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Determination of the relaxation behavior in time and frequency domains of a dipolar chain with Glauber dynamics using Monte Carlo simulation

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Abstract

In this paper, we have determined the relaxation behavior of one dimensional dipolar chain with the Glauber dynamics both in time and frequency domains using Monte Carlo simulation. Two algorithms are developed to simulate the decay function for a single dipole and for the whole dipolar chain in the time domain. MC simulations of the whole dipolar chain show that both exponential and KWW type behaviors for the decay function $\phi(t) = \exp[-(t/\tau)^{\beta}]$ $0 < \beta < 1$ are possible. The frequency domain transformation is also computed by using the Fourier transform of the corresponding time domain response of the decay function which is obtained by MC simulations. We have determined the components of the normalized complex dielectric permittivity. The observed behavior of loss curves are in full agreement with experiments performed on glass-forming materials in which two loss curves – called α- and β-relaxation processes – are observed.

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1. Introduction

Application of the Glauber's kinetic Ising model to the dipolar chain molecules has been used as a model for dielectric relaxation in time and frequency domains [1–12]. One of the first observation of non-Debye behavior in Ising systems based on Glauber's kinetic Ising model was reported by Anderson [2] and later by others [3–5], all of which were in the context of dielectric relaxation of infinite and/or finite dipolar chains where the dipole moment of each dipole is assumed to take either the value $(+\mu)$ or $(-\mu)$ [1–9]. These authors [2–5] have studied the frequency behavior of the complex permittivity which is expressed in terms of the Fourier transform of the dipole moment auto correlation function of a single dipole located in the middle of either an infinite or a finite chain. The complex permittivity $\varepsilon(\omega)$ is related to the correlation function $\phi(t)$ describing the dielectric response, by the expression [13]

$$\chi(\omega) = \frac{\varepsilon(\omega) - \varepsilon_{\infty}}{\varepsilon_{s} - \varepsilon_{\infty}} = 1 - i\omega \int_0^{\infty} e^{-i\omega t}\phi(t)dt. \quad (1)$$

Here ε_s is the equilibrium value of the total permittivity at zero frequency and ε_{∞} only represents the permittivity of the system at high frequency arising from the rapid polarization responses. The normalized complex permittivity can be written in terms of its real and complex components as $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$. $\phi(t)$ is defined by [13]

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$$\phi(t) = \frac{\langle M(0)M(t)\rangle}{\langle M(0)M(0)\rangle} = \frac{\sum_j \left[\langle \mu_j(0)\mu_j(t)\rangle + \sum_{k\neq j}\langle \mu_j(0)\mu_k(t)\rangle\right]}{\sum_j \left[1 + \sum_{k\neq j}\langle \mu_j(0)\mu_k(0)\rangle\right]}, \quad (2)$$

where the μ_j's are the individual dipole moments along the chain and $M(t)$ is the dipole moment for the whole chain at time t. For a chain containing equivalent dipole moments which may be expressed in terms of σ_k by $\mu_k = \mu_0\sigma_k$ where μ_0 is the magnitude of a single dipole and $\sigma_k = \pm 1$, the dipole correlation function is conveniently expressed as

$$\phi(t) = \frac{\sum_j \left[\langle \sigma_j(0)\sigma_j(t)\rangle + \sum_{k\neq j}\langle \sigma_j(0)\sigma_k(t)\rangle\right]}{\sum_j \left[1 + \sum_{k\neq j}\langle \sigma_j(0)\sigma_k(0)\rangle\right]}, \quad (3)$$

$\sigma_k(t)$ is a stochastic function of time making random transitions between values ± 1, due to interactions with a phonon bath. Analysis of dielectric relaxation of chain molecules with Glauber dynamics has been carried out by many authors and for the spin–spin time correlation functions. It is concluded that at low temperatures the complex permittivity approaches the Cole Davidson function with an exponent $\beta_{CD} = 1/2$ in frequency domain [2–10]. Consequently, this has been the value used to characterize the relaxation of the spin autocorrelation function in the one dimensional Ising model with Glauber dynamics.

