Simulations of the flipping images and microparameters of molecular orientations in liquids according to the molecule string model*

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The relaxation dynamics of liquids is one of the fundamental problems in liquid physics, and it is also one of the key issues to understand the glass transition mechanism. It will undoubtedly provide enlightenment on understanding and calculating the relaxation dynamics if the molecular orientation flipping images and relevant microparameters of liquids are studied. In this paper, we first give five microparameters to describe the individual molecular string (MS) relaxation based on the dynamical Hamiltonian of the MS model, and then simulate the images of individual MS ensemble, and at the same time calculate the parameters of the equilibrium state. The results show that the main molecular orientation flipping image in liquids (including supercooled liquid) is similar to the random walk. In addition, two pairs of the parameters are equal, and one can be ignored compared with the other. This conclusion will effectively reduce the difficulties in calculating the individual MS relaxation based on the single-molecule orientation flipping rate of the general Glauber type, and the computer simulation time of interaction MS relaxation. Moreover, the conclusion is of reference significance for solving and simulating the multi-state MS model.

Keywords: relaxation dynamics, glass transition, Ising model, molecular string

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1. Introduction

Glass transition is one of the central questions in condensed matter physics, and the relevant research mainly belongs to liquid physics, which include the dynamic structures, static and dynamical properties of liquids (including the supercooled liquids).[1−36]

Liquid is a fairly typical system with strong correlation, in which the kinetic energy nearly equates the potential energy.[9−11] For a strong correlated system, existing knowledge indicates that probing its collective unit is the key to solving the problem because the originally correlated system can be transformed into the weakly correlated system in the representation of the unit and it is easier to deal with.[9−11] However, there has been no general and feasible approach to searching for collective units in strong correlated systems till now.[9−11] Therefore, exploring the collective unit is a precondition of liquid physics, including the glass transition mechanism. So, the collective unit of liquids has been proposed to be the dynamic molecular string (MS),[9−14] which is based on the following considerations.

(i) Experiments,[33] analog simulations,[34] and computer simulations[35] show that individual dynamic MSs exist in the liquid structure. The "individual" means that the intra-string correlation with the motions of the internal molecules in an MS is much stronger than the inter-string correlation, while the "dynamic" expresses that, as time passes by, MSs can be broken by the thermal fluctuations and restructured by the intermolecular interaction.

(ii) For the most common dynamic molecular branch structures in liquids,[33−35] a) formally, supposing that the "walk" takes place along a branch, if it encounters the intersection of two or more branches,

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then we randomly select one of these branches, at the same time we imagine other branches to be "cut". After repeating this process, the branch structures will be formally divided into separate MSs; b) physically, the above process presents the branch structures as MSs with interactions, and the branch intersections are the interaction points among MSs, meanwhile, the interaction form is random and heterogeneous;[9−14] c) mathematically, the relevant description and solution will be relatively easy after the above treatments.[9−14]

Based on the MS assumption of a liquid collective unit, an MS model to describe the dynamic structure and relaxation dynamics of liquids was suggested.[9−14] This model deems that the random close packing of MSs of random spatial configuration forms the structure of a liquid, and the weak inter-string interaction only has subtle adjustment to the structure. When describing molecular orientation movements, the MS model divides the intermolecular interaction associated with the orientation degrees of freedom into three parts: 1) the mean field of others for a reference molecule is described by a double-well potential of a single molecule;[37] 2) the deviation of the interaction from the mean field is described by an intra-string homogeneous interaction and a weaker heterogeneous and random interaction between MSs. The dynamical Hamiltonian describing molecular orientation motion of the liquid is given as

$$\begin{cases} H = H_{\rm intra} + H_{\rm inter}, \\ H_{\rm intra} = -V_1 \sum\limits_{m=1}^{\infty} \sum\limits_{i=1}^{n-1} \sigma_i^{mn} \sigma_{i+1}^{mn}, \\ H_{\rm inter} = \dfrac{V_2}{2} \sum\limits_{m=1}^{\infty} \sum\limits_{i=1}^{n} \sum\limits_{m' \neq m, i'}^{nn(i)} \sigma_i^{mn} \sigma_{i'}^{m'n'} \Theta_{ii'}^{mm'}, \\ \nu_{\sigma_i^{mn} \to -\sigma_i^{mn}}^{{\rm SG}(1,n)} \\ = \tau_0^{-1} \dfrac{{\rm e}^{-E(-\sigma_i^{mn})/k_{\rm B}T}}{{\rm e}^{-E(-\sigma_i^{mn})/k_{\rm B}T} + {\rm e}^{-E(\sigma_i^{mn})/k_{\rm B}T}}, \end{cases} \quad (1)$$

