Theory of liquid-glass transition

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学位論文要旨

Abstract The liquid to glass transition and the slow relaxation phenomena of supercooled liquid and glass have been theoretically studied upon the dynamical point of view through the Trapping Diffusion Model (TDM), which is the meso-scopic model for the motion of an atom in such highly supercooled fluids. In the model, two type of motions of an atom are considered, stray motion and jump motion, where the rates of these two motions and the other parameters are determined by the results of Molecular-Dynamics (MD) simulations for the binary soft-sphere mixture system. Then, the micro-scopic dynamics of a atom can be represented by one particle's master equation. With adopting the solution of the master equation to the Green-Kubo formula, the self-part of the dynamical structure factor and the generalized susceptibility are calculated. The slow relaxations, α and α' relaxations are shown to be the consequences of the anomalous diffusion in glassy state and the sub-anomalous diffusions in supercooled fluids. Moreover, super-long-time MD simulation have been carried out for the purpose of the direct calculation of the generalized susceptibility of a supercooled fluid. In the results, the two kinds of the slow relaxation processes are observed, which are in good agreement with the TDM qualitatively and quantitatively.

The trapping diffusion model

In supercooled fluids and the other amorphous matters, the system has a strong cage effect, by which the atomic motion is strongly affected. It is very important how to set such cage effect into the theory of the dynamics in supercooled fluids. According to the MD simulation of a binary soft-sphere mixture system, an atom acts mainly two type of diffusive motions: One is a oscillatory motion within a local area, it is called stray motion, and the other is a jump motion in order of the interparticle distance. It is also observed that (i) jump distances have a narrow distribution for both diffusive motions, and (ii) the

waiting-time distribution can be well represented by a simple exponential function for the stray motion and by a power-law function for the jump motion, which indicates that the jump-rate distribution will be sharply peaked for the stray motion and be a power-law function for the jump motion. Thus, the following mesoscopic phenomenological model will be employed: An atom at a given site s performs a stray motion between s and neighboring position $\mathbf{u}_s$ ($|\mathbf{u}_s|$is of the order of 15% of the average interatomic distance) with a constant jump rate ω_b. Occasionally, it makes a long jump motion to site s′ with jump rate ω_s. The jump rate for this motion is assumed to depend only on the origin of the jump and not on the destination of the jump, because a structural relaxation following the jump will eliminate the correlation between forward and backward jumps. It is also assumed that the distribution of site {s} will not be important and sites {s} form a regular lattice, which can be conveniently assumed to be a simple cubic lattice. Consequently, the following trapping master equation is derived to describe the motion of a tagged atom.

$$\frac{\partial}{\partial t}P(s,t|s_0,\ 0)=\sum_{s'}\omega_{s'}P(s',t|s_0,0)+\sum_{u_s}\omega_b P(s+u_s,t|s_0,0)$$
$$-\left\{\sum_{s'}\omega_s+\sum_{u_s}\omega_b\right\}P(s,t|s_0,\ 0), \tag{1}$$

$$\frac{\partial}{\partial t}P(s+u_s,t|s_0,\ 0)=\omega_b P(s,t|s_0,0)-\omega_b P(s+u_s,t|s_0,0), \tag{2}$$

where $P(x,t|s_0,0)$ denotes the probability that the tagged atom is at $\mathbf{x}$ at time t when it was at s_0 at time t=0, the summation for s′ is taken over nearest neighbors of site s, and $\{\mathbf{u}_s\}$ represent neighboring sites to which the atom on s can stray. As discussed above, jump rate $\{\omega_s\}$ can be assumed to obey the power-law distribution

$$\Phi(\omega_s)=\begin{cases}\dfrac{\rho+1}{\omega_0^{\rho+1}}\omega_s^{\rho} & (0\leqq\omega_s\leqq\omega_0)\\ 0 & (\text{otherwise}),\end{cases} \tag{3}$$

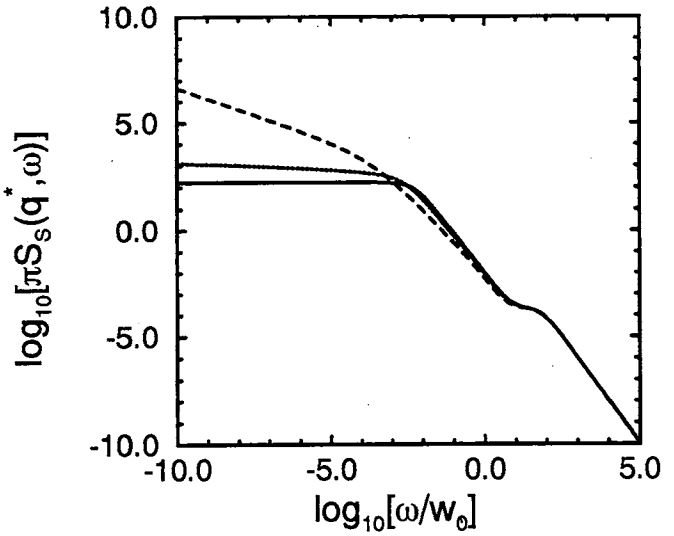
where ρ is a key parameter of the model which represents the thermo-dynamic state of the system. Since $\{\omega_s\}$ are random, the above master equation can be solved by using the coherent medium approximation.

