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LETTER TO THE EDITOR

Residence time distribution of a tracer atom in supercooled fluids

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Abstract. The residence time distribution of a tracer atom in soft-sphere supercooled fluids is discussed on the basis of the trapping diffusion model of the glass transition. An explicit relation between a parameter of the trapping diffusion model and the soft-sphere fluid is obtained.

The dynamics of atoms near a glass transition point is known to have two distinct modes; one is the rapid oscillation around a local equilibrium position and the other is a jump motion between those local equilibrium positions [1, 2]. The latter is responsible for a slow dynamics in mesoscopic time scales and determines the long-time dynamical behaviours such as the diffusion constant in liquids. Two approaches have recently been proposed to explain the dynamical characteristics of the glass transition: one is the mode-coupling approach [3, 4] and the other is the trapping diffusion approach [5]. In the mode-coupling approach, one concentrates on the density fluctuation and the non-decaying behaviour of the density fluctuation is considered to be the signature of the glass transition. A recent advanced mode-coupling theory has also revealed that if a coupling between the density and the momentum density fluctuations is taken into account, then no sharp transition can be expected to occur. An ideal glass transition is predicted only as a limiting condition.

The trapping diffusion model for the glass transition deals with the dynamics of atoms that is assumed to be described by the random walk on a simple cubic lattice with a random environment [5]

$$\frac{\partial}{\partial t}P(s,t|s_0,0) = \sum_{s'}[w_{s'}P(s',t|s_0,0) - w_s P(s,t|s_0,0)] \tag{1}$$

where $P(s',t|s_0,0)$ denotes the conditional probability of a tracer atom being at s at time t when it started from s_0 at $t = 0$, and the summation is taken over the nearest neighbours of site s. The jump-rate distribution is considered to be the most fundamental feature in a supercooled fluid affected by a random configuration of the neighbours surrounding the tracer atom, and is assumed to follow the power law function

$$P(w_s) = \begin{cases} \left(\dfrac{\rho+1}{w_0^{\rho+1}}\right)w_s^{\rho} & 0 \leqslant w_s \leqslant w_0 \\ 0 & \text{otherwise.} \end{cases} \tag{2}$$

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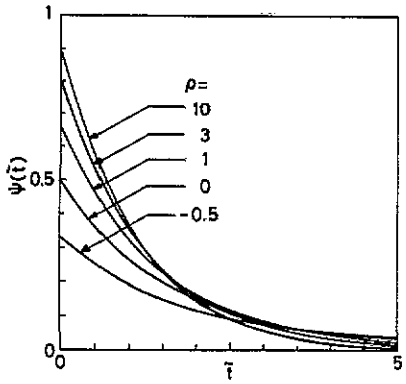

Figure 1. The residence time distribution $\psi(\bar{t})$ for the trapping diffusion model for various values of ρ.

It has been shown that the trapping diffusion model with this *ansatz* for $P(w_s)$ gives a successful explanation for the long-time behaviour of the mean square displacement, the diffusion constant and the non-Gaussian parameter of supercooled soft-sphere fluids [5,6], all consistent with the results of molecular dynamics simulations. In fact, using the maximum of the non-Gaussian parameter, the glass transition point is determined to be $\Gamma_g = 1.58$ (Γ is the effective coupling constant) for the binary soft-sphere system [6], which corresponds to $\rho = 0$ for the trapping diffusion model. This model also explains dynamical changes near $\Gamma = 1.45$ (a kinetic transition) observed in supercooled binary soft-sphere fluids with the molecular dynamics simulations [2, 7] as an apparent glass transition on the basis of the sub-anomalous dynamics predicted by the trapping diffusion model [8].

In this letter we present a direct comparison of the residence time distribution and the molecular dynamics simulation to give a further ground for adopting the trapping diffusion approach as a model for the glass transition in simple liquids. The residence time of an atom is defined as the time span before the first jump occurs after the observation started. The residence time distribution $\psi(t)$ for the trapping diffusion model is given by

$$\psi(t) = \int_0^{w_0} P(w_s) z w_s \exp(-z w_s t)\, \mathrm{d}w_s = z w_0 (\rho+1) G(\rho+2) \gamma^*(\rho+2, z w_0 t) \tag{3}$$

where $G(x)$ is the Gamma function and $\gamma^*(a,x)$ is the Tricomi incomplete Gamma function. Figure 1 shows $\psi(t)$ for various values of ρ. It is straightforward to obtain the limiting behaviours of $\psi(t)$.