where $H_{\rm intra}$ is the Hamiltonian of an individual MS, described by the chain Ising model, $\sigma_i^{mn} = \pm 1$ express the states of i-th molecule in an MS which is denoted as m and contains n molecules in a liquid, V_1 is the interaction constant within the string, which is independent of temperature (T) and $V_1 \ll V_0$, with V_0 being the barrier height of the double-well potential, $H_{\rm inter}$ is the random interaction between MSs, and we describe it by using a random interacting Ising model, V_2 is the inter-string interaction constant, which is independent of temperature (T) and $V_2 \leq V_1$, $\Theta_{ii'}^{mm'}$ is the random number whose value is between [0, 1]. The inter-string interaction weaker than the intra-string one is derived from the above random, $nn(i)$ means the number of the nearest neighbours of ith molecule, $\nu_{\sigma_i^{mn} \to -\sigma_i^{mn}}^{{\rm SG}(1,n)}$ is the orientation flipping rate of single molecule from the initial state σ_i^{mn} to the final one $-\sigma_i^{mn}$ in a liquid, which is of the special Glauber type,[33,38] $E(\sigma_i^{mn}) = -V_1 \left(\sigma_{i-1}^{mn} + \sigma_{i+1}^{mn}\right) \sigma_i^{mn} + V_2 \sum\limits_{m' \neq m, i'=1}^{nn(i)} \sigma_i^{mn} \sigma_{i'}^{m'n'} \Theta_{ii'}^{mm'}$ is the interaction energy between i-th molecule and its neighbours, the boundary conditions are $\sigma_0^{mn} = \sigma_{n+1}^{mn} = 0$ and $\tau_0 \equiv \nu_0^{-1}\, {\rm e}^{V_0/k_{\rm B}T}$ with ν_0 being the vibration frequency of the molecules at the bottom of the potential wells.[9−14]

In the present paper, the Monte Carlo method is used to simulate the orientation configuration change and the relevant microscopic parameters in MS relaxation processes according to Eq. (1). The main reasons are as follows.

(I) The physical significance of $\nu_{\sigma_i^{mn} \to -\sigma_i^{mn}}^{{\rm SG}(1,n)}$ in Eq. (1) is still not very clear.[38] Therefore, recently, Huang *et al.*[38] gave a single molecular orientation flipping rate $\nu_{\sigma_i^{mn} \to -\sigma_i^{mn}}^{{\rm GG}(1,n)}$ with a clear physical origin which belongs to the general Glauber type, and the corresponding computer simulation results are quite similar to those of $\nu_{\sigma_i^{mn} \to -\sigma_i^{mn}}^{{\rm SG}(1,n)}$. However, the relaxation equation of the MS based on $\nu_{\sigma_i^{mn} \to -\sigma_i^{mn}}^{{\rm GG}(1,n)}$ has not been given so far. Research on the molecular flipping images and relevant microscopic parameters would be beneficial to exploring the question.

(II) In existing studies of the MS model only the two-state problem ($\sigma_i = \pm 1$) has been dealt with, but for glassformers, the two-state is just a special case.[9−14] For the general multi-state problem, their relaxation dynamics remains unclear. Therefore, the present work will lay a foundation for solving and simulating the relaxation dynamics of multi-state MS.

(III) As Eq. (1) shows, it is very difficult to find the rigorous solution of the random interaction between the MSs. In Ref. [9], Huang *et al.*[9] have proposed a relaxation self-consistent field method, but its feasibility and accuracy need further verification. The investigations in this paper will provide groundwork for studying the inter-string heterogeneous interaction and verifying the validity of the relaxation self-consistent field method.

