research.

In this paper, we are concerned about the thermodynamic, dynamic and structural properties of supercooled liquid and glassy Ni during the cooling process. Three temperature regions can be divided by the variation of the internal energy. The evolutions of dynamic and structural relaxation in each region are discussed using time–correlation functions and Honeycutt–Anderson (HA) analysis.

2. Computational details

As we have already mentioned above, MD simulations are an important tool to study the properties of glass-forming systems. Horbach *et al* [20] suggested that a system with more than 1000 atoms should be necessary in simulations of the dynamics behaviour of silica to avoid finite-size effects. Therefore, the current MD simulations were performed using a system with 4000 atoms in a cubic box under periodic boundary conditions. The interactions among atoms were calculated via the embedded atom method (EAM). Details of the potential were given by Voter and Chen [21].

During the simulations the temperature was kept constant using the Nose–Hoover thermostat method. The equations of motion were integrated using the Verlet velocity

algorithm. To maintain the stability of the algorithm, the time step was chosen to be 3.5 fs in simulations.

We equilibrated the system for 35 ps in an isothermal and isobaric (*NPT*) condition at $T = 2000$ K. This was followed by a cooling process in which the system was cooled from 2000 to 400 K with a cooling rate of 2.86×10^{13} K s⁻¹. At selected temperatures, the velocities and positions of atoms were noted every 0.07 ps until we had 15 000 configurations, which were used to collect the data analysed and are shown in the following figures. The time dependence of the dynamic properties was studied in an isothermal and isochoric (*NVT*) condition. This means that the volume changes owing to crystallization have been neglected during the simulations. This is somewhat less realistic, but will clearly demonstrate the dynamic effects [22].

3. Structural analysis methods

3.1. Pair correlation function (PCF)

The PCF is regarded as a common parameter used to describe structural characteristics of liquid and amorphous states. It is defined as [23]:

$$g_{i,j}(r) = \frac{L^3}{N_i N_j} \left\langle \left(\sum_{\alpha=1}^{N_i} n_{\alpha j}(r) \right) / 4\pi r^2 \Delta r \right\rangle, \quad (1)$$

where L is the cell length of the cubic box, N_i and N_j are the numbers of atoms i and j , respectively, in systems, and $n_{\alpha j}$ is the average number of j -type atoms around i -type atoms in the spherical shell ranging from r to $r + \Delta r$. The PCF shows the probability of finding another atom in a distance ranging from r to $r + \Delta r$ and is used to detect the structural evolution in the melt.

3.2. Wendt–Abraham parameter (R^{WA})

To formulate a quantitative criterion for specifying the boundary between the supercooled liquid region and the amorphous region, Wendt and Abraham defined an empirical parameter as [24]:

$$R^{\text{WA}} = g_{\text{min}}/g_{\text{max}}, \quad (2)$$

where g_{min} and g_{max} are the magnitudes of the first shell maximum and the first minimum following this maximum in the PCF, respectively. The dependence of R^{WA} over distinct portions of the liquid section and glass section is linear and the slopes of the two sections are different. T_g is the temperature at which the discontinuity in the slope of the curve occurs.

3.3. The Honeycutt–Anderson index

For liquid or glass systems, a very useful assessment of local structure is provided by the Honeycutt and Anderson [25] analysis, in which four parameters, i , j , m and n , are used to distinguish the bonded pairs. The first integer indicates whether or not the atoms in the root pair are bonded, that is, if the root atoms A–B form a bond, $i = 1$; otherwise, $i = 2$. The second integer j denotes the number of near-neighbour atoms common to the root pair. The m represents the number of bonds formed among the shared neighbours. The fourth integer n is added to provide a unique correspondence between the cases when the first three integers are the same but the bond geometries are different. Each of the various phases in a dense bulk system has its own signature in the bonded pairs that characterizes its local structures. In general, the