The self-part of the dynamical structure factor $S_s(\mathbf{q},\omega)$ is shown in the figure, with the definition given by

$$S_s(\mathbf{q},\omega)=\frac{1}{\pi}\mathrm{Re}\left[1+\frac{\omega_b\beta(\mathbf{q})}{\omega_b+i\omega}\right]\sum_s e^{iq(s-s_0)}\left\langle\int_0^\infty e^{-i\omega t}P(s,t|s_0,0)dt\right\rangle, \tag{4}$$

where the angular brackets $\langle\cdots\rangle$ denotes an ensemble average and $\beta(\mathbf{q})=\Sigma_{u_s}e^{iqu_s}$ is assumed to be real and independent of s. In $S_s(\mathbf{q},\omega)$, two kinds of slow relaxations are observed: One appears near $\log_{10}\omega=-1.5$, which corresponds to the α relaxation, and the other appears near $\log_{10}\omega=1.2$, corresponds to the β relaxation. In $-1<\rho<0$, another slow relaxation, called α' relaxation, is found in the static limit. The α and α' relaxations are due to the jump motion which induce the sub-anomalous diffusion in supercooled liquid state ($0<\rho<1$) and the anomalous diffusion in glassy state ($-1<\rho<0$). The β relaxation

is caused by nothing but the crossover between the two dynamics (stray motion and jump motion).



The frequency dependence of $S_s(\mathbf{q},\omega)$ for $\rho=0.5$(solid line), 0.0(dotted line) and -0.5(dashed line).

Super-long-time MD simulation

The generalized susceptibility $\chi(\mathbf{q},\omega)$ has been computed directly through the MD simulation with a new algorithm described below. The Fourier and Laplace transformations, $S(\mathbf{q},\omega)$ and $G(\mathbf{q},\omega)$, of the intermediate scattering function $F(\mathbf{q},t)$ are defined as

$$S(\mathbf{q},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}F(\mathbf{q},t)e^{i\omega t}dt, \tag{5}$$

$$G(\mathbf{q},\omega)=\int_{0}^{\infty}F(\mathbf{q},t)e^{-i\omega t}dt, \tag{6}$$

where

$$F(\mathbf{q},t)=\left\langle\sum_{j}\exp\ i\mathbf{q}\cdot[\mathbf{r}_i(t+t_0)-\mathbf{r}_j(t_0)]\right\rangle_{i,t0}. \tag{7}$$

The averages are made over the configuration of atoms $\{r_i\}$ and the initial time t_0. It is known that the generalized susceptibility $\chi(\mathbf{q},\omega)$ is related to $G(\mathbf{q},\omega)$ and $S(\mathbf{q},\omega)$ in the following way,

$$\chi'(\mathbf{q},\omega)=1+\omega G''(\mathbf{q},\omega) \tag{8}$$

$$\chi''(\mathbf{q},\omega)=\omega G''(\mathbf{q},\omega) \tag{9}$$

$$=\omega\pi S(\mathbf{q},\omega), \tag{10}$$

where $\chi(\mathbf{q},\omega)=\chi'(\mathbf{q},\omega)+i\chi''(\mathbf{q},\omega)$and $G(\mathbf{q},\omega)=G'(\mathbf{q},\omega)+iG''(\mathbf{q},\omega)$.

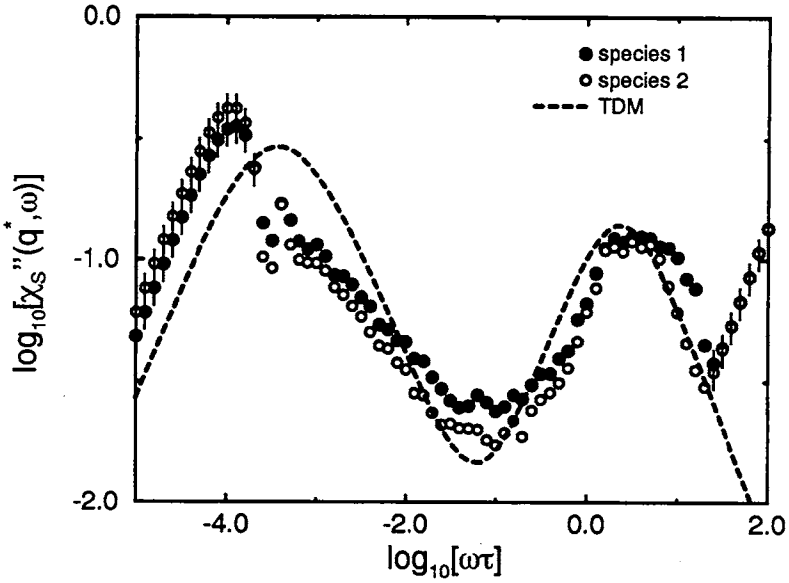
In the present MD simulation, $G(\mathbf{q},\omega)$ has been computed by the following formula,