Relaxation in kinetic Ising models has been extensively studied and stretched exponential behavior has been found for different choices of the transition rate. Shore and Zwanzig [6] studied the dielectric properties of a one dimensional lattice of interacting spins. They found a non-exponential decay function similar to KWW form. A new one dimensional kinetic Ising model was introduced by Skinner [7] to study the cooperative dynamics of linear chain molecules where relaxation functions are well represented by KWW function. Bauer and co-workers [8] studied dynamics correlation functions of one and two dimensional kinetic Ising models where they consider simultaneously high and low frequency behavior of observables and investigate, among others, the extent of non-exponential relaxation occurrence suggested by KWW function for such systems. In the low-temperature limit, an asymptotically valid continuous space equation was derived for the one dimensional Ising model with Glauber dynamics by Brey and Prados [9]. Monte Carlo (MC) simulations for the zero temperature dynamics have been studied by Derrida et al. [11] and Menon et al. [12]. However, these nearest-neighbors Ising model theories seem to explain only limited departures from Debye behavior, but not the major ones such as one found in the much broader and asymmetric loss peaks in a number of dielectric materials [14,16]. This type of behavior has been represented perfectly by a KWW function which is given by [17]

$$\phi(t) = \exp[-(t/\tau)^{\beta}], \quad 0 < \beta < 1. \quad (4)$$

In the present study, the relaxation behavior of one dimensional infinite dipolar chain with Glauber dynamics both in time and frequency domains are presented using MC simulation. This is an extension of a study on the subject previously carried out by the same authors [19]. In the previous study the correlation function for a single and dipolar chain in the time domain only was obtained. In the present study, this work is extended to the frequency domain where the number of particles used in the simulations is increased significantly to allow the presence of more points in the time domain needed for the Fourier transforms. In addition, using the Fourier transform of the decay function, the real and imaginary components of the complex dielectric permittivity is obtained. The latter are the main results of the present work. The plan of the paper is as follows: MC simulation of one dimensional dipolar chain with the Glauber dynamics is presented in Section 2. Section 3 contains the result of MC simulation of a linear chain of molecules in time domain. Dielectric relaxation in frequency domain is presented in Section 4. Finally, Section 5 contains summary and conclusions.

2. MC simulation of the dielectric relaxation of a chain molecule with Glauber dynamics

The relaxation behavior of one dimensional dipolar chain with Glauber dynamics has been determined by MC simulation in an earlier study by the present authors [19]. The simulation results shown in this section are the same as before but this time the number of particles N used in simulation is increased to 40 000 to both observe the behavior of the system in more detail and to have as many data points as possible for the Fourier transforms to be performed in Section 5. We will just summarize the two algorithms used before for the sake of completeness. We start with an initial configuration where all dipoles are aligned up (they take value +1) and then it is allowed to relax to its global minimum energy configuration. The probability of jth dipole to flip its alignment depends on the dipole moments of its neighbors and on its interaction with the surrounding heat bath. The probability $p_j(\sigma_j)$ of a dipole to flip its orientation to align itself antiparallel to its neighbors therefore can be taken to be of the form [19]

$$p_j(\sigma_j) = \frac{1}{2}\left\{1 + \frac{1}{2}\gamma\sigma_j(\sigma_{j-1} + \sigma_{j+1})\right\}, \quad (5)$$

which may be seen to take on only three possible values depending on the orientation of its neighbors. Here γ is a function of the temperature T of heat bath given by $\gamma = \tanh(2K)$ where $K = J/k_B T$ and J is the coupling constant describing the strength of interaction between nearest neighbor dipoles.

We have developed two algorithms to simulate the dipole behavior in time domain. In one algorithm (Algorithm A), the decay function of a single dipole and in the other (Algorithm B), the decay function of the whole dipolar chain is considered. For the details see [19] and the

references therein. The main difference between the two algorithms just mentioned is that only a single dipole is considered and updated in a MC step and then the total numbers of dipoles that are not flipped up to that time are counted in Algorithm A. The ratio of the number of dipoles which never flipped to the total number of dipoles gives the decay function $\phi_1(t)$ [12–19] for a single dipole. In Algorithm B, however, all dipoles in the system are considered and their orientations are updated at each MC step and then the total number of dipoles which have never flipped until time t are counted. In this case, the ratio of un-flipped dipoles to the total number gives the decay function $\phi_N(t)$ for the whole chain.

3. Dielectric relaxation in time domain

Let us first start with the decay function of a single dipole in the dipolar chain, namely with $\phi_1(t)$. We have plotted $\ln[-\ln(\phi_1(t))]$ vs $\ln(t)$ using the calculated values of $\phi_1(t)$. If the slope β of the curve is 1, then it means that $\phi_1(t)$ is in the form of an exponential function. If the slope is $0 < \beta < 1$, then $\phi_1(t)$ is in the form of a stretched exponential, which is the KWW form. The results of MC simulations using Algorithm A given above are shown in Figs. 1–3 for the parameter values $K = 0.01$, 1.0 and 1.8, respectively. For all three values of the parameter K, the slope of the curve at early times is exactly 1.0 as one can see in Figs. 1–3. Therefore the behavior for all parameter values at early times is Debye-type in the time domain. As the value of K increases, the exponential behavior is still observed at short times as we have already indicated. But at intermediate and late times it shows stretched exponential behavior but with different exponents. The slope at intermediate times is about 0.5 for Fig. 2 and it is about 0.3 for Fig. 3, the corresponding late time values of the exponent