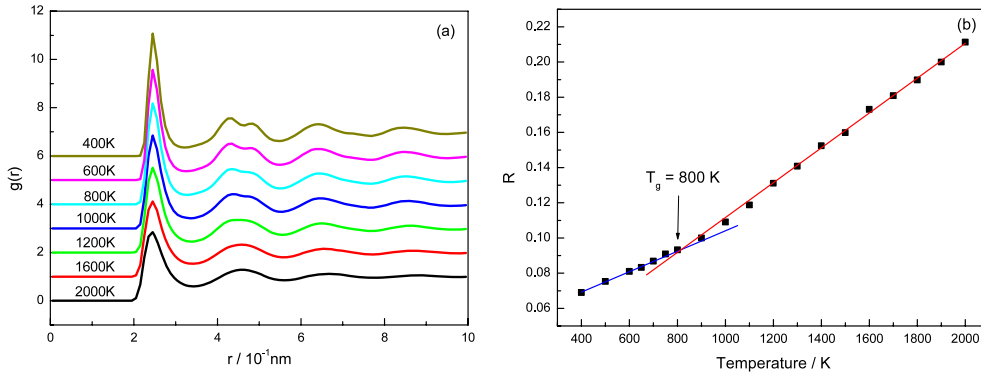


Figure 1. PCF and R^{WA} as a function of temperature for liquid Ni with 4000 atoms, implying a glass transition temperature of $T_g = 800$ K.

1551 pair are characteristic of an icosahedral order; the 1541 and 1431 pairs characterize the defect and disorder local structure; the 1421 pair is the typical pair for a face-centred cubic (fcc) crystal; the 1661 and 1441 pairs are the characteristic pairs for a body-centred cubic (bcc) crystal; while the 1421 and 1422 pairs are related to the hexagonal close packed (hcp) crystal.

4. Time correlation functions

4.1. Mean-square displacement (MSD)

The MSD is defined as:

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle, \quad (3)$$

where $r_i(t)$ is the atomic position of the atom i at time t and $\langle \cdot \rangle$ is the thermal average.

4.2. Non-Gaussian parameter (NGP) [26]

In order to quantify the dynamic heterogeneities of supercooled liquids and glasses, we introduce the non-Gaussian parameter (NGP) α_2 , which is expressed as:

$$\alpha_2(t) = 3 \langle r^4(t) \rangle / 5 \langle r^2(t) \rangle^2 - 1, \quad (4)$$

where $\langle r^2(t) \rangle$ is the MSD, and $\langle r^4(t) \rangle$ is the mean quartic displacement.

5. Results and discussions

To obtain the relevant temperature scale, we first determined the glass transition temperature T_g . The curve of the PCF plotted in figure 1(a) shows a split in the second peak at a temperature of 400 K, implying that the final state of the quenched sample is a glass state. A more sensitive measure of the phase transition is provided by extracting the Wendt–Abraham parameter R^{WA} from PCFs, as expressed in formula (2). The temperature dependence of R^{WA} , displayed in figure 1(b), leads to a clear intersection between two straight lines at $T_g = 800$ K, which indicates structural arrest by the glass transition.

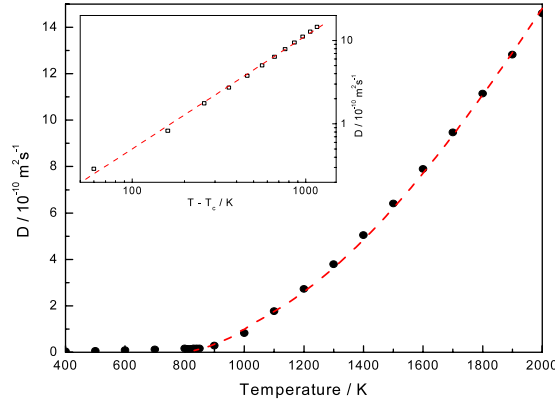


Figure 2. Diffusion constant of liquid and glassy Ni as a function of temperature. The full circles show the values obtained from simulations. The dashed line shows a fit using the power law $D \propto (T - T_c)^\gamma$. The inset shows the diffusion constant D versus $(T - T_c)$ in a log–log representation.

One of the simplest quantities for describing the dynamics of the system is the diffusion constant D , which can be calculated from the atomic mean square displacement by

$$D = \lim_{t \rightarrow \infty} \frac{\langle |r(t + t_0) - r(t_0)|^2 \rangle_{t_0}}{6t}. \quad (5)$$

The diffusion constant D that is obtained is shown in figure 2, and we can see that at higher and intermediate temperatures our data is fitted well by an Arrhenius law with an activation energy of 4.406 eV, which is in agreement with the experimental value of 4.45 eV [27]. In the inset of figure 2 we also show that the curve can be fitted well with a power law, i.e. $D \propto (T - T_c)^\gamma$, as predicted by MCT. Hence we obtain the critical temperature $T_c = 840$ K, with $\gamma = 1.355$.

