Supplementary Information (SI) for Soft Matter.

ELECTRONIC SUPPLEMENTARY INFORMATION

Unraveling molecular mechanisms of aging dynamics in the Kob-Andersen model: The role of free volume

Yifan Yang, Yuyuan Lu,* Yaozhang Yang, Xia Wang and Lijia An

State Key Laboratory of Polymer Science and Technology, Changchun Institute of Applied Chemistry,Chinese Academy of Sciences, Changchun 130022, P. R. China; University of Science and Technology of China, Hefei 230026, P. R. China.

E-mail:yylu@ciac.ac.cn

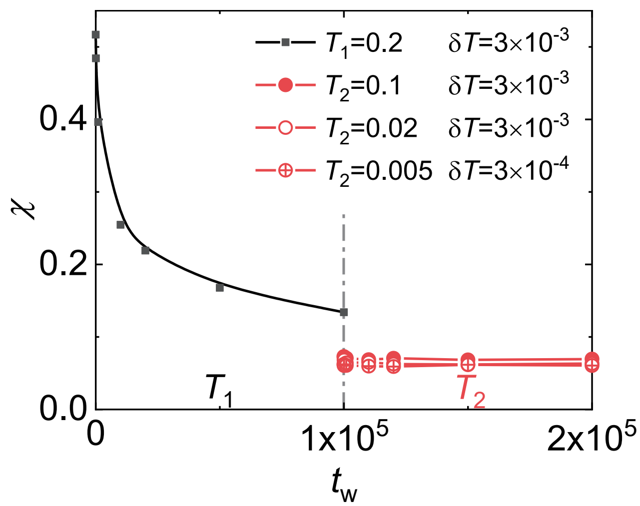

Fig. S1 Time evolution of χ at different T_2. No rejuvenation observed at lower temperatures. Cooling rate δT indicated. For $\delta T = 3\times10^{-3}$, samples at $T_2 = 0.005$ could not be obtained with current thermostat settings; thus, a slower cooling rate of 3×10^{-4} was used for $T_2 = 0.005$.

To verify that the temperature difference required to observe rejuvenation varies markedly between systems, we extended our simulations to even lower final temperatures, specifically $T_2 = 0.02$ and $T_2 = 0.005$, as shown in Fig. S1. Despite these substantially reduced values, no rejuvenation is observed—there is no upward jump in χ immediately following the temperature quench. Instead, χ remains flat or decreases slightly, in stark contrast to the behavior seen in the WCA model. It is crucial to note that rejuvenation is not solely indicated by a sudden increase in χ, but also by its subsequent decay with increasing waiting time. Although χ includes a $1/T$ normalization of displacements, this alone is insufficient to induce rejuvenation. Our results clearly demonstrate that the lack of rejuvenation in the KA model cannot be attributed to an insufficiently low T_2; rather, it reflects a more fundamental difference in dynamical response between the two systems.

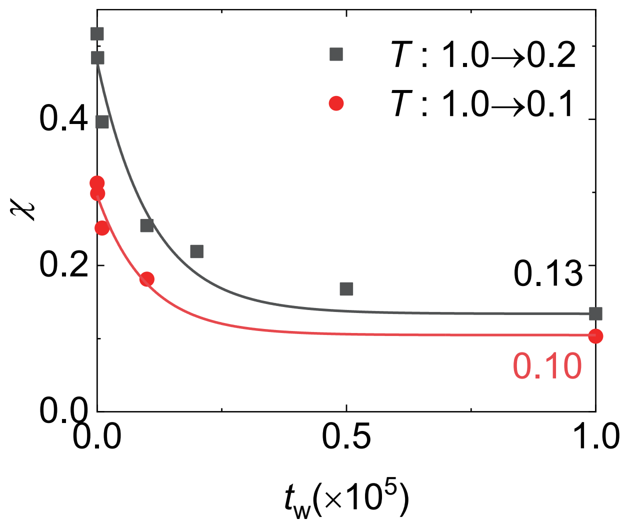

Fig. S2 Time evolution of dynamic susceptibility $\chi(t_\mathrm{w}, \Delta t = 10^5)$ as the temperature is rapidly decreased from the initial temperature $T_0 = 1.0$ to $T_1 = 0.2$ and $T_2 = 0.1$.

