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A theoretical framework for calculations of the structural relaxation time on the basis of the free energy landscape theory

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ABSTRACT

On the basis of the free energy landscape theory, we develop a framework to calculate the structural relaxation time in supercooled liquids and glasses. By the framework, the relaxation time is obtained by an escaping time from a basin in a given free energy surface. In order to demonstrate its usefulness, we apply the framework to monodisperse hard-sphere glass systems. Then we show that the relaxation time increases drastically with the density. Additionally, we discuss an explicit picture of the cooperatively rearranging region by analyzing the spatial distribution of an activation free energy of one particle.

1. Introduction

Despite numerous theoretical and experimental efforts, the glass transition is far from complete understanding. One of the reasons for this difficulty lies in the fact that various anomalous behaviors in the vitrification process are exhibited by both thermodynamic and dynamic properties [1]. For example, the specific heat changes abruptly at the glass transition temperature T_g. The structural relaxation time tends to diverge at a temperature below T_g. Therefore, it is important to construct a theory providing a unified understanding of these thermodynamic and dynamic anomalies.

A unified understanding of these behaviors has been provided by the free energy landscape (FEL) theory through dynamics on rugged free energy surfaces [2–9]. By the theory, the free energy surface is expressed as a function of coarse-grained configurations of liquid particles $\{\mathbf{R}_i\}$ [2]. The rugged structure of the free energy surface is obtained at low temperatures. The specific heat [3] and the relaxation time [8,9] have been calculated from dynamics on model free energy surfaces. The calculated specific heat changes abruptly at T_g [3]. Additionally, the temperature dependence of the relaxation time is agreement with that observed by the experiments [8,9].

Recently, Yoshidome et al. have constructed the FEL on the basis of a microscopic Hamiltonian [10–12]. From a microscopic Hamiltonian, the free energy functional was obtained by the density functional theory (DFT) [13]. In order to express the free energy function of $\mathbf{R}_i$, a sum of Gaussian functions with the center of $\mathbf{R}_i$ was employed as a density field [14,15]. Using the method, they obtained rugged free energy surfaces for monodisperse hard-sphere systems.

Since the FEL for actual systems has been constructed on the basis of a microscopic Hamiltonian, physical quantities such as the relaxation time for actual systems can be obtained using the FEL. In particular, it is desirable to calculate the relaxation time, because the time scale of the relaxation time is too long to obtain by the molecular dynamics simulation (MD). As described later, we can obtain it without executing MDs if the FEL is constructed.

It is known that a key concept for understanding the mechanism of the relaxation process is the cooperatively rearranging region (CRR) proposed by Adam and Gibbs [16]. The CRR is the minimum area required for particle rearrangements causing structural relaxations. Using the concept, Adam and Gibbs have shown that the relaxation time is in proportion to $\exp[N_{CRR}\Delta\mu]$. Here, N_{CRR} is a number of particles in a CRR, and $\Delta\mu$ is the activation free energy of a particle. In their theory, $\Delta\mu$ is assumed to have no spatial distribution and no temperature dependence.

We need to estimate $\Delta\mu$ microscopically in order to discuss validity of the theory developed by Adam and Gibbs. Adam and Gibbs expressed the relaxation time by N_{CRR} and $\Delta\mu$. Although N_{CRR} for a hard-sphere system was already studied before [11], there is no study of $\Delta\mu$. In particular, we examine the assumption that $\Delta\mu$ does not have a spatial distribution. We can consider that the assumption is not valid, if there is dynamical heterogeneity shown by the MD simulations [17].

In the present letter, on the basis of the FEL theory, we propose a method to calculate the relaxation time from free energy surfaces of actual systems. Applying the method to monodisperse hard-sphere particles in the CRR, we show density dependence of the relaxation time. Using the FEL, we define the activation free energy

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of a particle, and then analyze its spatial distributions. Calculating density dependence of the spatial distribution, we show that the activation free energy increases owing to contributions of particles at a boundary of the CRR.

On the basis of the potential energy landscape (PEL), other methods to treat the slow dynamics have been employed [18–20]. In the methods, jump motions among minima (inherent structures) and meta-basins are considered. The dynamics on the PEL, therefore, includes the fast vibrational motions of atom and the structural relaxation processes. In contrast, the structural relaxation processes are focused on in the FEL theory. Especially, hard-sphere systems can be treated only by the FEL.