Figure 3 shows results for the relaxation time dependence of internal energy at temperatures from 1100 to 400 K. It can be found from figure 3(a) that the curve at a temperature of 1000 K shows a time (t) dependence, while that at temperature of 1100 K shows a nearly constant internal energy during the relaxation. As the temperature is below 1000 K, three temperature regions of thermodynamic relaxation are defined by the time dependence of internal energy. In the temperature range $840 \text{ K} \leq T \leq 1000 \text{ K}$, a distinct decrease in energy is detected and the incubation time τ , determined by the onset time of the energy minimum, moves ahead with decreasing temperature (figure 3(a)). This is called the crystallization region of the supercooled liquid. In the temperature range $810 \text{ K} \leq T < 840 \text{ K}$, the internal energy exhibits relatively subtle changes and shows a higher value for long timescales compared with those at 840 and 800 K (figure 3(b)), which is consistent with the fact that metallic glass is in a metastable state. It is considered to be a complicated region. As the temperature is below 810 K, a dramatic drop appears in the energy–time curves and the τ increases rapidly with decreasing temperature, leading to a considerable time for crystallization at 400 K (figure 3(c)). This region is called the region of glass crystallization.

The results of PCFs for different relaxation times at temperatures of 1000, 830 and 800 K, as shown in figure 4, provide convincing support for the definition of three regions. In the crystallization region of supercooled liquid (figure 4(a)), the PCF retains the overall shape of the liquid phase at the beginning of relaxation ($t = 0.21$ ps). As relaxation time progresses, the crystal peak appears at $t = 350$ ps and becomes increasingly distinct with an increase in

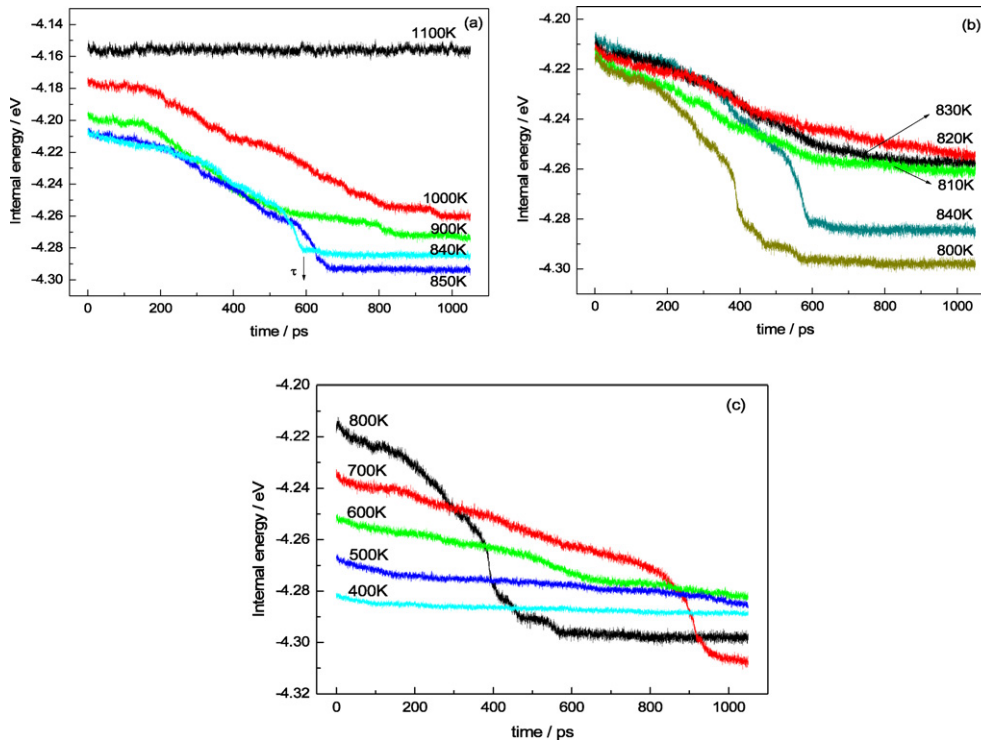


Figure 3. Time dependence of internal energy at several temperatures. Three regions of thermodynamic relaxation are defined: (a) $840 \text{ K} \leq T \leq 1000 \text{ K}$; (b) $810 \text{ K} \leq T < 840 \text{ K}$, where the energies are distinct from those at 840 and 800 K; (c) $T < 810 \text{ K}$.

