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Microscopic derivation of jump rate distribution and the glass transition

T Odagaki and A Yoshimori

Department of Physics, Kyushu University, Fukuoka 812-8581, Japan

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Abstract. A general framework is given for deriving the jump rate distribution function and the long-time behaviour of the waiting time distribution for the jump is shown to be a power-law function whose exponent is related to the contribution of fast modes relative to that of slow modes in the density fluctuation. A unified explanation for the vitrification process and glass transition singularities is presented.

1. Introduction

Understanding of the glass transition remains one of the most important unsolved problems in condensed matter physics and many reported experimental, theoretical and computational studies have been carried out with the aim of elucidating the solidification process of atoms in the glass transition. Extensive molecular dynamics simulations [1] have revealed that the diffusive dynamics in a supercooled fluid is separated into jump motion and localized stochastic motion and the jump motion is believed to be responsible for the slow dynamics. Odagaki [2] showed that the jump rate distribution behaves as

$$P(w) \sim w^{\alpha} \tag{1}$$

which gives rise to the power-law decay of the waiting time distribution

$$\psi(t) \sim t^{-(\alpha+2)} \qquad (t \to \infty) \tag{2}$$

and proposed a unified view for dynamical singularities based on the divergence of the moments of the waiting time distribution. From the comparison of the results from the trapping diffusion model [3] and experiments, it was concluded that (i) $\alpha = -1$ corresponds to the Vogel–Fulcher temperature, (ii) $\alpha = 0$, where the mean waiting time diverges, is the glass transition temperature and (iii) a crossover is expected at $\alpha = 1$. Furthermore, by exploiting the Adam–Gibbs approach and the chemical rate theory, the parameter α was related to the excess entropy $S_C(T)$:

$$\alpha = [TS_C(T) - T_g S_C(T_g)]/T_g S_C(T_g). \tag{3}$$

It is interesting to note that for a class of fragile glass formers the specific heat just above the glass transition temperature is scaled by α [4].

Götze [5] has proposed the mode coupling theory (MCT) for the dynamics of supercooled liquids and predicted that an ergodic-to-non-ergodic transition occurs at a certain critical temperature T_C. The critical temperature is now believed to be much higher than the glass transition temperature. The most important prediction of the MCT is the appearance of different timescales which distinguish fast and slow processes. In view of the success of the MCT in describing the dynamics in supercooled liquids, it is tempting to ask whether one can relate the frozen density fluctuation predicted by the MCT and the jump rate distribution and devise a unified concept for the vitrification process.

The aim of the present report is to present a general framework for the microscopic derivation of the jump rate distribution. To this end we employ a theory developed for chemical reactions [6] and show that the jump rate distribution becomes a power-law function in the small-jump-rate limit. In section 2, the general framework is presented. We obtain the jump rate distribution in section 3 utilizing the surrogate approximation and the Gaussian distribution of the density fluctuation. In section 4, the unified view for the vitrification process is discussed.

2. Basic formalism

It is now widely believed, from molecular dynamics simulations [1], that the relaxation process in supercooled liquids is split into fast and slow processes and that the latter is observed as a jump motion. When one identifies a jump motion of an atom or a group of atoms, one considers that during the jump process other atoms are localized—that is, the jump time is considered to be negligible compared to other characteristic times.

The jump motion occurs when the surrounding atoms produce a configuration (transition state) such that the energy of the initial state is equal to that of the final state. Thus, exploiting the theory of chemical reaction [6], we can write the average jump rate as

$$\bar{w} \propto \nu_A \left(\int \mathrm{d}\Gamma' \, \delta(H^I - H^F) \mathrm{e}^{-\beta H^I} \right) \Big/ \left(\int \mathrm{d}\Gamma' \, \mathrm{e}^{-\beta H^I} \right) \tag{4}$$

where H^I and H^F denote the energy of the system before and after a jump motion, respectively, and $\beta^{-1} = k_B T$ is the temperature multiplied by the Boltzmann constant. The integration is performed in the phase space spanned by coordinates other than those of atoms making the jump. The physical meaning of equation (4) is that the average jump rate is proportional to the total probability that the energy of the system is H^I under the condition of the transition state. Figure 1 illustrates this process schematically.

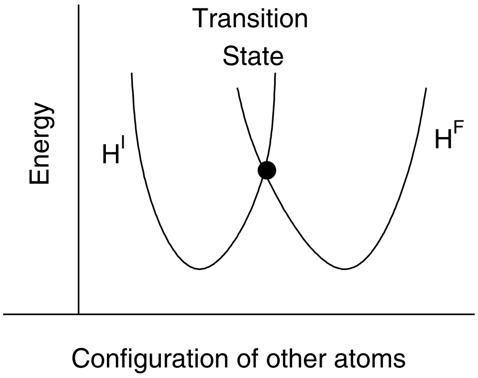

Figure 1. A schematic illustration of a jump process.

