

Molecular Dynamics Simulation of Binary liquid mixture Phase Separation and Glass Transition

Meili Li, Xingye Fu

College of Electrical Engineering of Suihua University, Suihua 152061, China
 meilili4683@163.com

This paper aims to study the phase separation of binary liquid mixture and two-phase glass transition process by using the method of molecular dynamics (MD) simulation. To this end, mainly taking B particle as research object in this paper, the temperature changes after the two-phase separation of binary liquid mixture were observed and compared. Through the study, it's found that under the external pressure, phase separation phenomenon appeared in the binary liquid mixture, and there existed the differences in the two-phase glass transition temperature after separation. Therefore, the phase separation of binary liquid mixture and glass transition may vary with the temperature, resulting in non-uniform microscopic phenomena.

1. Introduction

At certain cooling rate, the internal atoms of liquid may change, resulting in an amorphous structure. This solid structure belongs to amorphous material and can be made into glass material. In condensed matter physics, glass transition is one of the important research contents which has been studied by many scholars at home and abroad. Although the domestic glass transition process has been studied for a long time, there is no systematic understanding of the glass transition process. In the field of modern material performance research, the value of computer simulation technology has been gradually embodied. The researchers can conduct in-house material research through computer simulation techniques and use molecular dynamics methods to explore material properties. In materials science research, the researchers gradually began to deeply study the relationship between the macroscopic properties of materials and the structure of the material tube, and then combined the relevant theories to study the function of the material system and the specific structure of the material. If there are new materials that meet the requirements in the research process, the research will be conducted through simulation analysis and then the feasibility of the material will be explored.

This paper mainly studies the phase separation of binary liquid mixture and the two-phase glass transition process. First of all, the principle of MD simulation, the phase separation of binary liquid mixtures, and the glass transition process were studied, and then the related factors affecting phase separation and glass transition were analyzed and summarized.

2. Literature review

A binary system is cooled down rapidly starting from the miscible temperature, which drives the formation and growth of the two phases, that is, the phase separation of the system. The concept of spinodal decomposition in unstable region is first introduced by Gibbs. In a certain alloy system, after solid heat treatment, the solid solution is decomposed into an interphase distributed microstructure (Park, 2014). The solute content in these small areas form a certain waveform distribution in one direction. The composition at the crest is higher than the average composition, and the composition of the trough is lower than the average composition. These rich areas and poor areas retain the solid structure of the original solid solution. Such an uneven organization consisting of tiny regions of component amplitude modulation is called metastable subdomain organization. This decomposition process is called Spinodal decomposition and this decomposition does not require nucleation barrier, but only conducts through the growth of component fluctuations in the solid solution.

When the cooling rate is slow, the melt turns into crystal at the lower temperature, and the crystallization occurs. At this time, the energy and volume change, and the crystallization is the first order phase transition. When the cooling rate is faster, the melt can be kept below the temperature of the solidification point, and the velocity of molecular motion in the melt gradually slows down with the decrease of temperature. If the cooling rate of the melt is fast enough, the crystallization phenomenon may be completely avoided. At this time, the rate of atomic recombination is so slow that it cannot be fully reorganized in the time limit defined by the cooling condition, and the structure of the liquid is like freezing. Then, the glass transition occurs and the melt turns into an amorphous state.

