Solving the initial condition of the string relaxation equation of the string model for glass transition: part-II*

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The string model for the glass transition can quantitatively describe the universal α-relaxation in glassformers. The string relaxation equation (SRE) of the model simplifies the well-known Debye and Rouse–Zimm relaxation equations at high and low enough temperatures, respectively. However, its initial condition, necessary to the further model predictions of glassy dynamics, has not been solved. In this paper, the general initial condition of the SRE for stochastically spatially configurative strings is solved exactly based on the obtained special initial condition of the SRE for straight strings in a previous paper (J. L. Zhang *et al.* 2010 *Chin. Phys.* B **19**, 056403).

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1. Introduction

Though the glass transition is a fundamental property of the condensed matter, none of the theories and models proposed to explain this property has widely received acceptance, remaining a central unresolved issue in condensed matter physics.[1−64] Recently, a molecular level mechanism of coupling dynamical molecular strings was proposed by Huang, Wang, and Riande, called the string model for the sake of convenience.[22] Besides describing the single molecular orientational motion of Debye's mean-field theory approximation,[23,24] the string model represents the collective units of the structure and dynamics of glassformers by coupling molecular strings stochastically distributed in space, which has characteristics widely observed in well-designed experiments,[25] analog simulations[26] and molecular dynamics simulations.[27] The reasons about the basic structural and dynamical units of liquid state being the dynamical molecular string rather than the dynamical branched clusters are: 1) formally, supposing that the first 'walk' is along a branch of a cluster, and if we meet the cross point of two or more branches, then we will randomly choose a branch to 'walk', meanwhile 'cut' the other branches, by doing such process repeatedly, the cluster will formally be divided into 'individual' strings; 2) physically, the above processes re-express the cluster by some interacting strings, and the inter-string interacting points are the cross points of the branches; 3) mathematically, the above processes make the corresponding mathematical problems more easy to solve. Furthermore, the model assumes relative weak interactions between the strings, in comparison with the intra-string ones.

The Debye's theory[23,24] describes the orientational motions of a molecule in liquids by the well-known sin-Gordon potential,

$$\phi_i^{\mathrm{sG}} = \frac{V_0}{2}\sin 4\left(\theta_i - \theta_i^0\right)\delta(\varphi_i - \varphi_i^0),$$

where V_0 is the barrier height between the double wells, and θ_i $(0 \le \theta_i < \pi)$ and φ_i $(0 \le \varphi_i < 2\pi)$ are, respectively, the directional and rotational angles of the i-th molecule, $\delta\ (\varphi_i - \varphi_i^0)$ is the Dirac δ-function, θ_i^0 and φ_i^0 are the directional and rotational angles of the double wells in space, respectively.

Due to the fact that the factor $\mathrm{e}^{-V_0/k_{\mathrm{B}}T} \ll 1$ in liquids,[17−22] molecular jumping processes between

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the double wells are equivalent approximately to those between two states, $\sigma_i = \pm 1$, with a jumping rate or a jumping time $\tau_0 = v_0^{-1} \mathrm{e}^{V_0/k_\mathrm{B}T}$, where k_B is the Boltzmann's constant, T is the absolute temperature, and ν_0 is the vibration frequency of molecules in the wells.

Taking into account the two state approximation, the string model represents intra-string interactions by a finite one-dimensional Ising model $H_1 = -V_1 \sum_{m=1}^{\infty} \sum_{i=1}^{n-1} \sigma_i^{mn} \sigma_{i+1}^{mn}$,[20−22] whereas the inter-string interactions are represented by a random Ising model

$$H_2 = -\frac{V_2}{2} \sum_{m=1}^{\infty} \sum_{i=1}^{n} \sum_{m' \neq m, i'}^{nn(i)} \sigma_i^{mn} \sigma_{i'}^{m'n'} \Theta_{ii'}^{mm'},$$[20−22]

where V_1 and V_2 are, respectively, the intra- and inter-string interaction constants, independent of temperature, and $V_1 \geq V_2$. The symbol $\sigma_i^{mn} = \pm 1$ denotes the two states of the i-th molecule in a string (numbered m in the system) containing n molecules (called n-string hereafter), $nn(i)$ represents the nearest number of molecules surrounding the i-th molecule, and $\Theta_{ii'}^{mm'}$ is the random distribution function in the range of [0,1].

