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論 文 内 容 要 旨

Understanding the glass transition phenomenon is one of challenging problems in condensed matters. This phenomenon appears in various kinds of materials, such as polymers, colloidal suspensions, and metallic liquids. Hence, different types of approaches and models have been proposed to clarify characteristic features of statics and dynamics. As a result, a universal approach is somehow lacking. Thus, in this thesis, we shall regard the glass transition phenomenon as a diffusion process. In other words, our aim is to characterize dynamical and static quantities on the glass-forming materials by the self-diffusion coefficient D_S^L from the universal point of view. We perform extensively molecular dynamics (MD) simulations of several glass-forming models at different temperatures, pressures, and compositions in NpT ensembles. Then, we analyze the MD results by D_S^L and theoretical predictions, and explore a universality of the glass-forming liquids in the following. At first, we explore universal relationships between thermodynamics and dynamics. We can show thermal temperatures are consistent with dynamic temperatures obtained from D_S^L. Therefore, a peak temperature T_{peak} of the specific heat C_p or the thermal expansion coefficient α_p would be related to a deeply supercooled liquid temperature T_x of a mobile atom, and a thermal T_g to a dynamic T_g. These associations would be valid in other physical variables, that is, pressure, volume, and free energy. Next, we investigate structural changes and dynamics crossovers at $T_{peak} \sim T_x$. Our investigations suggest that peaks of C_p and α_p should be responsible for rearrangements of atoms around the second nearest orders and for a kind of hopping processes. Finally, we examine the composition dependence of a single particle dynamics by D_S^L from the universal standpoint. We can obtain a universal curve for D_S^L, which is independent of compositions and components. In addition, master curves for the mean-square

displacement $M_2(t)$ and mean-fourth displacement $M_4(t)$ are shown to be regardless of compositions. The above findings indicate that the D_S^L can be regarded as a universal parameter, and therefore this universal approach would play a significant role on quantifying fundamental features of the metallic glass-forming melts at different compositions and on developments of applications of them.

This Ph. D thesis is composed of 6 chapters. In chapter 1, we shortly introduce what happens on the glass transition phenomena and review a history of researches for them. Then, our objectives and methods of this thesis are presented. On the glass transition phenomena, three characteristic states show up, that is, liquid, supercooled liquid, and glassy states. These states are conventionally defined in thermal descriptions by the melting temperature T_m and a glass transition temperature T_g as follows. Enthalpy or specific volume behaves linearly as a function of T at each state. On crystallization, these properties drop discontinuously at T_m. However, in the glass-forming systems, they continuously change even below T_m. On further cooling, a slope value of them becomes more smoothly around T_g. A supercooled liquid state ($T_g < T < T_m$) is considered as a quasi equilibrium state, but glassy state ($T < T_g$) is as a non-equilibrium state from the thermal viewpoint. Thus, T_g is dependent on observable conditions such as a cooling rate and waiting time in experiments or simulations. In contrast to statics, glass-forming liquids exhibit dramatic changes in transport properties by approaching to T_g. In order to clarify the dynamics, it has been proposed that the long-time self-diffusion coefficient D_S^L characterize dynamics of a single atom in glass-forming materials by analysis of $M_2(t)$ in different classes of glass-forming materials. In the thesis, we examine general features in glass-forming materials by adopting this proposal. Thus, we explore not only $M_2(t)$ but also $M_4(t)$ and thermal quantities at wide regions by D_S^L from the universal standpoint.