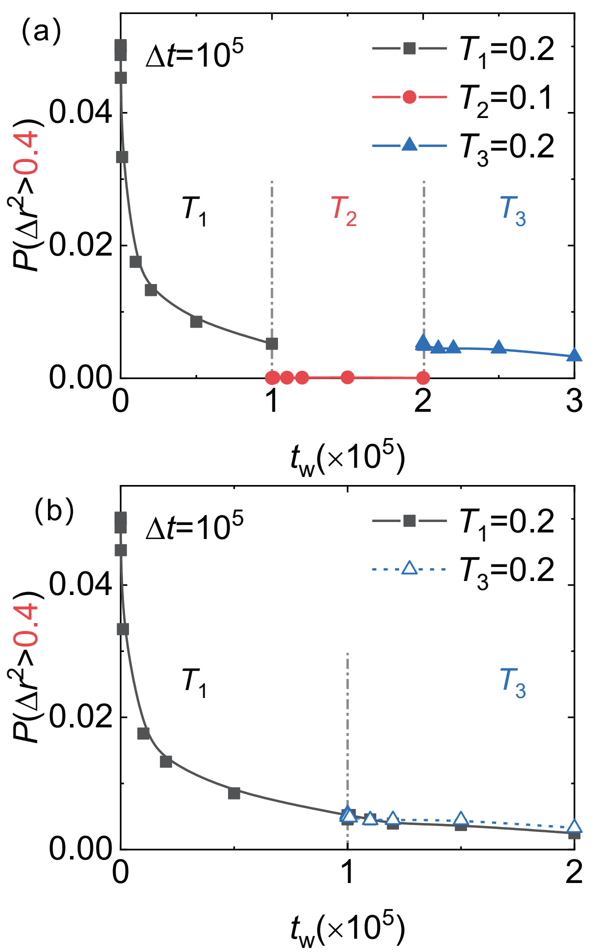

Fig. S3 (a) Time evolution of the fraction $P(\Delta r^2 > 0.4)$ of fast-moving particles at each cycle step, indicated by vertical dash-dotted lines. (b) Time evolution of $P(\Delta r^2 > 0.4)$ with the intermediate step omitted, highlighting the memory effect. No qualitative difference compared to Fig. 9, indicating the robustness of the results with respect to the reference value of Δr^2.

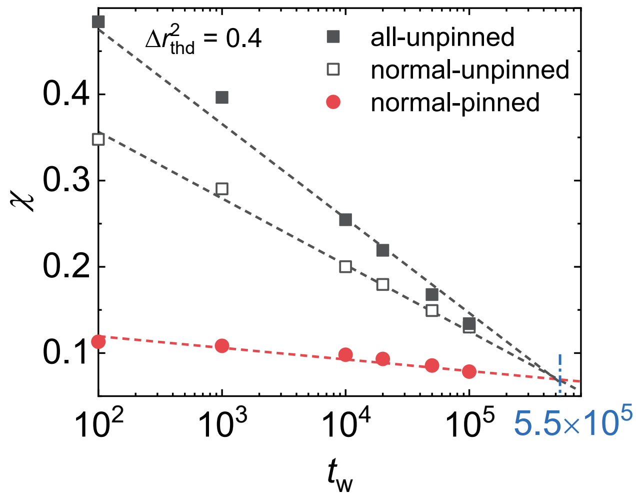

Fig. S4 Evolution of χ with waiting time tw for different systems. Solid black circles: all particles corresponding to black solid points in Fig.3a; open black circles: normal particles in the unpinned system; red circles: normal particles in the pinned system, i.e., unpinned particles. Fast particles are defined at $T_1 = 0.2$, $t_{\rm w} = 0$, and $\Delta t = 10^5$ as those with $\Delta r^2 > 0.4$; all others are classified as normal particles.

As shown in Fig. S4, we pinned the fast particles at $t_{\rm w} = 0$ and monitored the evolution of χ with waiting time t_w. The χ values of normal particles in the fast-pinned system (red circles) are significantly lower than those of all particles in the unpinned system (solid black circles) and also lower than normal particles in the unpinned system (open black circles). This demonstrates that pinning fast particles directly suppresses the mobility of surrounding normal particles, indicating that particle motion in our system is indeed cooperative. This observation aligns well with our proposed physical picture that particles achieve free volume diffusion through cooperative motion.

More specifically, due to the attractive interactions in the KA model, pinning restricts the cooperative rearrangements of neighboring particles, thereby hindering free volume diffusion and rearrangement, which slows down the aging dynamics. Furthermore, as Fig. S4 shows, extrapolation suggests that the three curves converge around $t_{\rm w} = 5.5 \times 10^5$, a timescale much longer than the β-relaxation time but shorter than the α-relaxation time. This indicates that free volume diffusion and rearrangement are relatively slow and localized processes occurring on timescales faster than the full structural relaxation of the system.

To further verify the impact of pinning on cooperative motion, we also explored various pinning protocols. These results confirm that aging dynamics are primarily governed by cooperative motion between fast particles and their neighbors, which requires sufficiently large local free volume. The cooperative rearrangements correspond to localized free volume redistribution toward a stable configuration.