Glass transition is a physical process of dynamics. The slower the melt cooling rate is, the longer the atom can be reorganized at each temperature. That is to say, it can be too cold to a lower temperature. Therefore, the glass transition temperature rises in theory as the cooling rate rises, and the glass state formed depends on the process of forming the glass. In glass transition, viscosity is a structural sensitive physical parameter. The viscosity of the melt is closely related to the microstructure. The change of structure inevitably causes the change of viscosity. Like other transport parameters, the viscosity reflects the state of the atom in the system (Mantaranon and Chirachanchai, 2016). With the decrease of melt temperature, the viscosity of liquid will increase sharply. The viscosity of the general equilibrium liquid is in the order of 10^{-3} - 10^{-1} Pa.S. When the melt is undercooled, the viscosity will become very large, which can reach the order of magnitude 10^{10} mPa.S. Viscosity is a widely studied physical property. However, the viscosity of undercooled state is still difficult to measure and calculate. Because of the atomic scale, the process of transition from super-cooled to glass state is not well understood. So far, no formula can be used to well describe the viscosity change of the whole process. Arrhenius formula can give the best description of the relationship of high temperature viscosity varying with temperature. This formula is very simple, the physical model is simple and the meaning of each parameter is clear. However, this formula can only describe the viscosity change of the high temperature melt when the Arrhenius formula is extended to the super-cooled state, except for some oxides such as SiO₂ (Aziz, 2016). The VTF formula is the most commonly used equation to describe the viscosity of the super-cooled melt. In the process of approaching the glass transition temperature, the viscosity of the super-cooled liquid with the change of temperature can be used to indicate that the glass is still applicable by the VTF equation. For most liquid systems, it cannot give the super-cooled liquid viscosity. For the VTF formula, some researchers have found that it does not give the change rule of the viscosity approaching the glass transition. Phalen and so on believed that the change of viscosity near the glass transition point should be faster than the viscosity expressed by the VTF formula (Phalen et al., 2016). Furthermore, a parameter T_0 appears in the VTF formula, which is mathematically an odd point separating the physical continuity of the glass transition temperature and physically difficult to explain. Both of these two formulas have their respective scope of application. If the VTF formula is extended to the high temperature region or the Arrhenius formula is extended to the super-cooled state, the results that are not consistent with the experimental data will be obtained. Viscosity can be used to judge brittleness, which is one of the hotspots in recent years. The amorphous formation ability of metal can be deduced by brittleness, thus the possibility of making amorphous is judged.

The brittleness of liquid is closely related to the structure of liquid material. According to this method, the liquid is divided into two types: fragile liquid and strong liquid. The behavior of the super-cooled state of a strong liquid presents a near Arrhenius characteristic. Since the concept of brittleness has been put forward, it has been widely used in the liquid study and has become an important parameter to distinguish the dynamic behavior of different liquid substances. Especially for glass forming liquid, brittleness is an important parameter for its glass forming ability. Although there are some small differences between different brittleness definitions, brittleness is of great importance in studying the relaxation process of super-cooled liquids. Many studies have shown that the relationship between the brittleness value and the other properties of the super-cooled liquid include the significant Bose peak, the attenuation of the relationship between the shear modulus of the liquid and the temperature in the correlation function of the glass transition temperature, the nonlinearity of the relaxation function and the vibrational properties of the glass.

Zhou and others found that the vibration property of glass was related to the brittleness value. Therefore, the brittleness concept was extended to the glassy state, and it was pointed out how to determine brittleness under the temperature alone by the nature of glass (Zhou and Zhao, 2016). The relationship between brittleness and the statistical properties of barrier was analyzed by Akinbinu. It was pointed out that the number, depth and shape of potential well are not enough to predict brittleness (Akinbinu, 2017). Karamloo studied the relationship between brittleness and Bose ratio. The analysis showed that there was a linear relationship between the ratio of the bulk modulus and the shear modulus of the glass, the ratio of the bulk modulus and the shear modulus to the brittleness of the liquid. They believed that the ratio determined the activation energy of the structural relaxation at high temperature, thus affecting the brittleness (Karamloo et al., 2016). However, 13 kinds of inorganic, organic and metal were studied by Távara. It was found that there

was no linear relationship between brittleness and the elastic properties of glass, and there was no linear relationship between brittleness and the ratio of bulk modulus to shear modulus (Távora et al., 2017).

In summary, the dynamic and thermodynamic properties of super-cooled liquid region and glass transition are two important problems and difficult problems in the basic theory of condensed matter physics. In view of this hot topic in condensed matter physics, molecular dynamics method is used to do some preliminary research on the glass transition of liquid phase separation. The glass transition of phase separated liquid by molecular dynamics simulation and the potential energy function of the system are optimized, thus the phase separation liquid is obtained, and the glass transition temperature and the thermodynamic and kinetic properties of the phase separation liquid in the super-cooled state are obtained. For the complete understanding of glass transition, much more work needs to be done. Therefore, the study of thermodynamic and dynamic characteristics of super-cooled liquid region is of great significance.