2. Microparameters describing the relaxation of MSs

According to the MS model, each orientation configuration change during the MS relaxation is achieved gradually by single-molecular orientation flipping processes, meanwhile the flipping rate $\nu^{\mathrm{SG}(1,n)}_{\sigma_i^{mn}\to-\sigma_i^{mn}}$ in Eq. (1) is determined by the orientation configurations of the molecular orientation states and its nearest neighbours. To describe it conveniently, the units composed of the orientation states of a molecule and its nearest neighbours are called local orientation configurations (LOCs). Because the nearest neighbour number of string-end molecules is different from that of the internal molecules of MSs, the corresponding LOCs are also different. So, we will discuss them in the following respectively and give out some microparameters describing the molecular orientation flipping details.

The LOCs of string-end molecules can be divided into two kinds, including the type with same states between itself and its nearest neighbour ($\sigma_1^{mn}=\sigma_2^{mn}$, including [1, 1] and [−1, −1]) and the type with different states between itself and its nearest neighbour ($\sigma_1^{mn}\neq\sigma_2^{mn}$, including [−1, 1] and [1, −1]), represented as LOC-S and LOC-D, respectively. It is easy to see that the orientation flipping of string-end molecules leads to the transformation between LOC-S and LOC-D. Since $\nu^{\mathrm{SG}(1,n)}_{-1-1\to1-1}=\nu^{\mathrm{SG}(1,n)}_{11\to-11}$, we can express them as $\nu^{\mathrm{SG}(1,n)}_{\mathrm{s}\to\mathrm{d}}=\tau_0^{-1}\,\mathrm{e}^{-V_1/k_{\mathrm{B}}T}/\left(\mathrm{e}^{-V_1/k_{\mathrm{B}}T}+\mathrm{e}^{V_1/k_{\mathrm{B}}T}\right)$, and the first microscopic parameter of MS relaxation can be described by the number $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\to\mathrm{d}}$ per unit time of the transformation from LOC-S to LOC-D in an n-MS. In the same way, since $\nu^{\mathrm{SG}(1,n)}_{1-1\to-1-1}=\nu^{\mathrm{SG}(1,n)}_{-11\to11}$, we can express them as $\nu^{\mathrm{SG}(1,n)}_{\mathrm{d}\to\mathrm{s}}=\tau_0^{-1}\,\mathrm{e}^{V_1/k_{\mathrm{B}}T}/(\,\mathrm{e}^{-V_1/k_{\mathrm{B}}T}+\mathrm{e}^{V_1/k_{\mathrm{B}}T})$, the second microparameter of MS relaxation can be described by the number $c^{\mathrm{SG}(1,n)}_{\mathrm{d}\to\mathrm{s}}$ per unit time of the transformation from LOC-D to LOC-S in an n-MS.

The LOCs of string-interior molecules can be divided into the following three kinds: i) the type with same states between itself and its nearest neighbours ($\sigma_{i-1}^{mn}=\sigma_i^{mn}=\sigma_{i+1}^{mn}$, including [1, 1, 1], [−1, −1, −1], simply represented by LOC-SS); ii) the type with different states between itself and its nearest neighbours ($\sigma_{i-1}^{mn}=-\sigma_i^{mn}=\sigma_{i+1}^{mn}$, including [1, −1, 1], [−1, 1, −1], expressed as LOC-DD); iii) the type with the different states between its neighbours ($\sigma_{i-1}^{mn}=-\sigma_{i+1}^{mn}$, including [1, 1, −1], [1, −1, −1], [−1, 1, 1], [−1, −1, 1], expressed as LOC-SD).