The density fluctuations of surrounding atoms which produce the transition state decay at various rates, and it is natural to assume that modes with characteristic time longer than the inverse of the attempt frequency ν_A are frozen and other modes are not. We introduce the basic assumption for the jump that the energy difference $\Delta H \equiv H^I - H^F$ can be written as the sum of two contributions; one is the contribution of fast modes ΔH_f and the other is that of slow modes ΔH_s. Then, equation (4) can formally be written as

$$\bar{w} = \int w(x)\Phi(x)\,\mathrm{d}x \tag{5}$$

where

$$\Phi(x) = \left(\int \mathrm{d}\Gamma'\,\delta(\Delta H_s - x)\mathrm{e}^{-\beta H^I}\right)\Big/\left(\int \mathrm{d}\Gamma'\,\mathrm{e}^{-\beta H^I}\right) \tag{6}$$

and

$$w(x) = \frac{A}{\Phi(x)}\left(\int \mathrm{d}\Gamma'\,\delta(\Delta H_s - x)\delta(\Delta H_f + x)\mathrm{e}^{-\beta H^I}\right)\Big/\left(\int \mathrm{d}\Gamma'\,\mathrm{e}^{-\beta H^I}\right). \tag{7}$$

Equation (5) indicates that the average jump rate is given by an average of the conditional jump rate $w(x)$ over the distribution function $\Phi(x)$. Therefore the jump rate distribution is given by

$$P(w) = \Phi(x^{-1}(w))\left|\frac{\mathrm{d}x}{\mathrm{d}w}\right|. \tag{8}$$

It is apparent from this formalism that the jump rate distribution originates from the fact that the jump occurs in various configurations of the slow modes.

3. Surrogate approximation and jump rate distribution

In order to evaluate the jump rate distribution, we write the energy difference in terms of the density function as

$$\Delta H = \int [V(\boldsymbol{r} - \boldsymbol{r}^I) - V(\boldsymbol{r} - \boldsymbol{r}^F)]\rho(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} \tag{9}$$

where $\boldsymbol{r}^I$ and $\boldsymbol{r}^F$ represent symbolically the positions of atoms making the jump motion before and after the jump, $\rho(\boldsymbol{r})$ is the conditional density function of the other atoms, which is assumed to be the same before and after the jump, and V is the potential energy between jumping atoms and the rest of atoms. Introducing the Fourier transform

$$\rho(\boldsymbol{r}) = \sum_{\boldsymbol{q}} \rho_{\boldsymbol{q}} \tag{10}$$

and assuming that the slow and fast modes can be distinguished in $\boldsymbol{q}$-space, we can write

$$\Delta H_f = \sum_{\text{F.M.}} \Delta V_{-\boldsymbol{q}}\rho_{\boldsymbol{q}} \tag{11}$$

$$\Delta H_s = \sum_{\text{S.M.}} \Delta V_{-\boldsymbol{q}}\rho_{\boldsymbol{q}} \tag{12}$$

where $\Delta V_{\boldsymbol{q}}$ is the Fourier transform of $V(\boldsymbol{r}-\boldsymbol{r}^I) - V(\boldsymbol{r}-\boldsymbol{r}^F)$ and F.M. and S.M. denote fast and slow modes, respectively. Furthermore, we employ an approximation in which the potential energy is replaced by the direct correlation function (the surrogate approximation [7–9]):

$$V(\boldsymbol{r}) = C(\boldsymbol{r}) \tag{13}$$

and the Boltzmann factor is replaced by the Gaussian distribution in density

$$\int \mathrm{d}\Gamma'\,\mathrm{e}^{-\beta H^I}\cdots = \int \prod_{\boldsymbol{q}} \mathrm{d}\rho_{\boldsymbol{q}}\,\cdots \exp\left(-\sum_{\boldsymbol{q}} \frac{|\rho_{\boldsymbol{q}} - \rho_{\boldsymbol{q}}^0|^2}{2S_{\boldsymbol{q}}}\right) \tag{14}$$

where S_q is the structure factor, ρ_q^0 and ρ_q are the densities of the average and temporal configurations, respectively. The replacement by the Gaussian distribution is equivalent to making the linear response approximation, and the surrogate approximation is employed to include nonlinear effects. The approximations were shown to be successful in the analysis of solvation dynamics [7–10].