2. Theory

All the calculations of the free energy landscape are executed by the procedure proposed by Yoshidome et al. [10–12]. On the basis of the DFT, the grand potential $\Omega[\rho(\mathbf{r})]$ is expressed as a functional of the density field $\rho(\mathbf{r})$. As the density field, the sum of Gaussian functions $\rho_G(\mathbf{r},\alpha,\{\mathbf{R}_i\})$ is employed. Here, α and $\mathbf{R}_i$ are the width and center of the Gaussian function [11,14,15]. By substituting $\rho_G(\mathbf{r},\alpha,\{\mathbf{R}_i\})$ into $\Omega[\rho(\mathbf{r})]$, the free energy is given by

$$\beta\Delta\Omega(\alpha,\{\mathbf{R}_i\}) \equiv \beta\Omega[\rho_G(\mathbf{r},\alpha,\{\mathbf{R}_i\})] - \beta\Omega(\rho). \tag{1}$$

Here, β is given by $\beta = 1/(k_BT)$ where k_B is the Boltzmann constant and T is the temperature, and ρ is given by $V^{-1}\int d\mathbf{r}\rho(\mathbf{r})$, where V is the volume. We note that $\beta\Omega[\rho_G(\mathbf{r},\alpha,\{\mathbf{R}_i\})]$ is a functional of $\rho_G(\mathbf{r},\alpha,\{\mathbf{R}_i\})$. In order to calculate $\Omega[\rho(\mathbf{r})]$, the Ramakrishnan–Yussouff (RY) free energy functional [21] is adopted. Eq. (1) is then given by

$$\beta\Delta\Omega[\rho(\mathbf{r})] = \int_V d\mathbf{r}\rho(\mathbf{r})\log\left[\frac{\rho(\mathbf{r})}{\rho}\right] - \int_V d\mathbf{r}\Delta\rho(\mathbf{r}) - \frac{1}{2}\int_V d\mathbf{r}\int_V d\mathbf{r}'c(|\mathbf{r}-\mathbf{r}'|)\Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}'), \tag{2}$$

where $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho$, and $c(|\mathbf{r}-\mathbf{r}'|)$ is the second direct correlation function.

The free energy is analytically calculated [10] by

$$\beta\Delta\Omega(\alpha,\{\mathbf{R}_i\}) = F_{id}(\alpha,\{\mathbf{R}_i\}) + F_0 - \frac{N}{2}I_0(\alpha) - \sum_i\sum_{j>i}I(\alpha,|\mathbf{R}_{ij}|), \tag{3}$$

where $|\mathbf{R}_{ij}|$ is the distance between $\mathbf{R}_i$ and $\mathbf{R}_j$, and N is given by ρV, and $I(\alpha,|\mathbf{R}_{ij}|)$ is defined by

$$I(\alpha,|\mathbf{R}_{ij}|) = \frac{1}{2}\left(\frac{\alpha}{\pi}\right)^3\int_V d\mathbf{r}_i\int_V d\mathbf{r}_j c(|\mathbf{r}_i-\mathbf{r}_j|)\times\exp[-\alpha(\mathbf{r}_i+\mathbf{r}_j)^2] \times\exp[-\alpha(\mathbf{r}_j+\mathbf{R}_{ij})^2]. \tag{4}$$

The $\mathbf{R}_i$-dependence of the ideal part $F_{id}(\alpha,\{\mathbf{R}_i\})$ in Eq. (3) can be omitted under a large-αcondition [14]. In the present letter, Eq. (4) is analytically calculated by the large-α [22] and Percus–Yevick [13] approximations. The detailed expressions of Eqs. (1), (3), and (4) are given in Refs. [10,22].