It is easy to see that the LOC-SS and LOC-DD can transform into each other. Because $\nu^{\mathrm{SG}(1,n)}_{-1-1-1\to-11-1}=\nu^{\mathrm{SG}(1,n)}_{111\to1-11}$ and $\nu^{\mathrm{SG}(1,n)}_{-11-1\to-1-1-1}=\nu^{\mathrm{SG}(1,n)}_{1-11\to-111}$, they can be expressed as $\nu^{\mathrm{SG}(1,n)}_{\mathrm{ss}\to\mathrm{dd}}=\tau_0^{-1}\,\mathrm{e}^{-2V_1/k_{\mathrm{B}}T}/\left(\mathrm{e}^{-2V_1/k_{\mathrm{B}}T}+\mathrm{e}^{-2V_1/k_{\mathrm{B}}T}\right)$ and $\nu^{\mathrm{SG}(1,n)}_{\mathrm{dd}\to\mathrm{ss}}=\tau_0^{-1}\,\mathrm{e}^{2V_1/k_{\mathrm{B}}T}/\left(\mathrm{e}^{-2V_1/k_{\mathrm{B}}T}+\mathrm{e}^{-2V_1/k_{\mathrm{B}}T}\right)$ respectively. So, the third and fourth microscopic parameters of MS relaxation process can be respectively described by the number $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\to\mathrm{dd}}$ per unit time of the transformation from LOC-SS to LOC-DD and the number $c^{\mathrm{SG}(1,n)}_{\mathrm{dd}\to\mathrm{ss}}$ per unit time of the transformation from LOC-DD to LOC-SS in an n-MS.

The transformation can occur in the same type in LOC-SD, and $\nu^{\mathrm{SG}(1,n)}_{-1-11\to-111}=\nu^{\mathrm{SG}(1,n)}_{-111\to-1-11}=\nu^{\mathrm{SG}(1,n)}_{1-1-1\to-11-1}=\nu^{\mathrm{SG}(1,n)}_{11-1\to1-1-1}$, so they can be expressed as $\nu^{\mathrm{SG}(1,n)}_{\mathrm{sd}\to\mathrm{ds}}=1/2\tau_0$. Here $1/2\tau_0$ is a constant independent of the string length and inter-string interaction. Therefore, the fifth microscopic parameter of MS relaxation process can be described by the number $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\to\mathrm{ds}}$ per unit time of the transformation occurring in the same type in an n-MS.

3. Simulation method

Simulation of an individual MS ensemble In this paper, because the simulated orientation flipping processes are independent of the spatial configuration of the MS, for convenience, only the linear spatial configuration of MS is simulated. Namely, the ensemble is thought of as being composed of M linear n-MSs which have no inter-string interactions in between them.

Simulation of single molecular orientation flips Based on the characteristic of Eq. (1), the time of the Monte Carlo simulation step is chosen as τ_0. And the corresponding orientation flipping probability of the i-th molecule in an n-MS is $q_i^{mn}\equiv\mathrm{e}^{-E_0(-\sigma_k^{mn})/k_{\mathrm{B}}T}/\left(\mathrm{e}^{-E_0(-\sigma_k^{mn})}+\mathrm{e}^{-E_0(\sigma_k^{mn})/k_{\mathrm{B}}T}\right)$, where, $E_0(\sigma_k^{mn})=-V_1\left(\sigma_{i-1}^{mn}+\sigma_{i+1}^{mn}\right)\sigma_i^{mn}$, $\sigma_0^{mn}=\sigma_{n+1}^{mn}=0$. For the n-MS with the sequence number m, firstly, we produce a random number r between [0, n], and then select the k-th molecule ($k=\mathrm{int}(r)+1$, $\mathrm{int}(r)$ represents choosing the integer part of r). Then we produce a random number q_r between [0, 1], if $q_r<q_k^{mn}$, the state σ_k^{mn} becomes $-\sigma_k^{mn}$; if $q_r\geq q_k^{mn}$, the status σ_k^{mn} remains the same. We repeat the above process n times, and the simulation of the relaxation process which occurs in the n-MS with the sequence number m in a Monte Carlo step time τ_0 is completed. Then we repeat the above process for

the M n-MSs of the ensemble, the simulation of the relaxation process of the whole ensemble which occurs in a Monte Carlo step time τ_0 is completed too. Then we calculate the relaxation function $\varphi(t)$ of the ensemble: $\varphi(t) = \dfrac{1}{Mn}\sum_{m=1}^{M}\sum_{i=1}^{n}\sigma_i^{mn}(t)$. We repeat the Monte Carlo steps in turn at the same time, and let $t = t + \tau_0$, then the relaxation process of the system can be simulated.