relaxation time. The results plotted in figure 4(b) show that, in the complicated region, there is a split in the second peak of PCF soon after the relaxation starts ($t = 3.5 \text{ ps}$), which is indicative of amorphous atomic packing. As the time increases, the appearance of a crystal-like peak at $t = 385 \text{ ps}$ indicates that a partial crystal structure has formed. The system becomes a glass state when the temperature drops to 800 K, since a visible split in the second peak of PCF exists in figure 4(c) at $t = 0.21 \text{ ps}$. The crystallization of the glass progresses with the relaxation time, and crystal peaks are very distinct when the relaxation time reaches to 1050 ps.

The time dependence of MSD at several temperatures, plotted in figure 5, shows threefold. (a) For short time ($t < 0.3 \text{ ps}$), the MSD increases with a quadratic dependence on relaxation time due to the free ballistic motion of atoms. (b) For intermediate time, a plateau appears and it becomes larger with a decrease in temperature. The microscopic explanation for the appearance of the plateau is the so-called ‘cage effect’ for a tagged particle [7, 17]. The lower the temperature is, the more extended the plateau is. (c) For longer time, the situation within the three temperature regions is quite different. At higher temperatures, the atomic motion becomes diffusive and MSD shows a linear dependence on time. As the temperature decreases to 850 K, a second plateau emerges in the MSD curve at relaxation times longer than 650 ps. The presence of the second plateau can be considered to be the result of nucleation and growth of crystal phases. Both the onset time and the height of the second plateau decrease with decreasing temperature. The second plateau can also be detected as the system is in the complicated region, whereas the onset time of the second plateau is independent of the decreasing temperature. In the region of glass crystallization, the MSD shows a slow increase

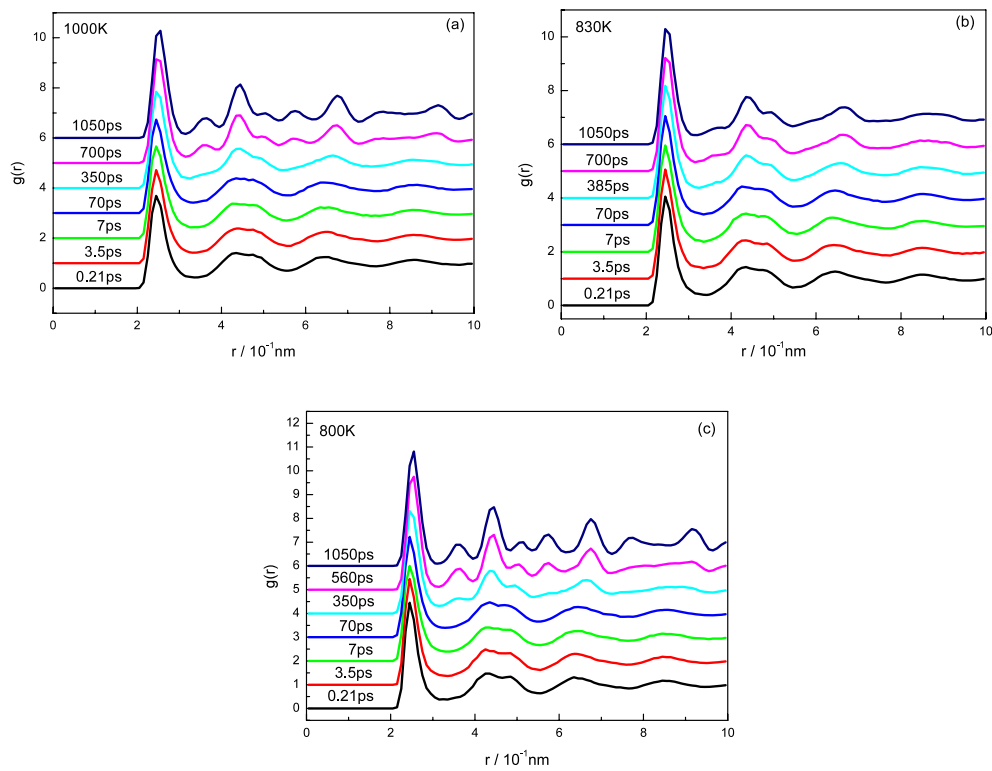


Figure 4. Time dependence of PCF at: (a) 1000 K; (b) 830 K; (c) 800 K.

