Supplementary Information for

Johari-Goldstein $\beta$ relaxation in glassy dynamics originates from two-scale energy landscape

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Supporting Information Text

Mode-coupling temperature

We plot $\tau_\alpha^{-1/\gamma}$ versus $T$ for several $\gamma$ and observe that the mode-coupling temperature of the dimer system is $T_c \approx 0.45$.

![Graph showing $\tau_\alpha^{-1/\gamma}$ versus $T$ for several $\gamma$.](image1)

**Fig. S1.** $\tau_\alpha^{-1/\gamma}$ versus $T$ for $\gamma = 2.5, 3.0, 3.5$. For all cases, the fitted lines (the dashed lines) cross zero at around $T_c \approx 0.45$.

Temperature dependence of basin potential energy

We calculated potential energy $E_{IS}$ of basin configurations quenched from equilibrated liquid configurations at each temperature $T$. As shown in Fig. S2, $E_{IS}$ shows a plateau at high-temperature region and decreases at around $T = 1.0$. At this temperature, the $\alpha$ relaxation time $\tau_\alpha$ deviates from the Arrhenius behavior. The decrease of potential energy $E_{IS}$ at the onset of glassy dynamics is consistent with the behavior of spherical Kob-Andersen system (1).

![Graph showing $E_{IS}$ versus $T$.](image2)

**Fig. S2.** The potential energy of basins quenched from configurations equilibrated at each temperature $T$. 
Bond state analysis

In the main text, we classify molecular bonds into 12 states (Table 1 in the main text) and report that more than 99% of the bonds dissociate in a specific pathway of states. Here, we discuss this analysis in detail. In the analysis, we checked the states of each bond in logarithmically spaced time intervals. We determined that the molecular bond had passed through the state if the state appeared at least once during the time evolution. The order and number of appearances were not taken into account. We carried out this analysis for all molecular pairs in trajectories of $T = 0.491$ and obtained the fraction of each set of states (Fig. S3). More than 80% of the molecular pairs visited the states 3B, 2A, and 1A in the trajectories; 12.8% of the pairs did not visit the states 3B or 1A but visited the others. As mentioned before, the analysis was conducted in logarithmically spaced times, therefore we consider all three patterns of appearances as a single path of states shown in Fig. 4 in the main text. We also observed that 0.07% of all bonds did not dissociate in any of the three states 3B, 2A, and 1A.

Simulations of the Kob-Andersen system

This section provides information on numerical procedures to obtain the data of the Kob-Andersen (KA) system in Fig. 5 in the main text and Fig. S4. The molecular dynamics (MD) simulations in the $NVT$ ensemble using the Nosé-Hoover thermostat were performed for equilibration runs, and subsequently, the MD simulations in the $NVE$ ensemble were performed for production runs. We consider $N = 1000$ particles enclosed in a square box with periodic boundary conditions. The number density is $\rho = N/L^3 = 1.204$. We use identical interaction parameters to those of the original paper by Kob and Andersen (2). We ensure the continuity at the cutoff length $r_c = 2.5\sigma_{ij}$ up to the first derivative of the potential as described in the main text. The number of samples is 3800 used in Fig. 5 of the main text. The relaxation time is measured with $F_s(k = 7.25, \tau_\alpha) = e^{-1}$.

Mean-squared displacement in inherent dynamics

In Fig. S4, we show mean-squared displacement (MSD) in the inherent dynamics of both the dimer and KA systems. For the KA system, the slow increase of inherent dynamics MSD at intermediate timescale $t \gtrsim 10^6$ is observed (3, 4). At the lower temperature of $T = 0.400$, this slow increase appear to be more pronounced. After this behavior, in the long-time diffusive regime, MSD in inherent dynamics and Newtonian dynamics converge for both temperatures. The number of trajectories is 1120 used for Fig. S4 (b).

Meanwhile, in the dimer system, the situation is much more evident. For both temperatures shown in Fig. S4 (a), the inherent MSD shows a complete plateau at the intermediate timescale. In the dimer system, the coincidence of inherent and Newtonian MSD starts at this timescale. In Newtonian dynamics, we assess that the dimer system forms a plateau at $t \sim 10^3$ at a height of $10^{-1}$ after JG $\beta$ relaxation (Fig. 2 in the main text). Results of Fig. S4 (a) suggest that the dimer system in inherent dynamics explores a metabasin structure in the PEL during JG $\beta$ relaxation. In the long-time $\alpha$ relaxation, the dimer system undergoes inter-metabasin transitions.

These results suggest the difference in PEL structures in the KA and dimer systems. In the dimer system that shows JG $\beta$ relaxation, there are typically two energy scales in their PEL, and they are hierarchically structured like Fig. 1 in the main text. The three-step relaxations of dimers are backed by the two-scale PEL structure. On the other hand, in spherical particles such as the KA system, we speculate the energy scales are distributed more continuously. We also speculate that those PEL structures of spherical particles causes the complex $\beta$ relaxation phenomena such as slow increase of inherent MSD (3, 4) and the excess wing spectrum (5).
Therefore, the PEL of dimer system and KA system is inherently different, as the former includes the two-scale hierarchical structure.

Figure S5. Mean-squared displacement (MSD) in inherent dynamics of (a) dimer system and (b) KA system. The lines show the MSD in Newtonian dynamics, whereas the square symbols show the MSD in inherent dynamics.