Simulation calculations of $c_{\mathrm{s}\to\mathrm{d}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{d}\to\mathrm{s}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{ss}\to\mathrm{dd}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{dd}\to\mathrm{ss}}^{\mathrm{SG}(1,n)}$, and $c_{\mathrm{sd}\to\mathrm{ds}}^{\mathrm{SG}(1,n)}$ Taking into account the fact that the existing methods of measuring liquid relaxation dynamics are in linear response generally and the liquids are nearly in equilibrium,[2−17] we will calculate the above parameters in the equilibrium state of the simulation ensemble. Specific process is, within the simulation error, the ensemble is already in an equilibrium state when the relaxation function $\varphi(t)$ of the simulated n-MS ensemble no longer changes with t. And we calculate the average values of $c_{\mathrm{s}\to\mathrm{d}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{d}\to\mathrm{s}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{ss}\to\mathrm{dd}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{dd}\to\mathrm{ss}}^{\mathrm{SG}(1,n)}$, and $c_{\mathrm{sd}\to\mathrm{ds}}^{\mathrm{SG}(1,n)}$ respectively with sufficient simulation steps in the equilibrium state.

4. Simulation results and discussion

Figure 1 shows the configuration changes with reduced time t/τ_0 in ranges of 0–200 (a), 400–600 (b), 1600–1800 (c), and 0–2000 (d) of 20 MSs containing 10 molecules when $V_1/k_{\mathrm{B}}T = 2.0$. The black and white points in Fig. 1 show 1 and −1 state of the molecules, respectively. The results show that when $V_1/k_{\mathrm{B}}T$ is relatively large, molecular orientation flipping images of MSs are similar to those of random walk.

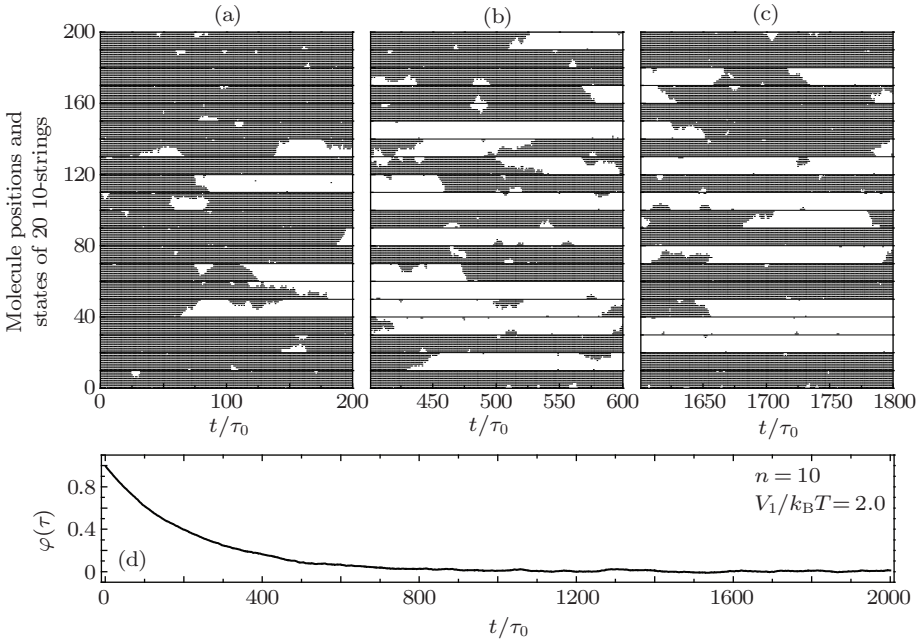


Fig. 1. Variations of configuration with reduced time t/τ_0 in ranges of 0–200 (a), 400–600 (b), 1600–1800 (c), and 0–2000 (d) of 20 MSs containing 10 molecules at $V_1/k_{\mathrm{B}}T = 2.0$. The black and white domains show 1 and −1 state of molecules respectively.

