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Metabasin dynamics of supercooled polymer melt*

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We employ molecular dynamic simulation to investigate metabasin dynamics for supercooled polymer melt. We find that, in a small system, the α-relaxation process is composed of a few crossing events that the monomers hops from one metabasin to another. Each crossing event is very rapid and involves a democratic movement of many particles, whereas such collective motion is not string-like. Evaluation on the contributions of metabasin exploration and democratic movement shows that the structural relaxation is mostly governed by the latter. Our calculated results show that the metabasin–metabasin transitions are not the main reason of spatially dynamical heterogeneity. It is different from the binary Lennard–Jones mixture model in which the metabasin–metabasin transitions are relevant for the spatially dynamical heterogeneity.

Keywords: metabasin dynamics, distance matrix, democratic movement, dynamic heterogeneity

PACS: 61.43.Fs, 64.70.Kj, 64.70.Km, 64.70.Pj **DOI:** 10.1088/1674-1056/ab4e82

1. Introduction

The physical mechanism of glassy dynamics remains a central open problem in condensed matter physics.[1–4] One concerned topic is the nature of the motion of particles in the α-relaxation process at low temperature. This relaxation has been believed to proceed by means of cooperatively relaxing regions whose time scale and size grow considerably as the temperature is lowered.[1–8] In this relaxation process, the dynamics may vary by orders of magnitude from one region of the system to another.[5–7] This spatially dynamic heterogeneity (DH)[9–16] has been observed both in experiment and simulation. From the simulations of binary Lennard–Jones mixture (BLJM) systems[10] and direct observations in colloidal suspension experiments,[12,13] it is also found that the spatially DH is related to the cooperative motion, in which a small number of particles (a few percent) undergo a string-like collective motion with the displacements comparable to the distance between the neighboring particles.

One way to understand the α-relaxation dynamics is through the potential energy landscape (PEL).[1,17–19] The PEL is very rugged with the presence of many barriers and the dynamics becomes slow at low temperature. Within the concept of the inherent structures, the "metabasin" (MB) is defined as some minima which are locally connected and are not separated by significant barriers. The motion of the system in the PEL can roughly be decomposed into two types:[20,21] i) The system moves from one MB to another by crossing over barriers. This process is believed to correlate to the α-relaxation,[3] i.e., it is the elementary event of the α-relaxation.[21] ii) The system explores in an MB.

By molecular dynamic (MD) simulation, Appignanesi *et al.*[22] found that the α-relaxation of a small BLJM system (150 particles) corresponds to a small number of barrier hopping events from one MB to a neighboring one. Such hopping events are also realized by the collective motion of a significant fraction of particles which form relatively compact clusters. This movement is very different in nature from the string-like motion driven by a few fast moving particles in the context of spatially DH.[8,12,13] For a small BLJM system, the dynamics is also quite heterogeneous in time as the consequence of MB–MB transitions,[22,23] which leads to sharp bursts of mobility. This MB–MB transition that involves the collective motion of a significant fraction of particles has also been identified in the supercooled water simulation[24] and colloidal suspension experiment.[25] Polymer is a major glass-forming material that has been extensively studied.[26,27] The α-relaxation behavior of the polymer melt has been investigated in a wide range of temperatures.[28] The spatially correlated dynamics of the glass-forming polymer melt has also been studied by MD simulations.[29] But, whether the MB–MB transition exists in the polymer system or whether there are qualitative or quantitative differences in MB–MB transition between polymers and simple molecules is not clear. Hence, in this paper, we perform MD simulations on a coarse-grained polymer model to study the MB–MB transitions. Since we are interested in individual MB–MB transitions, one has to avoid the presence of several independent local rearranging regions, but this will occur in a large system and obscures the analysis of the individual event. So a small (100 monomers) system is employed.

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The paper is organized as follows. Section 2 introduces the model for polymers and the simulation method. The results are discussed in Section 3. Then, the paper concludes in Section 4.

2. Model and simulation methods

We adopt a bead-spring model of linear chains and each chain contains $N = 10$ monomers.[28–33] All monomers interact via a truncated and shifted Lennard–Jones (LJ) potential

$$U_{\mathrm{LJ}}(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + U_{\mathrm{c}}, & r \leqslant r_{\mathrm{c}}, \\ 0, & r > r_{\mathrm{c}}, \end{cases} \tag{1}$$

where r is the center-to-center distance between the monomers, σ is the LJ diameter, and ε is the characteristic energy. The potential is cut off at $r_{\mathrm{c}} = 2r_{\mathrm{min}}$, where $r_{\mathrm{min}} = 2^{1/6}\sigma$ is the minimum position of the potential. U_{c} is a constant energy shift, ensuring that the potential is continuous at the cutoff. In the following, we use LJ units, i.e., $\varepsilon = 1$, $\sigma = 1$, the Boltzmann's constant $K_{\mathrm{B}} = 1$, and the monomer mass $m = 1$. The time scale $\tau_{\mathrm{LJ}} = \left(m\sigma^2/\varepsilon\right)^{1/2}$. Neighboring monomers along the polymer chains interact with each other through a finitely extensible nonlinear elastic (FENE) bond potential[34,35]

$$U_{\mathrm{FENE}}(r) = -\frac{K}{2}R_0^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right] + 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon. \tag{2}$$