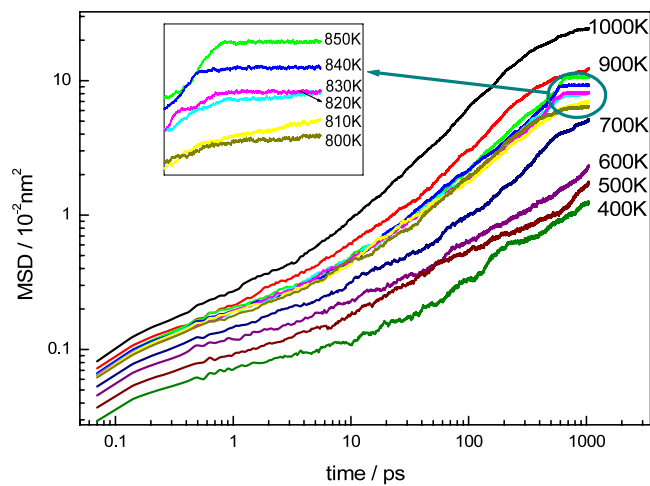


Figure 5. Mean square displacement as a function of time at various temperatures.

with time, indicating a retarded diffusive motion of atoms. The appearance of the second plateau at 800 K implies that the crystallization of glass also follows classical growth of nuclei, consistent with the crystallization model based on heterogeneous nucleation [28]. The onset time of the second plateau rapidly moves to a larger t -value with a decrease in temperature.

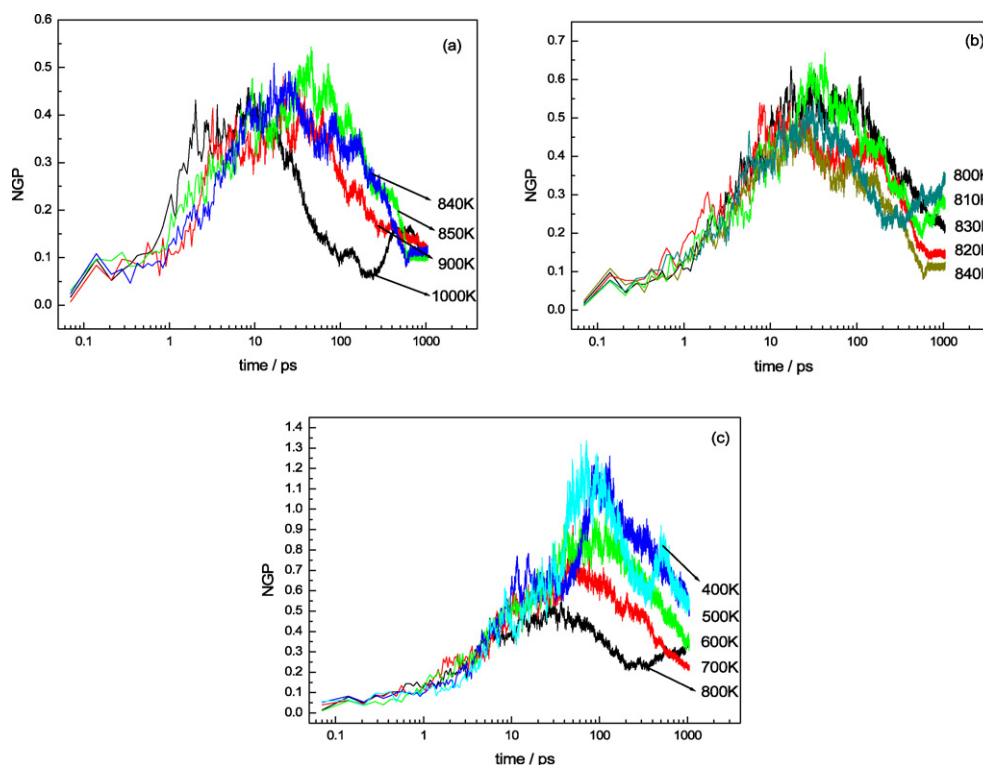


Figure 6. Non-Gaussian parameter as a function of time at different temperatures.