(i) Near $t = 0$:

$$\psi(\bar{t}) = \frac{\rho+1}{\rho+2} - \frac{\rho+1}{\rho+3}\bar{t} + \frac{\rho+1}{2(\rho+4)}\bar{t}^2 - \frac{\rho+1}{6(\rho+5)}\bar{t}^3 + \cdots. \tag{4}$$

(ii) Near $t = \infty$:

$$\psi(\bar{t}) = (\rho+1)G(\rho+2)\bar{t}^{-(\rho+2)} - (\rho+1)\exp(-\bar{t})\left(\frac{1}{\bar{t}} + \frac{(\rho+1)}{\bar{t}^2} + \frac{\rho(\rho+1)}{\bar{t}^3} + \cdots\right). \tag{5}$$

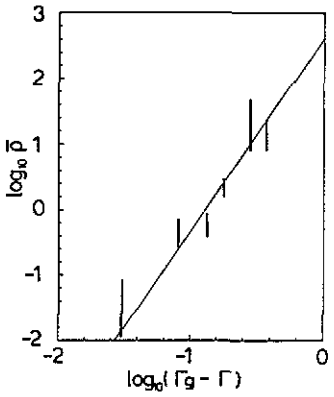

Figure 2. Log–log plot of $\bar{\rho}$ against $\Gamma_g - \Gamma$ with $\Gamma_g = 1.58$ for several values of Γ. The vertical bars denote the range of $\bar{\rho}$ estimated from $\psi(0)$ via (7). Γ is the effective coupling constant for the binary soft-sphere system.

Here, $\tilde{t} = zw_0 t$.

The mean residence time t_{MRT} defined by $\int_0^\infty t\psi(t)\,dt$ is given by

$$t_{MRT} = (\rho + 1)/zw_0\rho \tag{6}$$

for $\rho > 0$. The mean residence time diverges at $\rho = 0$, which corresponds to the glass transition point. For $\rho < 0$, t_{MRT} does not exist where the dynamics becomes anomalous and non-Gaussian character appears. We also note that the fluctuation of the residence time ceases to exist for $\rho \leqslant 1$, where the sub-anomalous diffusion takes place [9]. These behaviours are responsible for the dynamical characteristics of supercooled fluids explained above [5].

Detailed comparison of the residence time distribution expressions (3) with those obtained by the molecular dynamics simulation has been carried out [10]. The overall behaviours of the residence time distribution observed in supercooled binary soft-sphere fluids are qualitatively in good agreement with (3). We can use the behaviour of $\psi(t)$ at $t = 0$ to determine the relation between the parameters ρ and Γ of soft-sphere fluids. First we estimate $\psi(0)$ for each Γ from the residence time distribution observed for soft-sphere fluids. Then, we obtain corresponding $\bar{\rho}$ by the relation (see (4))

$$\bar{\rho} = \frac{1 - 2\psi(0)}{\psi(0) - 1}. \tag{7}$$

Unfortunately, since the statistics for $\psi(t)$ near $t = 0$ are not so good, it is hard to obtain a highly accurate estimate of $\psi(0)$. Our current best estimate of $\bar{\rho}$ as a function of Γ is shown in a log–log plot in figure 2, from which we find

$$\bar{\rho} = 398(\Gamma_g - \Gamma)^3. \tag{8}$$

Here we set the power to be 3 so that it can be consistent with the relation between Γ and ρ found for the diffusion constant and the non-Gaussian parameter [6], and the time scale $zw_0\tau$ is chosen to be 0.1, τ being the microscopic time scale for the soft-sphere system. It should be remarked here that the numerical constant may change if one gets better data for $\psi(t)$.

In summary, we conclude that the semi-quantitative behaviours of the residence time distribution observed in the supercooled binary soft-sphere fluids agree quite well with those predicted by the trapping diffusion model and that the function $\psi(t)$ can be used to determine the relation between the parameters in the trapping diffusion model and the soft-sphere system. Although the numerical factor in (8) will depend on the statistics of the data, we consider that the relation (8) will be fairly accurate. We propose an extensive study of the residence time distribution $\psi(t)$ near $t = 0$ to confirm relation (8).

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References

[1] Chudley C T and Elliot R J 1961 *Proc. Phys. Soc.* 77 353
[2] Miyagawa H, Hiwatari Y, Bernu B and Hansen J-P 1988 *J. Chem. Phys.* 88 3879
[3] Leutheusser E 1984 *Phys. Rev.* A 29 2765
Kirkpatrick T R 1985 *Phys. Rev.* A 31 939
Götze W 1988 *Z. Phys. Chem.* 156 S3
Krieger U and Bosse J 1987 *Phys. Rev. Lett.* 59 1601
Barrat J L and Latz A 1990 *J. Phys.: Condens. Matter* 2 4249
[4] Das S P and Mazenko G F 1986 *Phys. Rev.* A 34 2265; 1987 *Phys. Rev.* A 36 211
Götze W and Sjögren L 1987 *Z. Phys.* B 65 415; 1988 *J. Phys. C: Solid State Phys.* 21 3407
[5] Odagaki T and Hiwatari Y 1990 *Phys. Rev.* A 41 929
[6] Odagaki T and Hiwatari Y 1991 *Phys. Rev.* A 43 1103
[7] Roux J N, Barrat J L and Hansen J-P 1989 *J. Phys.: Condens. Matter* 1 7171
[8] Odagaki T and Hiwatari Y 1991 *preprint*
[9] Odagaki T 1988 *Phys. Rev.* B 38 9044
[10] Miyagawa H and Hiwatari Y 1991 *preprint*