The parameters $R_0 = 1.5$ and $K = 30$. This FENE potential yields a sharp minimum at $r_{\mathrm{b}} = 0.9606$.

Using the above model, we perform MD simulations for a small (10 chains) system to study the MB dynamics, and a large (270 chains) system is also used to calculate the characteristic time. The implementation has two steps[28,32] with a time step $\mathrm{d}t = 0.001$. The volume of the simulation box is first determined in an isobaric simulation at $P = 1$. Then, this volume is fixed and the simulation is continued in the canonical ensemble using the Nosé–Hoover thermostat. The simulation is under the temperature $T = 0.48$, which is slightly above the mode coupling theory critical temperature $T_{\mathrm{c}} = 0.45$.[28] The monomer density is $\rho_{\mathrm{m}} = 1.03$. All results are obtained from simulations in equilibrium.

3. Results and discussion

3.1. Characteristic time

To serve for the study of MB dynamics, a large system (270 chains) is used to calculate the characteristic time at $T = 0.48$, and twenty independent configurations are simulated for statistical average. An important quantity that is widely used to study the relaxation dynamics is the self-intermediate scatting function

$$F_{\mathrm{s}}(q,t) = \frac{1}{nN}\sum_{i=1}^{n}\sum_{j=1}^{N}\left\langle \exp\left\{\mathrm{i}\boldsymbol{q}\left[\boldsymbol{r}_{ij}(t) - \boldsymbol{r}_{ij}(0)\right]\right\}\right\rangle, \tag{3}$$

where $\boldsymbol{r}_{ij}(t)$ is the position of the j-th monomer in the i-th chain at time t. Usually, q is chosen to be the position of the first peak of the static structure factor. Such correlation function accounts for the loss in time of the memory of the initial structural configuration. The α-relaxation time τ_α is defined as when $F_{\mathrm{s}}(q, t = \tau_\alpha) = 0.1$. A quantity called non-Gaussian parameter is introduced to reflect the presence of the spatially DH. It is defined as

$$\alpha_2(t) = \frac{3\left\langle \boldsymbol{r}^4(t)\right\rangle}{5\left\langle \boldsymbol{r}^2(t)\right\rangle^2} - 1. \tag{4}$$

The position of the peak denotes a characteristic time t^*, at which the motion of monomers deviates most from the normal diffusion. The self-intermediate scatting function $F_{\mathrm{s}}(q,t)$ and non-Gaussian parameter $\alpha_2(t)$ at $T = 0.48$ are shown in Fig. 1. We have the α-relaxation time $\tau_\alpha \approx 550$, which is in agreement with the result calculated by Bennemann *et al.*[28] We also have $t^* \approx 40$.

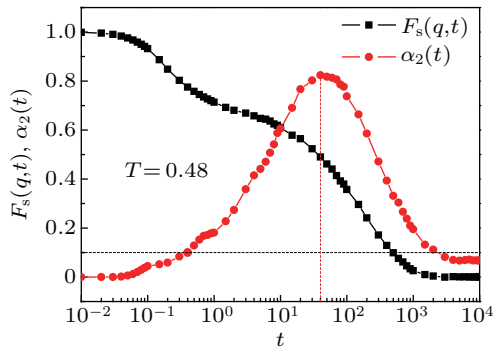


Fig. 1. The self-intermediate scatting function $F_{\mathrm{s}}(q,t)$ and non-Gaussian parameter $\alpha_2(t)$ of the system at $T = 0.48$. The $F_{\mathrm{s}}(q,t) = 0.1$ and $\alpha_2(t^*) = 0.82$ are marked out by dashed lines.