In chapter 2, we explain MD simulation models in this thesis. For qualitative discussions, we adopt simple models of glass-forming materials, that is, binary Lennard-Jones (LJ) $A_{80}B_{20}$ mixtures and ternary metallic glass-forming $Cu_{60}Ti_{40-x}Zr_x$ melts in NpT ensembles. We also use the Berendsen method in order to attain a constant temperature and pressure in the MD simulations. A motion of particles obeys the Newton equation and the particles interact with each other throughout the two-body potentials. For potential forms and parameter sets, we adopt the LJ potential of the Kob-Andersen model in $A_{80}B_{20}$ and Stillinger-Weber potential of the Han-Teichler model in $Cu_{60}Ti_{40-x}Zr_x$, respectively. The former model has been proposed originally in NVT ensembles. Thus, we set an external pressure p as a value estimated in NVT systems, for instance, $p=20$ at $T=2.0$ and $p=10$ at $T=1.0$. In the latter model, the electron gas potentials have been additionally considered. Although the latter model originates from $Cu_{60}Ti_{20}Zr_{20}$, we simply expand this

model to other compositions x of $Cu_{60}Ti_{40-x}Zr_x$. Such a simple model allows us to consider composition effects separately. Thus, they categorize into an effect of the potential and that of number of components.

In chapter 3, we focus on macroscopic correlations between thermodynamics and dynamics by MD simulations of $A_{80}B_{20}$ at different pressures p=0, 5, 10, 15, 20 and p=30 without attractive interactions. Understanding relationships between thermodynamics and dynamics is one of the essential topics on the glass transition phenomena. For the purpose, researchers have proposed relevant temperatures to specify static and dynamical quantities. In terms of thermodynamics, the glass transition temperature T_g is defined as a crossover point of specific volume and enthalpy by linear extrapolations. Around T_g, the specific heat C_p rapidly decreases. The decrease implies a dramatic slowdown of dynamics around T_g because C_p is associated with degrees of freedom of motions. Motivated by it, it has been discussed that transport properties such as the viscosity η and self-diffusion coefficient $D_S{}^L$ around the thermal T_g. Instead of linear fittings, in their works, several empirical functions have been used in order to obtain a dynamic T_g. Thus, the dynamic T_g can be defined as a crossover point where the transport properties obey one function from another function. It has been successfully shown that the dynamic T_g is consistent with the thermal T_g. However, a physical meaning of the dynamic T_g is still unclear because of the use in the empirical functions. In addition, other characteristic temperatures are somehow less focused. Thus, in this chapter, we shall explore how thermal temperatures correspond to dynamic temperatures. An analysis of $D_S{}^L$ by two theoretical curves gives rise to two characteristic temperatures of $D_S{}^L$, that is, a dynamic T_g and a deeply supercooled liquid temperature T_x. Thus, we can show not only a correspondence of T_g in between the thermal and dynamical definitions, but also that between a peak temperature T_{peak} of C_p and T_x of the mobile component B. In addition, we can check the above correspondences could be universal in various kinds of metallic glass-forming melts, regardless of the pressures, compositions, and components.

In chapter 4, we investigate what's going on dynamics and statics around $T_x \sim T_{peak}$ by the MD simulation studies of $A_{80}B_{20}$ at different pressures, p=10, 20 and p=30 without attractive interactions. Then, a second peak of the radial distribution function is split up and a peak height of the non-Gaussian parameter becomes more than 1 around the crossover point. This correspondence between a rearrangement and activation of particles is consistent with a coincidence of the peak between α_p and C_p. We also explore length and time scales of $M_2(t)$ and $M_4(t)$ at the caging regions, and confirm no significant change in differences between them around T_x. Thus, the time and length scales seem to behave in the same ways.

In chapter 5, we try to clarify the composition dependence of a single-particle dynamics in metallic

glass-forming melts by the universal parameter $D_S{}^L$. Recently, the bulk metallic glasses (BMGs) and glass-forming melts have received considerable attentions in application fields because they exhibit good mechanical properties such as a high strength, low Young's modulus, and so on. In order to develop BMGs to practical fields, one needs to fabricate a larger size of BMGs and better stability against crystallization. Then, a glass-forming ability (GFA) is a quite useful factor to evaluate better BMGs. In order to define GFA and to establish the way of evaluations, one needs to explore a composition-dependence of statics and of dynamics in multi-component metallic glass-forming melts. Thus, in the current chapter, we shall pay attention to a single dynamics for different compositions x by performing MD simulations of ternary metallic glass-forming $Cu_{60}Ti_{40-x}Zr_x$ melts at different compositions $x=10$, 20, and 30. It is expected that investigations for the composition-dependence of the single-particle dynamics in liquid and supercooled liquid regions might lead to understandings of GFA in static ways because the self-diffusion coefficient $D_S{}^L$ is associated to thermal quantities as discussed in chapters 3 and 4. We can show $D_S{}^L$ for different compositions x would have a universal curve, independently of x, as a function of induced temperature. The universal curve is obtained by analysis of theoretical predictions with singular temperatures. We can also show dynamics of $M_2(t)$ and $M_4(t)$ are governed by only $D_S{}^L$, which indicate a simple mechanism of them should be existed. These results suggest that once few data of dynamics in metallic glass-forming melts at a composition, we could expect their dynamics at wide temperature regions.