Figures 2 and 3 show the variations of $c_{\mathrm{s}\to\mathrm{d}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{d}\to\mathrm{s}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{ss}\to\mathrm{dd}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{dd}\to\mathrm{ss}}^{\mathrm{SG}(1,n)}$, and $c_{\mathrm{sd}\to\mathrm{ds}}^{\mathrm{SG}(1,n)}$ with $V_1/k_{\mathrm{B}}T$ and n respectively when $n = 50$ and $V_1/k_{\mathrm{B}}T = 2.5$. The results indicate that in the simulation error range, $c_{\mathrm{s}\to\mathrm{d}}^{\mathrm{SG}(1,n)} = c_{\mathrm{d}\to\mathrm{s}}^{\mathrm{SG}(1,n)}$ and $c_{\mathrm{ss}\to\mathrm{dd}}^{\mathrm{SG}(1,n)} = c_{\mathrm{dd}\to\mathrm{ss}}^{\mathrm{SG}(1,n)}$. As mentioned earlier, the LOC-S and LOC-D can only transform into each other, if $c_{\mathrm{s}\to\mathrm{d}}^{\mathrm{SG}(1,n)} \neq c_{\mathrm{d}\to\mathrm{s}}^{\mathrm{SG}(1,n)}$, it inevitably leads one of the LOCs to continually increase or decrease with time, thereby violating the equilibrium conditions. We have the same conclusion when LOC-SS and LOC-DD transform into each other. Therefore, $c_{\mathrm{s}\to\mathrm{d}}^{\mathrm{SG}(1,n)}$ and $c_{\mathrm{d}\to\mathrm{s}}^{\mathrm{SG}(1,n)}$ can be described by one parameter $c_{\mathrm{d}\leftrightarrow\mathrm{s}}^{\mathrm{SG}(1,n)}$; $c_{\mathrm{ss}\to\mathrm{dd}}^{\mathrm{SG}(1,n)}$ and $c_{\mathrm{dd}\to\mathrm{ss}}^{\mathrm{SG}(1,n)}$ can also be described by one parameter $c_{\mathrm{ss}\leftrightarrow\mathrm{dd}}^{\mathrm{SG}(1,n)}$.

Figure 2 also shows that as T decreases, $c_{\mathrm{s}\leftrightarrow\mathrm{d}}^{\mathrm{SG}(1,n)}$, $c_{\mathrm{ss}\leftrightarrow\mathrm{dd}}^{\mathrm{SG}(1,n)}$, and $c_{\mathrm{sd}\leftrightarrow\mathrm{ds}}^{\mathrm{SG}(1,n)}$ drop off, but the downward trend of $c_{\mathrm{s}\leftrightarrow\mathrm{d}}^{\mathrm{SG}(1,n)}$ and $c_{\mathrm{sd}\leftrightarrow\mathrm{ds}}^{\mathrm{SG}(1,n)}$ are slower than the trend of $c_{\mathrm{ss}\leftrightarrow\mathrm{dd}}^{\mathrm{SG}(1,n)}$. Figure 3 indicates that $c_{\mathrm{s}\leftrightarrow\mathrm{d}}^{\mathrm{SG}(1,n)}$ is indepen-

dent of n; $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\leftrightarrow\mathrm{dd}}$ and $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\leftrightarrow\mathrm{ds}}$ almost linearly increase with n increasing. From Figs. 2 and 3, we can find that when $V_1/k_{\mathrm{B}}T = 2.5$ and $n = 50$, $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\leftrightarrow\mathrm{dd}}$ is about 1/10 of $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\leftrightarrow\mathrm{d}}$, and about 1% of $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\leftrightarrow\mathrm{ds}}$, moreover, as T lowers and n decreases, $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\leftrightarrow\mathrm{d}}$ becomes smaller and smaller than $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\leftrightarrow\mathrm{ds}}$ and $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\leftrightarrow\mathrm{dd}}$, so its contribution to MS relaxation can be ignored.

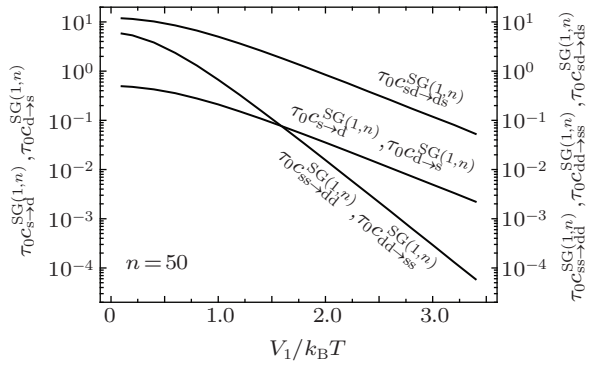


Fig. 2. Variations of $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\to\mathrm{d}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{d}\to\mathrm{s}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\to\mathrm{dd}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{dd}\to\mathrm{ss}}$, and $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\to\mathrm{ds}}$ with $V_1/k_{\mathrm{B}}T$ at $n = 50$.