3.2. Metabasins and metabasin–metabasin transitions

The MBs are studied in a single run of the small system (10 chains),[22–24] so that the two types of motion (exploring in an MB and MB–MB transition) are separated in time. In order to identify the MBs, the following distance matrix (DM), which has been described detailedly in Refs. [22] and [23], is calculated:

$$R^2(t',t'') = \frac{1}{nN}\sum_{i=1}^{n}\sum_{j=1}^{N}\left|\boldsymbol{r}_{ij}(t') - \boldsymbol{r}_{ij}(t'')\right|^2. \tag{5}$$

Thus, $R^2(t',t'')$ gives the system-averaged squared displacement of the monomers in the time interval that starts at t' and ends at t''. Since $R^2(t',t'') = R^2(t'',t')$, this is a symmetric matrix. In other words, the DM contains the average squared distances between each pair of the recorded configurations. In our simulation, the total run time $t = 2400$ is larger than

the α-relaxation time $\tau_\alpha \approx 550$. We record 101 equal-time-interval configurations. The time interval between two successive recorded configurations is $\Delta t = 24$.

Figure 2 shows a typical graph of DM as a function of t' and t'' at $T = 0.48$. The small value of $R^2(t',t'')$ means that the relation of the two paired configurations is close. The color represents the value of $R^2(t',t'')$. Clearly, island structures can be seen in the DM graph. Note that the typical value of $R^2(t',t'')$ within an island structure is around 0.035, while the value reaches larger than 0.105 in between the island structures (see legend on the right of the figure). The island structures are the "landscapes" of MBs, i.e., MBs are composed of closely related configurations. The MBs are separated by rapid increases of $R^2(t',t'')$, which correspond to the MB–MB transitions. The transitional process is quite short on the order of 20.

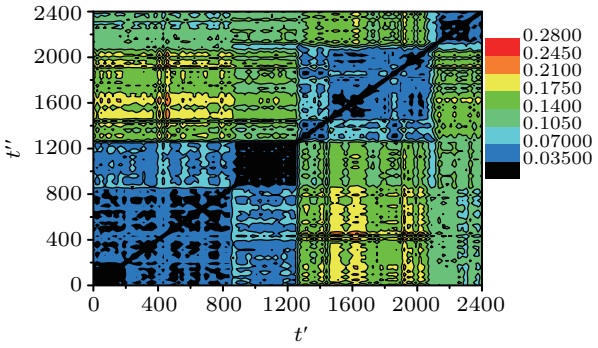


Fig. 2. Distance matrix $R^2(t',t'')$ of the small system (10 chains) at $T = 0.48$. The different colors correspond to values of $R^2(t',t'')$ (see the color bar).

The typical sojourn time within one MB is around 200–400, which is around 50% of $\tau_\alpha \approx 550$. So the α-relaxation is realized after several (1–3) MB–MB transitions. We have $t^* \approx 40$, which is much smaller than the MB sojourn time. Hence, we can conclude that the MB–MB transition is not the main reason of spatially DH, and the same conclusion has been obtained through an experiment of glassy colloidal systems.[25] However, it is different from the BLJM system,[22] in which the time scale of t^* corresponds to the sojourn time within one MB, and the MB–MB transitions are relevant for the spatially DH.

It is also found that the typical sojourn time within one MB is much larger than the MB–MB transitional time. Hence, the dynamics of the system is quite heterogeneous in time, i.e., the system stays for a significant time in an MB before it finds a pathway out. The occurrence of the MB–MB transitions is not regular but random.

To investigate the physical mechanism of MB dynamics, we calculate the averaged squared displacement (ASD) of the monomers within a time interval Δt. It is defined as

$$\delta^2(t,\Delta t) = R^2(t-\Delta t/2, t+\Delta t/2) = \frac{1}{nN}\sum_{i=1}^{n}\sum_{j=1}^{N}\left|\boldsymbol{r}_{ij}(t-\Delta t/2)-\boldsymbol{r}_{ij}(t+\Delta t/2)\right|^2. \quad (6)$$

Thus, $\delta^2(t,\Delta t)$ is $R^2(t',t'')$ measured along the diagonal $t'' = t' + \Delta t$. At the same time, the mobile monomers are defined as those having moved farther than $r_{\rm th} = 0.30$ and the number fraction of mobile monomers is denoted by $m(t,\Delta t)$. The calculated $\delta^2(t,\Delta t)$ (solid line) and $m(t,\Delta t)$ (vertical bars) for $\Delta t = 24$ are shown in Fig. 3. We can see that $m(t,\Delta t)$ varies in steps with $\delta^2(t,\Delta t)$. Compared with Fig. 2, $\delta^2(t,\Delta t)$ shows pronounced peaks exactly when the system leaves an MB. At the large peaks of $\delta^2(t,\Delta t)$, i.e., MB–MB transitions, the number fraction of mobile monomers $m(t,\Delta t)$ is around 20%.