Based on the above results, the string model describes the coupled orientational jumping motion of molecules in glass systems by the following kinetic and partly-random Ising-model,

$$\begin{cases} H_\mathrm{e} = -V_1 \sum_{m=1}^{\infty} \sum_{i=1}^{n-1} \sigma_i^{mn} \sigma_{i+1}^{mn} + \dfrac{V_2}{2} \sum_{m=1}^{\infty} \sum_{i=1}^{n} \sum_{m' \neq m, i'=1}^{nn(i)} \sigma_i^{mn} \sigma_{i'}^{m'n'} \Theta_{ii'}^{mm'}, \\ \nu_{\sigma_i^{mn} \to -\sigma_i^{mn}}^{\mathrm{SG}(1,n)} = v_0 \mathrm{e}^{-V_0/k_\mathrm{B}T} \dfrac{\exp\left[-E_{-\sigma_i^{mn}}^{(1)}/k_\mathrm{B}T\right]}{\exp\left[-E_{-\sigma_i^{mn}}^{(1)}/k_\mathrm{B}T\right] + \exp\left[-E_{\sigma_i^{mn}}^{(1)}/k_\mathrm{B}T\right]}, \end{cases} \tag{1}$$

where $\nu_{\sigma_i^{mn} \to -\sigma_i^{mn}}^{\mathrm{SG}(1,n)}$ is the special-Glauber type flip rate of the i-th molecule in an n-string from the σ_i^{mn} to $-\sigma_i^{mn}$ states, $E_{\sigma_i^{mn}}^{(1)} = -V_1 \left(\sigma_{i-1}^{mn} + \sigma_{i+1}^{mn}\right) \sigma_i^{mn} + V_2 \sum_{m' \neq m, i'=1}^{nn(i)} \sigma_i^{mn} \sigma_{i'}^{m'n'} \Theta_{ii'}^{mm'}$, and $\sigma_0^{mn} = \sigma_{n+1}^{mn} = 0$.

The main conclusions of the model for a glassy system under a first-order approximation (the calculation error is estimated to be about 1% near the glass transition temperature T_g) are:[20−22] a) the relaxation behaviour of a molecular string is equivalent to that of an effective molecule (EM), characterized by a definite relaxation time and dipole moment; b) high temperature ordinary liquids are renormalized to an EM gases, this approach presents a possible brand-new kind picture about the ordinary liquids; c) low temperature strong correlated supercooled liquids are renormalized to weak correlated EM liquids; d) there exists a crossover transition from the EM gases to the EM liquids.

The polarizability predicted by the model gives a unified and quantitative description of the universal α-relaxation dynamics in glass-formers including: i) the crossover of the relaxation time from the high temperature Arrhenius behaviour to the low temperature Vogel–Fulcher–Tammann law;[65−67] ii) the crossover of the relaxation function from the high temperature Debye exponential to the low temperature Kohlrausch–Williams–Watts[68,69] or Cole-Davidson[70] function; iii) the departure of the relaxation intensity from the Curie law.[17−19] In addition, comparing with other models, we find that least parameters of clear physical origins are involved in the string model.[20−22]

Both mathematical and physical core of the string model arises from the stronger intra-string interaction H_1 described by Eq. (1), which leads to the following relaxation equation for an individual n-string,[20−22]

$$\frac{\mathrm{d}}{\mathrm{d}t} \begin{bmatrix} \delta_1 \\ \delta_2 \\ \vdots \\ \vdots \\ \vdots \\ \delta_{n-1} \\ \delta_n \end{bmatrix} = -\frac{1}{\tau_0} \begin{bmatrix} 1 & 2u-1 & 0 & \cdots & 0 & 0 & 0 \\ w-1/2 & 1 & w-1/2 & \cdots & \vdots & 0 & 0 \\ \vdots & w-1/2 & 1 & \cdots & \vdots & \vdots & 0 \\ \vdots & \vdots & w-1/2 & \cdots & w-1/2 & \vdots & \vdots \\ 0 & \vdots & \vdots & \cdots & 1 & w-1/2 & \vdots \\ 0 & 0 & \vdots & \cdots & w-1/2 & 1 & w-1/2 \\ 0 & 0 & 0 & \cdots & 0 & 2u-1 & 1 \end{bmatrix} \begin{bmatrix} \delta_1 \\ \delta_2 \\ \vdots \\ \vdots \\ \vdots \\ \delta_{n-1} \\ \delta_n \end{bmatrix}, \tag{2}$$