In chapter 6, we summarize and conclude the present work in this thesis. We have examined the pressure, temperature, and composition dependences of dynamical and thermal quantities in several kinds of glass-forming materials in NpT ensembles by the MD simulations. We have figured out that simple universalities of them are obtained by using the self-diffusion coefficient $D_S{}^L$. Thus, we could regard $D_S{}^L$ as a universal parameter on the diffusion processes in different kinds of glass-forming materials. These facts indicate the current simple approaches by $D_S{}^L$ shed light on understanding of mechanism behind a slow dynamics and rearrangement of atoms at short and medium range orders on the glass transition phenomena from the unified point of view. In addition, it is expected that the current results would make applied and engineering fields be more developed.

論文審査結果の要旨

多成分混合や急冷などによって，コロイド分散系や金属系などは液体から過冷却液体へと遷移し，ガラス状態へと至る。このガラス転移現象に潜む静的及び動的機構を普遍的視点より解明することは重要な課題の一つである。本研究では，ガラス転移現象を拡散過程として捉え，その普遍性を理解することを目的として分子動力学法による計算機実験を行っている。拡散係数と熱力学量との対応関係を明らかにしたとともに，この対応関係は系の組成比や構成元素，あるいは設定圧力や密度にも依存しない普遍性を持つことが示されている．本論文は，これら研究成果をまとめたものであり，全編6章からなる。

第1章は，序論であり，本研究の背景，目的および構成を述べている。

第2章は，主に金属溶融体のモデル化について考察し，分子動力学法による計算機実験方法の詳細について述べている。実験との定性的比較を目的とした場合には，本研究のシンプルな実験モデルは測定時間が短縮され，非常に有益である。

第3章は，定圧系における2成分レナード・ジョーンズ流体に対して計算機実験を行い，熱力学量と自己拡散係数に関する考察結果について述べている。定圧比熱及び熱膨張係数のピークは液体から過冷却液体への動的遷移と相関しており，また過去に提案されている熱力学的ガラス転移温度と動的ガラス転移温度も一対一対応であることを明らかにしている。この普遍的対応関係から過冷却液体領域を推定することが可能であり，ガラス形成能を評価する上で非常に有益な成果である。

第4章は，定圧比熱や熱膨張係数のピーク温度近傍での構造変化及び動的挙動について考察している。熱力学量のピークの要因は，第二近接距離近傍の構造変化と関係しているとする従来の研究報告を再確認しただけでなく，さらに位置変位分布におけるガウス分布からのずれであることも明らかにしている。この結果は，液体と過冷却液体の相違点の解明するために非常に重要な知見である。

第5章は，3成分金属ガラス溶融体に対する計算機実験を行い，動的物理量の組成比依存性を普遍的観点より検証している。自己拡散係数を普遍変数と考えた場合，異なる組成比間の動的挙動は一致することを明らかにしている。この結果から，高いガラス形成能を有する組成比を推定することが示唆され，材料工学的に有益である。

第6章は，結論である。

以上要するに本論文は，拡散係数を用いることで，熱力学量及び動的物理量を普遍的に解析できる研究手法を実証したものであり，ナノメカニクス，流体工学の発展に寄与するところが少なくない。よって，本論文は博士（工学）の学位論文として合格と認める。