Time-dependent variance of potential energies

In the main text, we introduce the time-dependent variance of potential energies \( V(t) = \text{Var}[E_{\text{IS}}(t) - E_{\text{IS}}(0)] \) to quantify the size of the phase space explored by IS trajectories. \( E_{\text{IS}}(t) \) is the potential energy of a configuration in an IS trajectory at time \( t \).

Figure S5 (a) shows \( V(t) \) for various temperatures. Horizontal lines are the long-time limits \( V_\infty \), which was estimated from \( V(t) \) at \( t \geq \tau_n \). For temperatures \( T = 0.403, 0.445, 0.491 \), we used configurations generated by the parallel tempering method as initial configurations. The number of initial configurations is 95, and the number of the isoconfigurational trajectories is 6 for \( T = 0.403 \) and \( T = 0.445 \) and 24 for \( T = 0.491 \). For \( T = 1.500, 0.800 \), we generated initial configurations by the MD simulation in the NVT ensemble using the Nosé-Hoover thermostat and subsequent NVE runs were performed. The number of trajectories is 1000 for \( T = 1.500 \) and 5600 for \( T = 0.800 \). For these temperatures, the simulation time is sufficiently long that \( V(t) \) converges to the long-time limit \( V_\infty \). At a short time scale, \( V(t) \) at \( T = 1.500 \) and \( 0.800 \) does not start from 0. The reason is that even one MD step shifts the system to a different basin of attraction at these high temperatures. On the other hand, at low temperatures, \( V(t) \) continuously deviates from 0 because the system does not leave the initial basin in just one MD step. A similar observation was made from the overlap function of IS trajectories of the KA system (6).

In the right panel of Fig. S5, we show \( V(t) \) for the KA system. The same IS trajectories used for Fig. S4 were also used in this calculation. In contrast with dimer system in the left panel, the plateau of \( V_{\text{GO}} \) is absent in \( V(t) \) of the KA system. Therefore, the PEL of dimer system and KA system is inherently different, as the former includes the two-scale hierarchical structure.

Figure S5. \( V(t) \) for (a) dimer system and (b) KA system. (a) \( V(t) \) of dimer system for various temperatures are shown. Horizontal lines with each color represent the long-time limit \( V_\infty \). (b) \( V(t) \) of KA system for \( T = 0.400 \) and \( T = 0.450 \) are shown. Horizontal line represent the long-time limit \( V_\infty \) reached at \( T = 0.450 \).
System-size effects in time-dependent variance of potential energies

We checked the system-size effect in $V(t)$ which is introduced in this paper. We performed molecular dynamics simulations to equilibrate the system of $N_{\text{mol}} = 300$ at temperatures $T = 0.800, 0.491$. We also performed a parallel tempering simulation to equilibrate the system at $T = 0.400$. The number of trajectories is 2040 for $T = 0.800$ and 1100 for $T = 0.491$. For $T = 0.400$, the number of initial configurations is 56 and the number of isoconfigurational trajectories is 10 for each configuration. In Fig. S6, $V(t)$ of $N_{\text{mol}} = 300$ is shown. The behavior is identical to that of Fig. S5 (a). At the high temperature, $V(t)$ smoothly increases to a long-time limit of $V_\infty$. At $T = 0.491$, $V(t)$ shows a slow increase at the intermediate timescale of $\tau_\beta$. At the lowest temperature of $T = 0.400$, $V(t)$ does not increase higher than the plateau of $V_{\text{JC}}$. Further studies on the system-size effect are beyond the scope of the present study.

![Fig. S6. $V(t)$ for the system of $N_{\text{mol}} = 300$. Horizontal lines with each color represent the long-time limit $V_\infty$.](image)

Correlation between low-frequency vibrational modes and relaxations in the Kob-Andersen system

We carried out a parallel tempering simulation to equilibrate the KA system in $T = 0.4308$. The parameters and setups are identical to the above. In our MD simulations, 18 replicas were used, and each replica corresponded to a temperature from 0.7800 to 0.3971. The MD simulations were performed in the NVT ensemble using the Nosé-Hoover thermostat with a time step of 0.005. Exchange trials were performed every 2800 MD steps using the Metropolis criterion. Sampling was started after 80000 exchange trials and was performed every 10000 trials thereafter. We checked the equilibration by the absence of aging in $F_\alpha(k, t)$. Using these configurations as initial positions, we carried out the simulations in the NVE ensemble for production runs. The number of initial configurations is 72, and the number of the isoconfigurational ensemble is 5. We used the norms of eigenvectors of each particle summed over the lower 1% of all modes (i.e. the 30 lowest-frequency modes) at IS corresponding to the initial configuration as the predictor and the propensity of motion $|r_i(t) - r_i(0)|$ as the actual relaxations. For the definitions of the evaluators (the Rank, Pearson, and Spearman correlations), see the main text. The correlation persists to the timescale of $\alpha$ relaxation in Fig. S7.
Various correlations between low-frequency vibrational modes and relaxations in the dimer system

In Fig. S8, various correlations between low-frequency vibrations and relaxations are plotted. The correlations are evaluated by the Pearson, Spearman, and Rank correlations, whereas the relaxations are evaluated by propensity of motion, $\theta_i(t)$, and atomic bond-break correlation. The definitions of the quantities are described in the section of Materials and Methods in the main text.

References

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