3. Methods

3.1 Basic principle of molecular dynamics simulation

Molecular dynamics is the most important and widely used method in molecular mechanics. The basic principle is to calculate the trajectories of each atom in the physical system by Newtonian classical mechanics, and then use certain statistical method to calculate the mechanics, thermodynamic, and dynamic properties of the system. In MD, a system of N particles was first abstracted into N interacting particles. Each particle had coordinates (usually in Cartesian coordinates), mass, charge, and bond formation; as per the target temperature. the initial velocity of each particle was randomly assigned according to the Boltzmann distribution. Then, the interaction energy between the particles and the force of each particle were calculated according to the corresponding bonding and non-bond energy expression in the selected force field. The core idea of the finite difference method is to divide the integral into many small segments. The fixed time of each segment is: the total force of each particle at any time t is the vector sum of its interaction with other particles. The acceleration of the particle can then be obtained. In conjunction with the position and velocity of the particle at time t , the position and velocity of the particle at time $t + \Delta t$ can be calculated. The force of the particles is considered constant during the time period Δt . In the new position, the force of the particles can also be calculated by molecular mechanics, so that the position and velocity of the particles can be obtained at $t + 2\Delta t$, and then the new position and velocity can be continuously achieved.

The interaction potential between atoms is the basis of all atom simulations. The accuracy of the interaction potential between atoms will directly affect the accuracy of simulation results, while the computer machine-hour required for computer simulation depends on the complexity of the potential function. With the application of computer technology in physics and other fields, the research on atomic computational model has also been widely carried out. Figure 1 shows the interaction potential of Lennard-Jones. The potential between atoms is divided into two types in terms of their complexity: Lennard-Jones potential is established to describe the interaction forces between inert gas molecules. The formula is as follows:

$$\phi(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

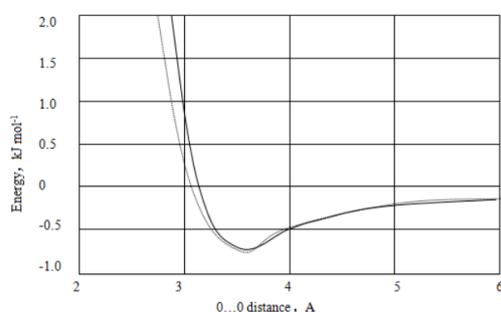


Figure 1: Lennard-Jones

3.2 Binary liquid mixture phase separation method

In MD studies, more people have studied the evolution of phase separation processes over time, while relatively fewer have studied the dynamics growth law of phase separation with temperature; in addition, the

component size (atomic size) has a great influence on the phase separation process, but the study for the influence of the change in the component size on the phase separation has not been conducted. In this paper, MD simulation method was used to study the growth kinetics of the two blend systems with temperature, and the influence of different component sizes on the phase separation process was discussed. The binary system composed of two types of particles A and B was studied in this paper; the interaction potential used was "LJ \pm " potential. In LJ \pm potential, pure repulsive potential was used between A and B particles. Lennard-Jones potential was adopted between same types of potentials. Under the action of LJ \pm potential, only heterogeneous particles had repulsion. The MD simulation was performed in a cube of 2,000 particles. The time step was 1.5×10^{-16} s, the initial temperature was 240K, and the simulation was performed in 200000 steps to obtain an equilibrium state. The temperature was then reduced to 10K at the speed of 6.7×10^{12} K/s, to observe the phase separation process and diffusion coefficient of different components. Molecular dynamics simulation has been most widely used since its creation. The molecular dynamics method has been used to study the solid-state defects of metallic materials, the thermodynamic properties of the liquid structure under special conditions that are inaccessible under experimental conditions, colloids, proteins, atomic clusters, and thin-film growth etc. It can be said that various types of materials can be studied by means of molecular dynamics simulation.