Since the Boltzmann factor is factorized in equation (14), equation (7) can be simplified as follows:

$$w(x) = \left[A \int \prod_{\mathrm{F.M.}} \mathrm{d}\rho_q \, \delta(\Delta H_f + x) \exp\left(-\sum_{\mathrm{F.M.}} \frac{|\rho_q - \rho_q^0|^2}{2S_q} \right) \right] \times \left[\int \prod_{\mathrm{F.M.}} \mathrm{d}\rho_q \, \exp\left(-\sum_{\mathrm{F.M.}} \frac{|\rho_q - \rho_q^0|^2}{2S_q} \right) \right]^{-1} \tag{15}$$

$$\Phi(x) = \left[\int \prod_{\mathrm{S.M.}} \mathrm{d}\rho_q \, \delta(\Delta H_s - x) \exp\left(-\sum_{\mathrm{S.M.}} \frac{|\rho_q - \rho_q^0|^2}{2S_q} \right) \right] \times \left[\int \prod_{\mathrm{S.M.}} \mathrm{d}\rho_q \, \exp\left(-\sum_{\mathrm{S.M.}} \frac{|\rho_q - \rho_q^0|^2}{2S_q} \right) \right]^{-1}. \tag{16}$$

It is tedious but straightforward [11] to show by calculation that

$$w(x) \propto \exp\left[-\frac{1}{4\lambda_f} (\lambda_f + x)^2 \right] \tag{17}$$

and

$$\Phi(x) \propto \exp\left[-\frac{1}{4\lambda_s} (\lambda_s - x)^2 \right]. \tag{18}$$

Here, λ_f and λ_s are defined by

$$\lambda_f = \sum_{\mathrm{F.M.}} \frac{S_q |C_q^I - C_q^F|^2}{2} \tag{19}$$

$$\lambda_s = \sum_{\mathrm{S.M.}} \frac{S_q |C_q^I - C_q^F|^2}{2} \tag{20}$$

where C_q^I and C_q^F are the Fourier transforms of the direct correlation function before and after the jump, respectively.

Eliminating x from equations (17) and (18), we can obtain the jump rate distribution $P(w)$ and show that in the limit of $w \to 0$, $P(w)$ behaves as

$$P(w) \propto w^{\lambda_f/\lambda_s - 1} \tag{21}$$

where an unimportant term proportional to $\ln w$ is neglected.

4. Waiting time distribution and glass transition singularities

According to the unified view given by Odagaki [2], the glass transition singularities can be understood from the divergence of the various moments of the waiting time distribution of a jump which is defined by

$$\psi(t) = \int w \mathrm{e}^{-wt} P(w) \, \mathrm{d}w. \tag{22}$$

The singularity of moments of the waiting time distribution is determined by the long-time behaviour of the waiting time distribution. It is easy to show from equation (21) that $\Psi(t)$ behaves as

$$\Psi(t) \sim t^{-(\lambda_f/\lambda_s+1)}. \tag{23}$$

Thus in the present theory, the glass transition point is given [2] by

$$\frac{\lambda_f}{\lambda_s} = 1. \tag{24}$$

Similarly, the Vogel–Fulcher point and a crossover point are given by $\lambda_f = 0$ and $\lambda_f/\lambda_s = 2$, respectively.

5. Discussion

We have presented a general framework for derivation of the jump rate distribution. According to molecular dynamics simulations [1], the diffusive dynamics in supercooled liquids changes its nature at a certain temperature and a description based on the jump motion becomes possible. This means that for a theory which does not include the jump motion the system will appear frozen. Since the relaxation time τ_q depends on the wavenumber, it is natural to assume that modes can be classified into fast and slow modes by the wavenumber as we have done in this paper. The present mode coupling theory [5] discusses the divergence of the relaxation time or the disappearance of diffusion on the basis of the basic equation without jump motions and predicts the divergence to occur at a critical temperature independent of the wavenumber. The view from the MCT suggests that modes whose relaxation time exceeds the inverse of the attempt frequency can be considered as frozen in the jump process. Once the existence of fast and slow modes is accepted, then the jump rate distribution can be shown to behave as a power-law function for the small-jump-rate limit as we have seen in this paper, and the glass transition singularities are related to the divergence of various moments of the waiting time distribution, following the argument of the trapping diffusion model [2]. Therefore, we now have a unified description of the vitrification process and the glass transition singularities on the basis of a microscopic model.

To understand the separation of slow and fast modes, let us consider the relaxation in liquids where the relaxation time is $\sim(Dq^2)^{-1}$, D being the diffusion constant. Thus, if the attempt frequency is ν_A and the diffusion constant expected for the dynamics without jumps is denoted by D, then $q_C \sim \sqrt{\nu_A/D}$ is a rough estimate of the demarcation wavenumber, where the slow and fast modes at a given temperature are classified as having $q < q_C$ or $q \geqslant q_C$. In fact, on this assumption, we can obtain the glass transition point by analysing the structure factor. We will report an analysis for the hard-sphere system elsewhere [11].

It should be remarked here that the relaxation time may not be a monotonic function of the wavenumber and thus one might need more careful analysis of the relaxation time to distinguish slow and fast modes.

The remaining problem is that of whether the thermodynamic anomalies can be understood in the same framework. It is very encouraging to see that the specific heat of a class of fragile glass formers can be scaled by α defined in equation (3). Therefore, it is plausible to expect the same framework to also explain the thermodynamic singularities, which will be an important future problem.

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