where $\delta_i^{(n)}(t) \equiv p_i^{(n)}(t) - p_i^{(n)}(\infty),\ i = 1, \ldots, n,\ p_i^{(n)}(t)$ is the probability that the i-th molecule of the n-string is at the orientational state $\sigma_i^{mn} = 1$, and $p_i^{(n)}(\infty)$ is the relevant probability at equilibrium. Therefore, $\delta_i^{(n)}(t)$ is the departure of the quantity from equilibrium, $u \equiv \left(1 + \mathrm{e}^{2v}\right)^{-1}$, $w \equiv \left(1 + \mathrm{e}^{4v}\right)^{-1}$, and $v \equiv V_1/k_{\mathrm{B}}T$.

For the sake of convenience, equation (2) will be called the string relaxation equation (SRE), whereas the square matrix on the right-hand side of Eq. (2) will be named M_{SR}. At high enough temperature, i.e. $v \to 0$, M_{SR} becomes a unit matrix and the SRE simplifies the Debye relaxation equation.[20−24] On the other hand, at low enough temperature, i.e. $v \to \infty$, and M_{SR} is the Rouse–Zimm matrix, the SRE becomes the Rouse–Zimm relaxation equation.[71,72] Since the Debye theory and the Rouse model are, respectively, the two most successful relaxation theories for monomers and macromolecules, respectively, the string model can be considered, at least mathematically, a universal model that describes the relaxation dynamics of the amorphous condensed matter.

It can be proven mathematically that the relaxation of the n coupled molecules in an n-string is described physically by n individual relaxation modes, according to the SRE. The first-order approximation in Ref. [19] only gives the main relaxation mode corresponding to the largest relaxation intensity and the longest relaxation time, the other modes are omitted.

We would like to point out that, in addition to the universal α-relaxation, glass-formers exhibit another well-known universal Johari–Goldstein β-relaxation at high frequencies.[17−19] The microscopic mechanism associated with the Johari–Goldstein β-relaxation is not clear till now, though there are some phenomenological theories, such as the coupling model[11] and the mode-coupling theory,[12] which give some import elicitations of the characteristics of this process.

The relaxation mode scenario of the string model possibly provides a unified mechanism of the α- and β-relaxation. It can be assumed that, with the exception of the main relaxation mode associated to the α-relaxation, all the other modes correspond to the Johari–Goldstein β-process. To carry out the exact analysis and quantitative comparisons of this assumption with experiments, it is necessary to calculate the intensities of all the modes. To accomplish this goal, it is necessary to solve the initial condition of the SRE, that is,

$$\delta_i^{(n)}(0) \equiv p_i^{(n)}(0) - p_i^{(n)}(\infty),\ i = 1, \ldots, n. \quad (3)$$

In a previous paper,[73] the authors have presented the exact solution of the initial condition of the SRE for the case of straight molecular strings and for the dielectric spectrum technique which is one of the most common methods to investigate the glassy dynamics, so the main goal of this paper is to calculate the general initial condition (GIC) of the molecular strings stochastically configurative in space also for the dielectric spectrum technique.

2. General calculation project

Similar to the method shown in Ref. [19], the relevant question of the coupled n molecules in an n-string is first transformed to that of the individual 2^n orientational complexions, so that it can be calculated exactly based on the Boltzmann principle in allusion to the individual complexions, then the calculated results of the orientational complexions are transformed back to those of the coupled molecules.

For the dielectric spectrum technique, the relevant GIC of the SRE of an n-string (Eq. (3)) is induced by an external electric field. Without losing generality and in the linear response regime,[20−24] we consider an individual n-string ensemble perturbed by a small enough step electric field,

$$F(t) = \begin{cases} F_0,\ t < 0, \\ 0,\ \ t \geq 0. \end{cases} \quad (4)$$

Mathematically, the linear response condition is the reduced energy of the molecule in the electric field $f \equiv \mu_0 F_0/k_{\mathrm{B}}T \ll 1$ and $\mathrm{e}^f \approx 1 + f$, where μ_0 is the permanent electric dipole moment of the molecule along the string direction.