The time dependence of NGP at simulation temperatures is presented in figure 6. The value of NGP is nearly zero on very short timescales, and then rises till it reaches a maximum value. After this, the NGP curves show dissimilar declines in the different regions. In the crystallization region of a supercooled liquid, an obvious Gaussian approximation is observed, since the NGP finally drops back to nearly zero, while at the lower temperatures of 850 and 840 K this process is interrupted by a nonzero plateau at a time corresponding to the occurrence of the second plateau in MSD. With a decrease in temperature, besides the appearance of the nonzero plateau at longer times, it is found that the maximum value of NGP in the complicated region is much higher than that at the adjacent temperatures, namely 840 and 800 K, which demonstrates a more pronounced heterogeneity of the relaxations in this region. When the temperature drops to the crystallization region of glass, as shown in figure 6(c), the nonzero plateau of the NGP also occurs at a temperature of 800 K, while it cannot be observed as the temperature is below 800 K due to the great difficulty in observing dynamical behaviours for large times at low temperatures. An increasing maximum in NGP indicates a more distinct non-Gaussian property with a drop in temperature.

Variations in these time–correlation functions are consistent with each other in different temperature regions. The above results indicate similar dynamics behaviours occurring in the crystallization region of supercooled liquid and the crystallization region of glass, implying a close relation between the atomic rearrangements and the heterogeneous dynamics. As the temperature approaches T_g , the variations of MSD and NGP show distinct characteristics and a reasonable explanation is not available, remaining an area for further research.