We apply Eq. (3) to three-dimensional random packing structures (RPS) of hard-sphere particles constrained in a spherical shell (see Figure 1). We prepare the RPS by the infinitesimal gravity protocol [11]. The number of particles was 486 and the number density was 1.04. To obtain the positions of particles at an objective density $\rho\sigma^3$ (σ is the diameter of the hard-sphere particle), we modulate the position of particles by multiplication of $(1.04/\rho\sigma^3)^{1/3}$. From the RPS, we choose particles shown by green color[1] in Figure 1. We leave the particles (white particles in Figure 1) surrounding the green particles over 2σ and remove other particles outside the white particles. While we calculate the FEL, we move the green particles and fix the positions of white particles. Here, $\sum_i$ in Eq. (3) represents the summation over green particles, while $\sum_{j>i}$ represents the summation over both green and white particles. Before the calculation of the FEL, the green particles are relaxed to minimize $\Omega(\alpha,\{\mathbf{R}_i\})$ in the $\{\mathbf{R}_i\}$ space by the steepest descent method with the positions of white particles fixed. The initial configuration giving the minimum of $\Omega(\alpha,\{\mathbf{R}_i\})$ is denoted by $\{\mathbf{R}_i^0\}$.

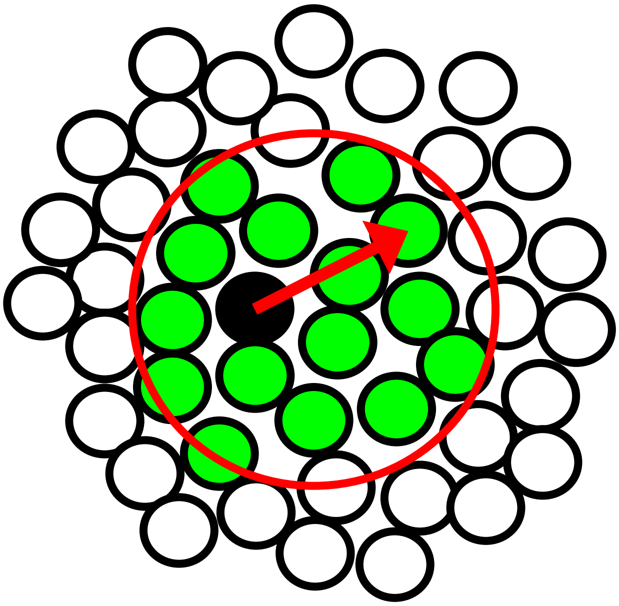

Figure 1. A schematic picture of the system. The black particle is the A-particle.

We determine the number of green particles so that the number is in agreement with that of the CRR. In the previous paper [11], the number of particles of a CRR N_{CRR} was estimated by modulating the number of green particles as follows. After the positions of the white particles are fixed, a FEL is first constructed by one particle (A-particle shown by black in Figure 1) forced to displace toward one direction. When the number of the green particles is large, the system can transit from the initial basin to an adjacent basin. For a small number, in contrast, the system cannot transit. Then, N_{CRR} is defined by the smallest number of the green particles. By the procedure, the density dependence of N_{CRR} was obtained: $N_{CRR}(\rho\sigma^3) = 2.5/(1.3-\rho\sigma^3)^{1.7}$[11]. Using this equation, we estimate N_{CRR} for all the density employed in the present calculation.

In order to produce a structural relaxation in the constrained particles, we force the A-particle to displace toward one direction. We choose the A-particle whose position is away from the center of green particles about σ. After the A-particle is forced to displace, the green particles are relaxed to minimize the free energy with the position of the A-particle fixed.

The explained procedure allows us to focus on a one-dimensional motion of the tagged particle (A-particle). The other particles than the A-particle are relaxed to minimize the free energy. Then we can uniquely determine the path connected between given two basins in a multi-dimensional phase space. The free energy landscape along the one-dimensional path can be given by a function of the displacement of the A-particle ΔR_A.

The free energy difference between the initial and new configurations $\{\mathbf{R}_i^0\}$ and $\{\mathbf{R}_i\}$ is given by

$$\beta\delta\Omega(\Delta R_A;\rho\sigma^3) \equiv \beta\Delta\Omega(\alpha,\{\mathbf{R}_i\}) - \beta\Delta\Omega(\alpha,\{\mathbf{R}_i^0\}) = \sum_i^{N_{CRR}}\sum_{j>i}\left[-I(\alpha,|\mathbf{R}_{ij}|) + I(\alpha,|\mathbf{R}_{ij}^0|)\right]. \tag{5}$$

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[1] For interpretation of color in Figure 1, the reader is referred to the web version of this article.