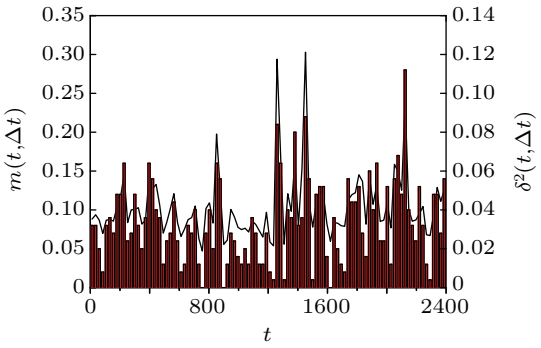


Fig. 3. Solid line (right scale): averaged squared displacement $\delta^2(t,\Delta t)$ for the trajectory given in Fig. 2. The Δt is 24. Vertical bars (left scale): the function $m(t,\Delta t)$, which gives the number fraction of mobile particles (particles that moved farther than the threshold value $r_{\rm th} = 0.30$ in the time interval $[t-\Delta t/2, t+\Delta t/2]$).

In order to further understand the nature of the motion of monomers when the system leaves an MB, the distribution of the displacement r of the monomers is calculated, which is defined as

$$G_{\rm s}(r,t,t+\Delta t) = \frac{1}{nN}\sum_{i=1}^{n}\sum_{j=1}^{N}\delta\left(r-\left|\boldsymbol{r}_{ij}(t)-\boldsymbol{r}_{ij}(t+\Delta t)\right|\right). \quad (7)$$

Note that the average of $G_{\rm s}(r,t,t+\Delta t)$ over time gives $G_{\rm s}(r,\Delta t)$, which is the self part of the van Hove function. The distribution for $\Delta t = 24$ is shown in Fig. 4. In Fig. 4(a), t is chosen to be time that ASD is small, i.e., the system is exploring in an MB. The self part of the van Hove function $G_{\rm s}(r,\Delta t)$ is also included in the graph. We find that the distributions of $G_{\rm s}(r,t,t+\Delta t)$ within the uncertainty of noise are identical to $G_{\rm s}(r,\Delta t)$, implying that within the time interval of Δt, the motion of a system exploring in an MB is statistically roughly the same as the time-averaged motion. In Fig. 4(b), the same distributions are shown, but now t is chosen to be the time when the system leaves an MB. In these time regimes, the distributions of $G_{\rm s}(r,t,t+\Delta t)$ shift to the right of $G_{\rm s}(r,\Delta t)$, indicating that the motion of the system is faster than average. Notably, the shift is global, which implies that a substantial part of the monomers moves faster than average, i.e., the MB–MB transition or the peak of ASD involves a democratic movement

of many particles. This is in contrast to the behavior of cooperative motion on the time scale of t^*,[10,12,13] in which the cooperative motion is contributed by the string-like motion of a few fast moving monomers.[13,36]

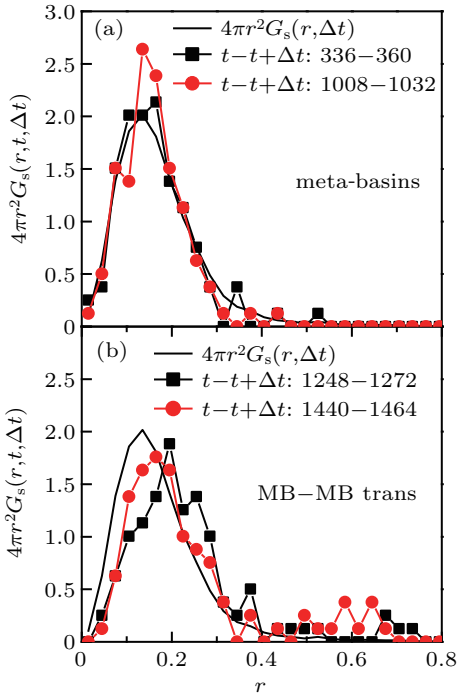


Fig. 4. The distribution function $G_s(r,t,t+\Delta t)$ for different values of t (curves with symbols): (a) values of t at which the system is inside a MB, (b) values of t at which the system is about to leave an MB. The Δt is 24. The bold black curve is $G_s(r,\Delta t)$, the self-part of the van Hove function.

To further clarify that the number of monomers that participate in the democratic motion is indeed substantial, the number fraction of mobile monomers is extracted by integrating the distribution of $G_s(r,\Delta t)$ from $r_{th} = 0.30$ to infinity and gets 0.065. From Fig. 3, the number fraction $m(t,\Delta t)$ is around 0.20 for the MB–MB transitions, which is significant larger than that extracted from $G_s(r,\Delta t)$.