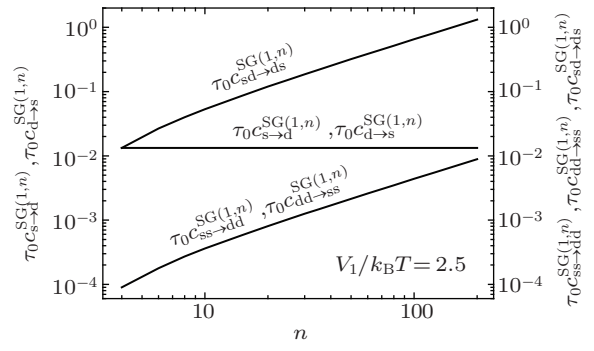


Fig. 3. Variations of $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\to\mathrm{d}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{d}\to\mathrm{s}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\to\mathrm{dd}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{dd}\to\mathrm{ss}}$, and $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\to\mathrm{ds}}$ with n at $V_1/k_{\mathrm{B}}T = 2.5$.

Considering the data of the typical glassformer glycerol, its boiling point ~ 290 °C, and the crossover temperature from liquid to the supercooled liquid $T_{\mathrm{co}} \approx 290$ K,[6−8] the MS model predicts that $V_1 \approx 640$ K, and the average length of the MS ~ 20 at T_{co}.[9−14] So it is clearly seen that the values of $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\leftrightarrow\mathrm{dd}}$ in liquids and supercooled liquids are much smaller than $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\leftrightarrow\mathrm{d}}$ and $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\leftrightarrow\mathrm{ds}}$, and its contribution to MS relaxation can be neglected as a good approximation.

It can be expected that the above results is also correct for the single-molecule orientation flipping rate of general-Glauber-type,[33,38] so that the above approximation will effectively reduce the difficulties in calculating the individual MS relaxation based on the rate and the computer simulation time of interaction MS relaxation process. In addition, the approximation is no doubt of reference significance for solving and simulating the multi-state MS model.

In short, based on the dynamical Hamiltonian of MS model, we first gave microscopic parameters $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\to\mathrm{d}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{d}\to\mathrm{s}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\to\mathrm{dd}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{dd}\to\mathrm{ss}}$, and $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\to\mathrm{ds}}$ describing the MS relaxation process in this paper, and then simulated the molecular orientation flipping images of individual MS ensemble, at the same time we calculated $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\to\mathrm{d}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{d}\to\mathrm{s}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\to\mathrm{dd}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{dd}\to\mathrm{ss}}$, and $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\to\mathrm{ds}}$ of the equilibrium state. The results show that in liquids (including supercooled liquids), the main molecular orientation flipping image in MS is similar to those of random walk. In addition, $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\to\mathrm{d}} = c^{\mathrm{SG}(1,n)}_{\mathrm{d}\to\mathrm{s}}$, $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\to\mathrm{dd}} = c^{\mathrm{SG}(1,n)}_{\mathrm{dd}\to\mathrm{ss}}$, can be described only by two parameters $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\leftrightarrow\mathrm{d}}$ and $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\leftrightarrow\mathrm{dd}}$, respectively. Moreover, $c^{\mathrm{SG}(1,n)}_{\mathrm{ss}\leftrightarrow\mathrm{dd}}$ can be ignored compared with $c^{\mathrm{SG}(1,n)}_{\mathrm{sd}\to\mathrm{ds}}$ and $c^{\mathrm{SG}(1,n)}_{\mathrm{s}\leftrightarrow\mathrm{d}}$. This approximation will effectively reduce the difficulties in calculating the individual MS relaxation based on the single-molecule orientation flipping rate of general Glauber type and the computer simulation time of the interaction MS relaxation process. In addition, the conclusion is undoubtedly of reference significance for solving and simulating the multi-state MS model.

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