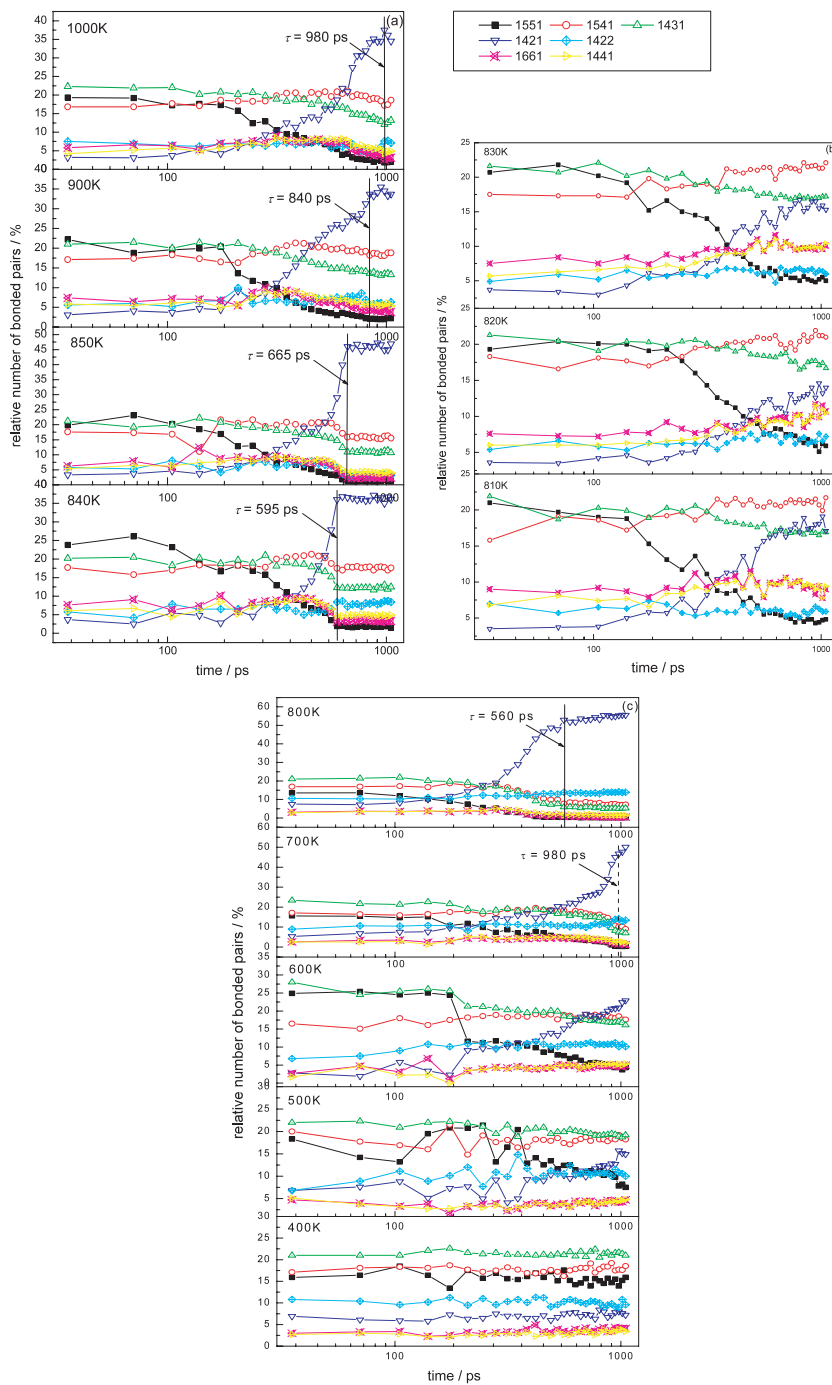


Figure 7. Honeycutt–Andersen pair fraction as a function of time in these three regions.

Figure 7 presents curves of the time dependence of HA pairs during relaxation. At each temperature, the system starts with a disordered structure, leading to numerous 1551, 1541 and

1431 bonded pairs. As the temperature decreases from 1000 to 840 K, the fraction of 1551 bonded pairs clearly decreases with increasing relaxation time, while the 1421 bonded pairs increase rapidly with time, indicating that the final state of the system belongs to fcc structure. In contrast, other pairs, such as 1541, 1431, 1422, 1661 and 1441 bonded pairs, exhibit only a slight change, as shown in figure 7(a). All the pairs remain nearly constant after a long timescale (i.e. the incubation time τ) and τ shortens with the decreasing temperature. When the temperature ranges from 830 to 810 K, the structural transition shown in figure 7(b) reveals a very slow increase in the 1421 bonded pair, reaching less than 20% after relaxation. Although the fraction value is less than 5% for 1551, the 1541 and 1431 bonded pairs, representing amorphous characteristics, are maintained at a considerable number during relaxation. Hence, it can be concluded that, within the complicated region, the structure of the system exhibits a sluggish transition, with only a partial crystal structure included. It seems that the incubation time τ cannot be determined in this region, since the bonded pair fractions are still at a rising stage, even if the relaxation time is longer than 1050 ps. When the temperature decreases to 800 K, the 1421 bonded pair shows a sharp increase to around 55% at $\tau > 560$ ps, while the 1551 bonded pair drops to nearly zero, suggesting a crystallized sample with fcc structure. At the end of relaxation, the number of 1421 bonded pairs in the final state of the system decreases smoothly with decreasing temperature and the τ increases so rapidly that the simulation time is not long enough to detect fully the crystallization of the glass state at low temperatures. At a temperature of 400 K, various pairs remain almost constant during relaxation, suggesting that it is difficult for aging to occur in glasses.

Both theoretical and experimental results [25, 29–31] suggest that there is a cluster size at which the crossover from icosahedral to crystalline order occurs, with consequent nucleation and crystallization. The HA results in figure 7 show that the 1421 bonded pair is anti-correlated with respect to the 1551 and 1431 bonded pairs, suggesting the existence of two major competing local orders, i.e. close-packed fcc order (1421 bonded pair) and icosahedral order (1551 and 1431 bonded pairs). Thus it can be deduced that the fcc order, characterized by the 1421 bonded pair, will become more stable when its size is beyond the critical size with a decrease in temperature, causing the crystallization of supercooled liquid or glass. Additionally, the number of 1541, 1661 and 1441 bonded pairs stays constant or even increase with time at every region, and then declines, having a crossover with increasing 1421 bonded pairs (see figure 7). Studies of homogeneous nucleation indicate that bcc is favoured near the melting line and transforms to other structures at low temperatures [32]. Honeycutt and Andersen [25] revealed that the normalized abundance of 1551 bonded pairs in a nucleated solid is 0.002, while that of 1541 is 0.09. Accordingly, it is inferred that 1541, 1661 and 1441 bonded pairs contribute greatly to the formation of incipient embryos, but transform to other stable forms in subsequent relaxations.