In order to study the relation between the structural relaxation and MB dynamics, we define the following function:

$$F_s(q,t,\Delta t) = \frac{1}{nN}\sum_{i=1}^{n}\sum_{j=1}^{N}\exp\left\{i\boldsymbol{q}\left[\boldsymbol{r}_{ij}(t+\Delta t/2)-\boldsymbol{r}_{ij}(t-\Delta t/2)\right]\right\}. \quad (8)$$

It estimates the memory of the configuration at time $t+\Delta t/2$ to the configuration at time $t-\Delta t/2$. Small $F_s(q,t,\Delta t)$ means the structure relaxes a lot in the time interval $[t-\Delta t/2, t+\Delta t/2]$. The behaviors of $F_s(q,t,\Delta t)$ (vertical bars) and $\delta^2(t,\Delta t)$ (solid line) for $\Delta t = 24$ are shown in Fig. 5. Note that $F_s(q,t,\Delta t)$ shows the presence of valleys, which coincide with the peaks of the function $\delta^2(t,\Delta t)$ or MB–MB transitions. This result again manifests that the existence of MB dynamics and most of the decay of the correlation function arises from the MB–MB transitions.

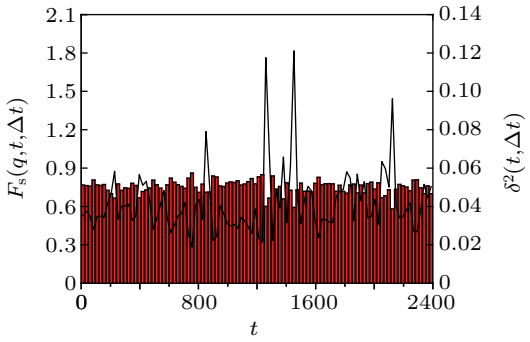


Fig. 5. Solid line (right scale): averaged squared displacement $\delta^2(t,\Delta t)$ for the trajectory given in Fig. 2. The Δt is 24. Vertical bars (left scale): the function $F_s(q,t,\Delta t)$ for the trajectory given in Fig. 2, the memory of the configuration at time $t+\Delta t/2$ for the configuration at time $t-\Delta t/2$, using $\Delta t = 24$.

To check whether the MB dynamics appears in large systems, the DM of a large system (270 chains) is shown in Fig. 6. Instead of island structures (landscapes of MBs), the gradient of $R^2(t',t'')$ is perpendicular to the diagonal line in the DM plot, i.e., the DM depends only on $|t'-t''|$. Hence, the relaxation of the system is gradual. The reason of the gradual relaxation of the large system lies in the randomness of the MB–MB transitions of different small parts of the large system, which gives smooth global dynamics on average.

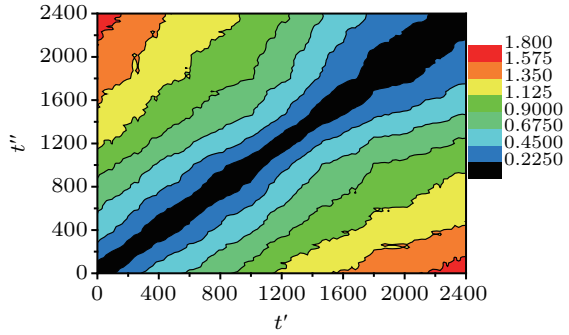


Fig. 6. Distance matrix $R^2(t',t'')$ of the large system (270 chains) at $T = 0.48$. The different colors correspond to values of $R^2(t',t'')$ that are given by the color bar.

4. Conclusions

The metabasin dynamics of the supercooled polymer melt is investigated by molecular dynamic simulation. In a small system, the α-relaxation process is composed of a few crossing events that the monomer hops from one metabasin to another. Each crossing event is very rapid and involves a democratic movement of many particles. Evaluation on the contributions of metabasin exploration and democratic movement shows that the structural relaxation is mostly governed by the latter. The dynamics of a small system is heterogeneous in time, i.e. the averaged motion does not evolve gradually with time but exhibits rapid bursts of mobility signaling a democratic movement of many particles. The MB–MB transitions of different small parts of the large system appear randomly. Hence, the relaxation of the large system is gradual on average.

At last, we note that the metabasin dynamics are also found for the BLJM model[22] and colloidal suspension experiment.[25] Through comparing the maximum non-Gaussian time with the sojourn time of metabasin, our polymer melt simulation and the colloidal suspension experiment[25] show that the metabasin–metabasin transitions are not the main reason of spatially dynamical heterogeneity. However, the metabasin–metabasin transitions of the BLJM model[22] are relevant for the spatially dynamical heterogeneity.

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