3. Specific calculations of GIC and results

Let $E_j^{(n)}(F)$ and $q_j^{(n)}(t)$ be the energy and the probability of the j-th orientational complexion of the n-string in the electric field respectively, and assume that the angle between the i-th molecule dipole moment in the n-string and the external electric field equals $\theta_i^{(n)}$ that depends on the spatial configurations of the string, first $E_j^{(n)}(F)$, then $q_j^{(n)}(0)$ and finally $q_j^{(n)}(\infty)$ can be calculated according to the Boltzmann principle and the intra-string Hamiltonian H_1 of Eq. (1),

$$\begin{cases} q_j^{(n)}(0) = \mathrm{e}^{-E_j^{(n)}(F_0)/kT} \Big/ \sum_{k=1}^{2^n} \mathrm{e}^{-E_k^{(n)}(F_0)/kT} \approx \left[1 + f\sum_{i=1}^{n} \sigma_i^{mn} \cos\theta_i^{(n)}\right] \exp\Big(v \sum_{i=1}^{n-1} \sigma_i^{mn}\sigma_{i+1}^{mn}\Big) \Big/ Q_n, \\ q_j^{(n)}(\infty) = \mathrm{e}^{-E_j^{(n)}(0)/kT} \Big/ \sum_{k=1}^{2^n} \mathrm{e}^{-E_k^{(n)}(0)/kT} = \exp\Big(v \sum_{i=1}^{n-1} \sigma_i^{mn}\sigma_{i+1}^{mn}\Big) \Big/ Q_n, \end{cases} \tag{5}$$

where $Q_n = 2\,(2\mathrm{ch}v)^{n-1}$ is the orientational partition function of the n-string,[20–22] and $\mathrm{ch}v \equiv (\mathrm{e}^v + \mathrm{e}^{-v})/2$.

As an example, the 2^4 orientational complexions of a 4-string are shown in Table 1. For the two orientational states $\sigma_i^{mn} = 1$ and $\sigma_i^{mn} = -1$ of a molecule can be formally expressed by "0" and "1", respectively, the total orientational complexions of an n-string can be denoted by the binary digits, as shown in the 2nd columns of Table 1. For example, "0000" indicates that $\sigma_i^{m4} = 1,\ i = 1, \ldots, 4$. $E_j^{(n)}(F)$ has two parts, one originates from the intra-string interaction H_1 of Eq. (1), and the other from the permanent electric dipole moment of the molecule in the electric field. Such as the "0000" orientational complexion, the intra-string energy and the energy of string molecules in the electric field are $-3V_1$ and $-\mu_0 F\left(\cos\theta_1^{(4)} + \cos\theta_2^{(4)} + \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)$, respectively.

The calculated $q_j^{(4)}(0),\ j = 1, \ldots, 2^4$ are shown in the 3rd columns of the Table 1. We would like to point out a simple method to calculate the energy of string molecules in the electric field, that is if the orientational state of the i-th molecule in an n-string is "0", the sign before the $\cos\theta_i^{(n)}$ is negative otherwise is positive. Such as "1010", the energy in the electric field is $-\mu_0 F\left(-\cos\theta_1^{(4)} + \cos\theta_2^{(4)} - \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)$.

Table 1. Expressions of the total orientational complexions of a 4-string and the calculated $q_j^{(4)}(0)$.