Considering the time dependence of thermodynamic, dynamic and structural functions in supercooled liquid and glassy Ni, we plot τ schematically as a function of temperature in figure 8, which follows a nonmonotonic relationship with T , resembling the typical TTT (temperature–time–transformation) diagram. It can be inferred that, in the crystallization process of supercooled liquid, the formation of incipient embryos is a direct consequence of heterogeneous dynamics in supercooled liquids. Facilitated by the collective fluctuations of atoms, the critical nuclei for crystal growth tend to form only after sufficient incubation time τ via structural rearrangements of atoms in terms of the results of HA analysis (see figure 7(a)). The driving force for the nucleation increases with further supercooling and the time τ goes ahead clearly. However, the diffusive motion of atoms is lowered drastically near T_c . Despite the number of embryos increasing due to the increasing heterogeneity of relaxations, the slow dynamics decelerates atomic motions, as revealed by the slight changes of bonded pairs. That

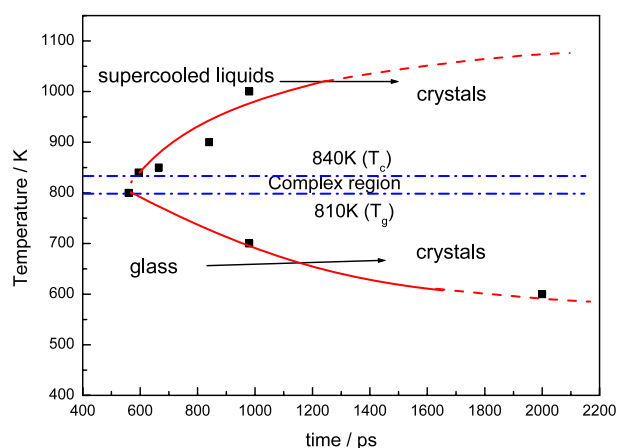


Figure 8. Schematic plot of the temperature dependence of the time needed for the system to crystallize.

means that the atoms have not enough time to find their more stable local configurations via moving fast, and then to minimize the internal energy of the system. Consequently, only partial crystallization of glass can be detected at the end of relaxations. With the decrease in temperature, homogeneous nucleation will take too much time, and nucleation due to quenched-in fluctuation or nuclei is responsible for crystallization. The time required for the atomic rearrangements extends sharply because of the decline of relaxation dynamics. Hence, the nucleation and subsequent crystallization are inhibited and the time τ moves to a large value obviously upon relaxation. Our results also reveal that structural rearrangements of atoms are of great importance to the nucleation and growth kinetics of any crystalline phase. Such a structural transition is directly related to the dynamical heterogeneity in either supercooled liquid or glassy system.

6. Conclusion

In this paper, molecular dynamics simulations using the embedded atom method have been performed to explore the thermodynamic, dynamic, and structural relaxations in supercooled liquid and glassy Ni. In a system with 4000 atoms, the glass transition temperature T_g is 800 K and the critical temperature T_c is estimated to be 840 K, with a cooling rate of $2.86 \times 10^{13} \text{ K s}^{-1}$.

We find three characteristic regions in relaxation processes with distinct thermodynamic, dynamic, and structural properties. In the temperature range $840 \text{ K} \leq T \leq 1000 \text{ K}$, crystallization of supercooled liquid occurs with a gradually advancing incubation time τ ; at a lower temperature region of $810 \text{ K} \leq T < 840 \text{ K}$, the internal energy shows a relatively higher value for long timescales and the final state of the system exhibits a more complicated structure, characterized by the coexistence of partial crystal and glassy matrix; while as the temperature is below 810 K, crystallization of the glass will arise and the τ is prolonged rapidly with decreasing temperature.

Results of time–correlation functions MSD and NGP indicate that dynamic behaviour occurring in the crystallization region of supercooled liquid is comparable with that obtained in the crystallization region of glass, characterized by the appearance of a second-plateau in the MSD and the nonzero plateau in the NGP at larger timescales. This means that the crystallization process from a supercooled liquid or glass occurs through the nucleation and

growth of crystal nuclei. Relaxation at the temperature of approaching T_g has an abstruse effect on the dynamic variations.

Thermodynamic and dynamic relaxations are accompanied by a structural rearrangement of atoms. The 1551 bonded pair characterizing local fivefold symmetry decreases in the process of relaxation; correspondingly, the 1421 bonded pair representing fcc structural order increases. The incubation time can be determined as the number of bonded pairs changes sharply, while in the complicated region only a sluggish transition in the structure of the system will be found. The curve of τ as a function of temperature resembling the typical TTT diagram is finally plotted.

Acknowledgments

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