$$G(\mathbf{q},\omega)=\frac{1}{T}\left\langle\sum_j\int_0^T dt_0 e^{i\mathbf{q}\cdot\mathbf{r}_i(t_0)}e^{-i\omega t_0}\int_0^{t_0}dt e^{-i\mathbf{q}\cdot\mathbf{r}_j(t)}e^{i\omega t}\right\rangle_i, \tag{11}$$

where $< \ldots >$ means an average over the configuration of atoms $\{\mathbf{r}_i\}$, and T is the total time step of the simulation. The above equation is valid provided that the condition $\omega T \gg 1$ is satisfied. The self part $G_s(\mathbf{q},\omega)$of $G(\mathbf{q},\omega)$is similarly obtained by setting $i=j$ in the summation.

The imaginary part of the self part of the generalized susceptibility $\chi_s''(\mathbf{q},\omega)$ is shown in the following figure. The α peak is clearly seen around $\log_{10}\omega\tau=-3.2$, which can be represented by the power-law function $\chi_s''(\mathbf{q},\omega)\propto\omega^{-0.47}$. This exponent value gives the approximate value of the stretched exponent which differs from Debye value -1. The β peak appears in the higher frequency region around $\log_{10}\omega\tau=0.6$. For the Cole-Cole analysis, it is concluded that the β peak seems to be the Debye type. The fact that the decrement of $\chi''(\mathbf{q},\omega)$in high frequency is seen as ω^{-1} in the figure supports this conclusion.

The result of TDM is represented by dashed line in the same fugure. It is remarkable that the MD results are in good agreement with the TDM.



The frequency dependence of $\chi_s''(\mathbf{q},\omega)$ for $\Gamma_{\text{eff}}=1.50$.

Circles represent the MD results and the dashed line the TDM results. Unreliable data due to the numerical integration are marked by | to their data points.

学位論文の審査結果の要旨

提出された学位論文をもとに，審査委員会の慎重な内容の検討を行い，平成７年２月７日に行われた口頭発表およびその後開かれた最終審査会を得て以下のような結論を得た。

本学位論文は液体－ガラス転移の理論的考察を行ったものである。ガラス転移現象は実験的にはよく知られている現象であるが理論的考察，特にそのダイナミックスについての考察，は極めて少なく，

ガラス転移の本質はまだ解明されるに至っていない現状である。本論文ではガラス転移点近傍のみならず，高過冷液体からガラス状態にいたるまでの広い範囲の状態についてこれらの状態のダイナミックスを中心とした独創的な理論の展開を行っている。

過冷液体の分子動力学シミュレーションから粗視化された原子運動には異なる2種類のジャンプ運動が存在することが明らかにされる。また，過冷液体中の原子配位およびケージ効果の特徴を反映してこれらのジャンプ運動の一方（平均のジャンプ率が小さい方）のジャンプ率は一定ではなくある分布をしていて通常のジャンプ拡散と質的に異なる。このような原子運動の特徴を取り入れて，1粒子拡散方程式(マスター方程式)を解くことから種々のダイナミックス(緩和関数など)の異常性が求められる。この結果以下のことが明らかにされた。

(1) 高過冷液体で準異常拡散が生じる。これから中間時間帯での動的異常の振る舞い(α緩和, β緩和)の機構が明らかにされた。

(2) ガラス転移温度以下で異常拡散が現われる。これより拡散運動は存在するが拡散係数はゼロとなる。これは長時間極限でも動的異常性が現われることを示すものである。液体－ガラス転移はガウシアン－ノンガウシアン転移として理解されるとの新しい概念の提案やまた新しい緩和(α')の存在も示唆されている。

(3) (1)の結果は分子動力学シミュレーションによる過冷液体（二成分ソフトコアモデル）の一般化された複素感受率の計算を行うことからもその妥当性が示されている。また近年の中性子回折実験の結果ともよく符号することが示されている。

このように本論文はその発想が独創性に豊んでいることはもとより，内容，記述の論理性，正確さのいづれにおいても優れているので博士（理学）の学位に値するものと判断する。