serial number	orientational complexions	$q_j^{(4)}(0)$
1	0000	$q_1^{(4)}(0) = \left[1 + f\left(\cos\theta_1^{(4)} + \cos\theta_2^{(4)} + \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{3v} \Big/ Q_4$
2	0001	$q_2^{(4)}(0) = \left[1 + f\left(\cos\theta_1^{(4)} + \cos\theta_2^{(4)} + \cos\theta_3^{(4)} - \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{v} \Big/ Q_4$
3	0010	$q_3^{(4)}(0) = \left[1 + f\left(\cos\theta_1^{(4)} + \cos\theta_2^{(4)} - \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{-v} \Big/ Q_4$
4	0011	$q_4^{(4)}(0) = \left[1 + f\left(\cos\theta_1^{(4)} + \cos\theta_2^{(4)} - \cos\theta_3^{(4)} - \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{v} \Big/ Q_4$
5	0100	$q_5^{(4)}(0) = \left[1 + f\left(\cos\theta_1^{(4)} - \cos\theta_2^{(4)} + \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{-v} \Big/ Q_4$
6	0101	$q_6^{(4)}(0) = \left[1 + f\left(\cos\theta_1^{(4)} - \cos\theta_2^{(4)} + \cos\theta_3^{(4)} - \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{-3v} \Big/ Q_4$
7	0110	$q_7^{(4)}(0) = \left[1 + f\left(\cos\theta_1^{(4)} - \cos\theta_2^{(4)} - \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{-v} \Big/ Q_4$
8	0111	$q_8^{(4)}(0) = \left[1 + f\left(\cos\theta_1^{(4)} - \cos\theta_2^{(4)} - \cos\theta_3^{(4)} - \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{v} \Big/ Q_4$
9	1000	$q_9^{(4)}(0) = \left[1 + f\left(-\cos\theta_1^{(4)} + \cos\theta_2^{(4)} + \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{v} \Big/ Q_4$
10	1001	$q_{10}^{(4)}(0) = \left[1 + f\left(-\cos\theta_1^{(4)} + \cos\theta_2^{(4)} + \cos\theta_3^{(4)} - \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{-v} \Big/ Q_4$
11	1010	$q_{11}^{(4)}(0) = \left[1 + f\left(-\cos\theta_1^{(4)} + \cos\theta_2^{(4)} - \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{-3v} \Big/ Q_4$
12	1011	$q_{12}^{(4)}(0) = \left[1 + f\left(-\cos\theta_1^{(4)} + \cos\theta_2^{(4)} - \cos\theta_3^{(4)} - \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{-v} \Big/ Q_4$
13	1100	$q_{13}^{(4)}(0) = \left[1 + f\left(-\cos\theta_1^{(4)} - \cos\theta_2^{(4)} + \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{v} \Big/ Q_4$
14	1101	$q_{14}^{(4)}(0) = \left[1 + f\left(-\cos\theta_1^{(4)} - \cos\theta_2^{(4)} + \cos\theta_3^{(4)} - \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{-v} \Big/ Q_4$
15	1110	$q_{15}^{(4)}(0) = \left[1 + f\left(-\cos\theta_1^{(4)} - \cos\theta_2^{(4)} - \cos\theta_3^{(4)} + \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{v} \Big/ Q_4$
16	1111	$q_{16}^{(4)}(0) = \left[1 + f\left(-\cos\theta_1^{(4)} - \cos\theta_2^{(4)} - \cos\theta_3^{(4)} - \cos\theta_4^{(4)}\right)\right] \mathrm{e}^{3v} \Big/ Q_4$

As to $q_j^{(4)}(\infty),\ j = 1, \ldots, 2^4$, they can be calculated by setting $f = 0$ in the expressions corresponding to $q_j^{(4)}(0),\ j = 1, \ldots, 2^4$.

From the definition given for $p_i^{(n)}(t)$ above and taking into account Table 1, the following relationships between $p_i^{(4)}(0)$ and $q_j^{(4)}(0)$ are obtained:

$$\begin{cases} p_1^{(4)}(0) = q_1^{(4)}(0) + q_2^{(4)}(0) + q_3^{(4)}(0) + q_4^{(4)}(0) + q_5^{(4)}(0) + q_6^{(4)}(0) + q_7^{(4)}(0) + q_8^{(4)}(0), \\ p_2^{(4)}(0) = q_1^{(4)}(0) + q_2^{(4)}(0) + q_3^{(4)}(0) + q_4^{(4)}(0) + q_9^{(4)}(0) + q_{10}^{(4)}(0) + q_{11}^{(4)}(0) + q_{12}^{(4)}(0), \\ p_3^{(4)}(0) = q_1^{(4)}(0) + q_2^{(4)}(0) + q_5^{(4)}(0) + q_6^{(4)}(0) + q_9^{(4)}(0) + q_{10}^{(4)}(0) + q_{13}^{(4)}(0) + q_{14}^{(4)}(0), \\ p_4^{(4)}(0) = q_1^{(4)}(0) + q_3^{(4)}(0) + q_5^{(4)}(0) + q_7^{(4)}(0) + q_9^{(4)}(0) + q_{11}^{(4)}(0) + q_{13}^{(4)}(0) + q_{15}^{(4)}(0). \end{cases} \tag{6}$$

For example, the specific method to calculate $p_1^{(4)}(0)$ is first finding all the orientational complexions with the 1st (from left to right) binary digits being "0" as shown in the 2nd column of Table 1, and then adding them together. The $p_i^{(4)}(0),\ i = 2,\ 3,\ 4$ can be obtained by the same way.