3.3 Molecular dynamics simulation of liquid glass transition

The MD simulation was performed in a cube of 1000 particles, where A particles accounted for 80% and B particles for 20%. The time step was 3×10^{-16} s, the initial temperature was 400K, and under the external pressure of 0GPa, 0.75GPa, 1.75GPa, and 2.75GPa respectively, 200,000 steps of simulation were performed to obtain an equilibrium state. Then, the temperature was lowered to 10 K at a speed of 6.7×10^{12} K/s. Thus, the phase separation process and glass transition process of system under different external pressure were observed to explore the effect of external pressure on the glass transition of phase separation liquid and the effect of phase separation on glass transition. Radial distribution function $g(r)$ is widely used in the study of liquid-state and amorphous structure. In this paper, the radial distribution function was used to analyze the effect of external pressure on the formation ability of phase-separated liquid glass. At the relatively low cooling rate, the melt turns into crystal at the temperature, and crystallization occurs. At this time, the energy and the volume mutate at the temperature, and the crystallization is the process of first-order phase transition. At the high cooling rate, the melt can be stored until the freezing point temperature below. At this time, the molecular motion speed in the melt gradually becomes slower as the temperature decreases. If the melt cools fast enough, crystallization can be completely avoided, when the reorganization of the atoms is so slow that they cannot be fully recombined within the time limit defined by the cooling conditions. The liquid structure is just like freezing. At this time, glass transition occurs and the melt turns into an amorphous state. In the curve of volume-temperature change, the glass state and the liquid state are different, and there is a point of intersection between them. The temperature of this intersection is defined as the glass transition temperature. Usually the glass transition temperature is about $2/3$. Glass transition is not a true phase transition because at the glass transition temperature, most of the system's physical properties do not mutate.

4. Results and discussions

4.1 Simulation results of binary liquid mixture phase separation

During the simulation, the system temperature was reduced from 240K to 10K at the same cooling rate of 6.7×10^{12} K/s. During this process, the system was phase separated. The phase separation process of the particles was also visually displayed. For the sake of clarity, only the distribution of Class B particles is shown in the figure. It can be seen that at 240K, the particles in the system are nearly homogeneously mixed and the system is in a state of miscibility. As the temperature decreases, similar particles continue to converge, heterogeneous particles gradually separate, and the phase separation domain gradually grows to form two different phases. At 10K, it's clearly observed that the system forms two separate phases.

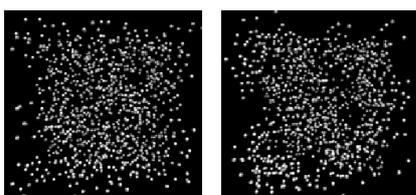


Figure 2: Partial atom distribution in system 1

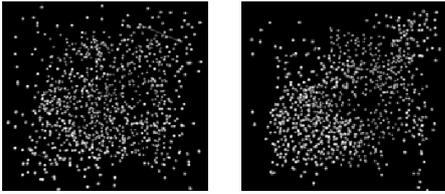


Figure 3: Partial atom distribution in system 2

Figure 2 and 3 shows the atom distribution of the first and second parts of the system.

Under the potential action of different component sizes σ , the physical quantities of the system all change with the temperature in the phase separation process, resulting in different phase separation degree of the system. Under pure repulsive potential, if the size of certain component decreases, the growth rate of the phase separation will increase, the particles of the same kind will converge more easily, the phase separation will become more significant, and the diffusion coefficient will be greatly influenced by σ . Table 1 lists the fitting results of diffusion activation energy parameters for different components.

Table 1: Parameters of the fit using our data

constant	Types of particles			
	A1	A2	A3	A4
A(J)	439.34458	446.31704	439.69075	444.98194
B(J)	0.00202	0.00281	0.00238	0.00779
C(Boundless just)	2.05244	2.00838	2.1718	1.85012

4.2 Simulation results analysis of liquid glass transition

In the MD simulation, the system temperature was reduced from 400K to 10K at the same cooling rate of $6.7 \times 10^{12} \text{K/s}$. During this cooling process, phase separation occurred in the system, and the degree of phase separation increased as the external pressure increased. For clear observation, the phase separation process of the system under different external pressures at a temperature of 100K was visually displayed. Besides, only the distribution of Class B particles is shown in the figure. The black ball represents B particles and the blank space is A particles. It can be clearly seen that at 100 K the scattered distribution of B particles at 0GPa is changed to the aggregated distribution at 2.75GPa, indicating two different phases are gradually formed in the system; at 2.75GPa, it's obvious that the system forms two separate phases. Figures 4 and 5 below show the distribution of B particles under different external pressures.