According to Eq. (6) and Table 1, we obtain,

$$\begin{aligned} p_1^{(4)}(0) = {} & (2\mathrm{ch}3v + 6\mathrm{ch}v)/Q_4 \\ & + [(2\mathrm{ch}v)^3 \cos\theta_1^{(4)} + 2(\mathrm{sh}3v + \mathrm{sh}v)\cos\theta_2^{(4)} + 2(\mathrm{ch}3v - \mathrm{ch}v)\cos\theta_3^{(4)} + 2(2\mathrm{sh}v)^3 \cos\theta_4^{(4)}]f \ / \ Q_4, \end{aligned}$$

and $p_1^{(4)}(\infty) = (2\mathrm{ch}3v + 6\mathrm{ch}v)/Q_4$ can be readily obtained by setting $f = 0$ in $p_1^{(4)}(0)$, where $\mathrm{sh}v \equiv (\mathrm{e}^v - \mathrm{e}^{-v})/2$. And $p_i^{(4)}(0),\ p_i^{(4)}(\infty),\ i = 2, \ldots, 4$ can also be calculated by the same method. Thus $\delta_i^{(4)}(0),\ i = 1, \ldots, 4$ can exactly be obtained by Eq. (3) and the calculated $p_i^{(4)}(0),\ p_i^{(4)}(\infty),\ i = 1, \ldots, 4$. The results are,

$$\begin{cases} \delta_1^{(4)}(0) = [(2\mathrm{ch}v)^3 \cos\theta_1^{(4)} + 2(\mathrm{sh}3v + \mathrm{sh}v)\cos\theta_2^{(4)} + 2(\mathrm{ch}3v - \mathrm{ch}v)\cos\theta_3^{(4)} + (2\mathrm{sh}v)^3 \cos\theta_4^{(4)}]f \ / \ Q_4, \\ \delta_2^{(4)}(0) = [2(\mathrm{sh}3v + \mathrm{sh}v)\cos\theta_1^{(4)} + (2\mathrm{ch}v)^3 \cos\theta_2^{(4)} + 2(\mathrm{sh}3v + \mathrm{sh}v)\cos\theta_3^{(4)} + 2(\mathrm{ch}3v - \mathrm{ch}v)\cos\theta_4^{(4)}]f \ / \ Q_4, \\ \delta_3^{(4)}(0) = [2(\mathrm{ch}3v - \mathrm{ch}v)\cos\theta_1^{(4)} + 2(\mathrm{sh}3v + \mathrm{sh}v)\cos\theta_2^{(4)} + (2\mathrm{ch}v)^3 \cos\theta_3^{(4)} + 2(\mathrm{sh}3v + \mathrm{sh}v)\cos\theta_4^{(4)}]f \ / \ Q_4, \\ \delta_4^{(4)}(0) = [(2\mathrm{sh}v)^3 \cos\theta_1^{(4)} + 2(\mathrm{ch}3v - \mathrm{ch}v)\cos\theta_2^{(4)} + 2(\mathrm{sh}3v + \mathrm{sh}v)\cos\theta_3^{(4)} + (2\mathrm{ch}v)^3 \cos\theta_4^{(4)}]f \ / \ Q_4. \end{cases} \tag{7}$$

From Eq. (7), we can find that the dependence of $\delta_i^{(4)}(0),\ i = 1, \ldots, 4$ on v and $\theta_i^{(4)},\ i = 1, \ldots, 4$ looks quite complicated, and though we have calculated $\delta_i^{(n)}(0), \ldots, n$ for n= 1 to 9 by the same way mentioned above, unfortunately we still cannot find a simple relation between $\delta_i^{(n)}(0),\ i = 1, \ldots, n$ and v for arbitrary n.

However, by comparison of Eq. (7) with the calculated SIC for a straight n-string in Ref. [66], i.e. $\theta_i^{(n)} = 0,\ i = 1, \ldots, n$ of the present case, we can find a regularity in Eq. (7). For example, according to Eq. (12) of Ref. [66], $\delta_1^{(4)}(0) = \dfrac{f}{2}\left(1 + \tanh v + (\tanh v)^2 + (\tanh v)^3\right)$, and by Eq. (7), $\delta_1^{(4)}(0) = [(2\mathrm{ch}v)^3 + 2(\mathrm{sh}3v + \mathrm{sh}v) + 2(\mathrm{ch}3v - \mathrm{ch}v)]f \ / \ 2\,(2\mathrm{ch}v)^3$. These two results would be the same, so we obtained that $2(\mathrm{sh}3v + \mathrm{sh}v) = (2\mathrm{ch}v)^2\, 2\mathrm{sh}v$ and $2\,(\mathrm{ch}3v - \mathrm{ch}v) = 2\mathrm{ch}v\,(2\mathrm{sh}v)^2$, and these can be easily checked. Accordingly, equation (7) can be simplified to the following matrix form:

$$\begin{pmatrix} \delta_1^{(4)}(0) \\ \delta_2^{(4)}(0) \\ \delta_3^{(4)}(0) \\ \delta_4^{(4)}(0) \end{pmatrix} = \frac{f}{2} \begin{pmatrix} 1 & \tanh v & (\tanh v)^2 & (\tanh v)^3 \\ \tanh v & 1 & \tanh v & (\tanh v)^2 \\ (\tanh v)^2 & \tanh v & 1 & \tanh v \\ (\tanh v)^3 & (\tanh v)^2 & \tanh v & 1l \end{pmatrix} \begin{pmatrix} \cos\theta_1^{(4)} \\ \cos\theta_2^{(4)} \\ \cos\theta_3^{(4)} \\ \cos\theta_4^{(4)} \end{pmatrix}, \tag{8}$$

and from Eq. (8), it could be obtained that for an arbitrary string length n,

$$\delta_i^{(n)}(0) = \frac{f}{2} \sum_{k=1}^{n} (\tanh v)^{|k-i|} \cos\theta_k^{(n)},\ i = 1, \ldots, n. \tag{9}$$

The physics of Eq. (9) show quite clearly that the polarization contribution of the k-th molecule to the i-th molecule, arising from the intra-string interaction, obeys a power law $(\tanh v)^{|k-i|}$ decay with the distance $|k - i|$ between them. Moreover, $\delta_i^{(n)}(0),\ i = 1, \ldots, n$ also depends on $\theta_i^{(n)}(0),\ i = 1, \ldots, n$, i.e. the

spatial configurations of the n-string, and this dependence will be discussed in the following.

We would like to point out that, the spatial configurations of the n-string, with $\theta_i^{(n)},\ i = 1, \ldots, n$ randomly distributing in the range of $[0, \pi]$, correspond to the contrails of random walks, with walking step equal to the distance between the two near neighbouring molecules in the strings, and they are straight chains for $\theta_i^{(n)} = 0,\ i = 1, \ldots, n$. The more general spatial configurations of the n-string, such as the rotational chains, worm chains, or self-avoiding chains etc.,[74−76] can be described equivalently, at least approximately, by setting $\theta_i^{(n)},\ i = 1, \ldots, n$ randomly distributing in a range of $[0, \alpha_p]$ with $0 \leq \alpha_p \leq \pi$, and α_p can be considered as a characteristic angle to describe the spatial configurations of the n-strings.

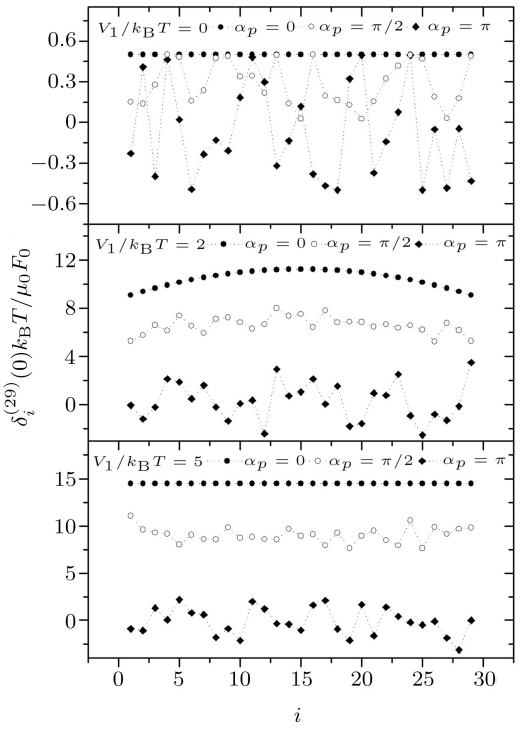


Fig. 1. The $\delta_i^{(29)}(0)/f$ versus the molecule position i in a 29-string for a set of positive v and α_p values.