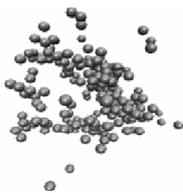


Figure 4: B distribution of particles under 0GPa

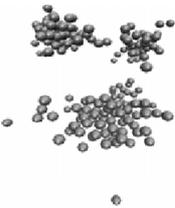


Figure 5: B distribution of particle at 1.75GPa

The binary mixing system composes of A and B particles. During its rapid cooling process, the phase-separated liquid is obtained and the glass transition occurs. The higher the external pressure is, the higher the phase separation temperature and the glass transition temperature are, and then the diffusivity is weaker.

Under the same external pressure, the separated two-phase glass transition temperature is different. The phase glass transition temperature of A particles is higher than that of B particles. In the glass transition process, microscopic non-uniformity appears in the system.

5. Conclusion

In this paper, the MD simulation method was mainly adopted to explore binary liquid phase separation and glass transition process. Through study, it has been found that under the action of Lennard-Jones the phase separation shall occur to the binary liquid mixtures. As the temperature of particles increases, the diffusion activation energy of the particles shall change accordingly. With the phase separation of the binary liquid mixture, the two-phase glass transition temperature will change, resulting in non-uniform microscopic phenomena. As the external pressure gradually increases, the particle freezing speed will gradually increase and then the glass transition temperature will also increase accordingly.

This study mainly simulates and analyze the phase separation of binary liquid mixture and the changes that occur during the two-phase glass transition. Due to limited research space and the author's professional ability, only the binary liquid mixture phase separation and glass transition process were simply analyzed, without further study about the glass transition temperature and diffusion results. Binary liquid mixture phase separation and glass transition process has certain applied research value, and it is of great significance for study of condensed matter physics.

Reference

- Akinbinu V.A., 2017, Relationship of brittleness and fragmentation in brittle compression, *Engineering Geology*, 221, 82-90, DOI: 10.1016/j.enggeo.2017.02.029.
- Aziz S.B., 2016, Role of dielectric constant on ion transport: reformulated arrhenius equation, *Advances in Materials Science and Engineering*, 1-11, DOI: 10.1155/2016/2527013.
- Karamloo M., Mazloom M., Payganeh G., 2016, Influences of water to cement ratio on brittleness and fracture parameters of self-compacting lightweight concrete, *Engineering Fracture Mechanics*, 168, 227-241, DOI: 10.1016/j.engfracmech.2016.09.011.
- Mantaranon N., Chirachanchai S., 2016, Polyoxymethylene foam: from an investigation of key factors related to porous morphologies and microstructure to the optimization of foam properties, *Polymer*, 96, 54-62, DOI: 10.1016/j.polymer.2016.05.001.
- Park J.C., 2014, Generalization of gibbs entropy and thermodynamic relation, *Physica A Statistical Mechanics & Its Applications*, 395(4), 135-147, DOI: 10.1016/j.physa.2013.10.012.
- Phalen R.N., Cousins K., Usher T., Young M., Zhang R., 2016, Revising the formulization of the narayanaswamy equation using the adam-gibbs theory, *Journal of Non-Crystalline Solids*, 453, 59-65, DOI: 10.1016/j.jnoncrysol.2016.09.025.
- Távora L., Reinoso J., Castillo D., Mantić V., 2017, Mixed-mode failure of interfaces studied by the 2d linear elastic–brittle interface model: macro- and micro-mechanical finite-element applications in composites, *Journal of Adhesion*, (8),1-30, DOI: 10.1080/00218464.2017.1320988.
- Zhou M., Zhao P., 2016, Prediction of critical cutting depth for ductile-brittle transition in ultrasonic vibration assisted grinding of optical glasses. *International Journal of Advanced Manufacturing Technology*, 86(5-8), 1775-1784, DOI: 10.1007/s00170-015-8274-9.