Figures 1 and 2 show the calculated reduced $\delta_i^{(n)}(0)/f$ ($f \equiv \mu_0 F_0/k_BT$) versus the molecule position i in a 29-string for a set of positive $v \equiv V_1/k_BT$ and α_p values. It is found that $\delta_i^{(n)}(0)$ is a spatial randomly distributed quantity due to the random distribution of $\theta_i^{(n)}$ in space, and we introduce the spatial average

$$\bar{\delta}^{(n)}(0) \equiv \sum_{i=1}^{n} \frac{\delta_i^{(n)}(0)}{n},$$

i.e. local polarization originating from the intra-string interaction, and the spatial fluctuation

$$\Delta^{(n)}(0) \equiv \frac{1}{n} \sum_{i=1}^{n} \left[\delta_i^{(n)}(0) - \bar{\delta}^{(n)}(0)\right]^2,$$

i.e. depolarization from the random spatial configurations of the strings, to describe this fluctuation quantity.

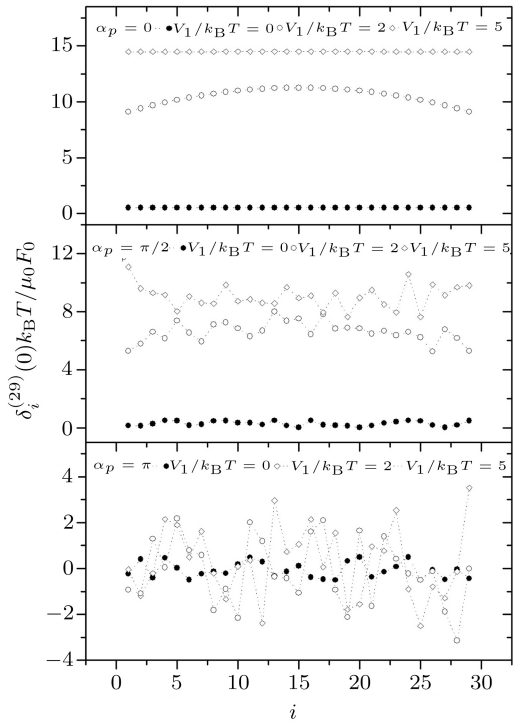


Fig. 2. The $\delta_i^{(29)}(0)/f$ versus the molecule position i in a 29-string for a set of α_p and positive v values.

Specifically, for definite v as shown in Fig. 1, the spatial average $\bar{\delta}^{(n)}(0)$ decreases but the spatial fluctuation $\Delta^{(n)}(0)$ increases with increasing α_p, which means that the randomness of the string spatial configurations eliminates, more or less, the spatial polarization arising from the intra-string interaction. On the other hand, for definite α_p as shown in Fig. 2, the spatial average $\bar{\delta}^{(n)}(0)$ increases except for $\alpha_p = \pi$, meanwhile the spatial fluctuation and $\Delta^{(n)}(0)$ go up except for $\alpha_p = 0$ with increasing v, which indicates that the intra-string interaction boosts up both the local polarization and the amplitude of the spatial polarization fluctuations.

As a comparison, the $\delta_i^{(n)}(0)/f$ as functions of i for a set of α_p and negative $v = -5$ was presented in Fig. 3. In contrast to the positive v cases, the average $\bar{\delta}^{(n)}(0)$ is always about zero for all the α_p values, but

the spatial fluctuation $\Delta^{(n)}(0)$ increases with increasing α_p.

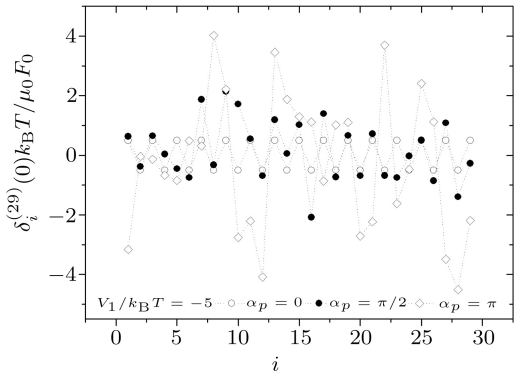


Fig. 3. The $\delta_i^{(29)}(0)/f$ versus molecule position i in a 29-string for $v=-5$ and a set of α_p values.

In conclusion, the GIC of the SRE has been calculated from the allusions of the obtained SIC in a previous paper.[73] With the solved GIC, the relaxation times and intensities of all the relaxation modes of the strings can be calculated exactly, so we could check whether the string model gives a good and unified account of the universal α- and Johari–Goldstein β-relaxation at molecular level by comparing with experiments.[17−19] Moreover, the relevant studies also present a quantitative molecular level description of the static dielectric constants of liquids, a long time standing question of condensed matter physics.[23−24,77,78] These items will be described in separate publication.

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