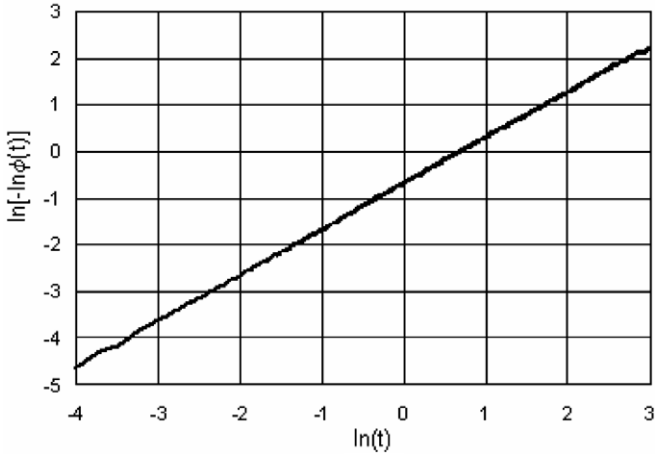

Fig. 1. The decay function of a single dipole as obtained from MC simulations using Algorithm A mentioned in the text with a parameter value of $K = 0.01$. The axes are arranged to make the degree of the correspondence between Eq. (4) and the results of the simulation visible where the slope gives the value of exponent β in Eq. (4). The behavior is clearly exponential in time domain.

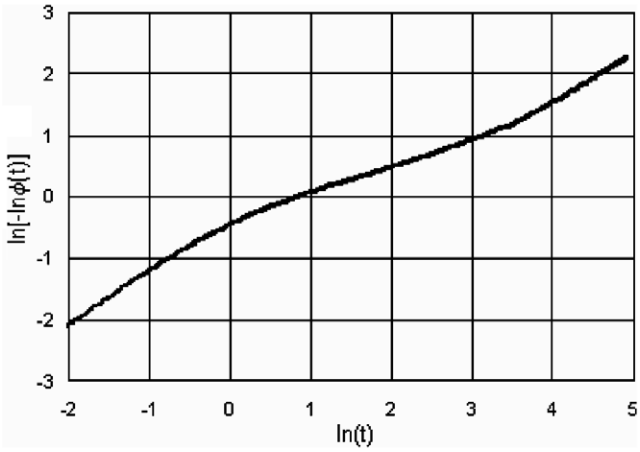

Fig. 2. The same as Fig. 1 but with a parameter value of $K = 1.0$. There are three regimes in which the behavior is exponential at early times, shifts to stretched exponential at intermediate and late times with different exponents.

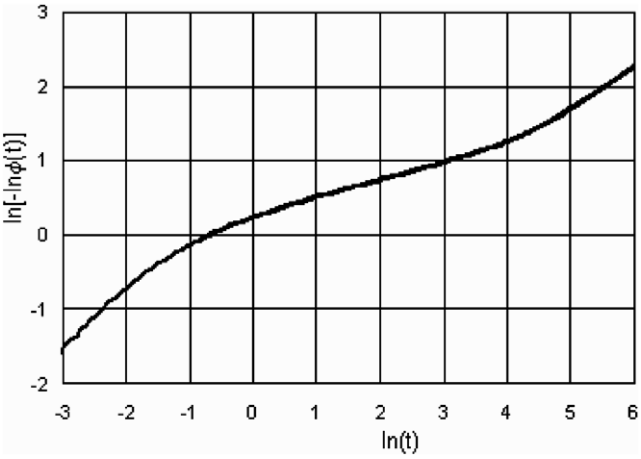

Fig. 3. The same as Fig. 2 but with a parameter value of $K = 1.8$. In this case the non-exponential behavior becomes more dominant compared to the case of small values of K.

are 0.7 for Fig. 2 and 0.5 for Fig. 3. This behavior is similar to the one found in Ref. [9] for the Ising model with Glauber dynamics and in Ref. [6] for the one dimensional lattice model.

Now let us consider the decay function for the whole chain. Unlike the decay function for a single dipole, the results obtained using Algorithm B mentioned above shows exponential behavior only for small values of parameter K. For large values of K the behavior resembles more that of a KWW function. The results are depicted in Figs. 4–6 for parameter values $K = 0.01$, 1.0 and 1.8, respectively, on a logarithmic scale to test their correspondence with the KWW function in Eq. (4). For small values of K, the exponent β is close to unity, indicative of an exponential behavior as shown in Fig. 4. As K increases, the decay function deviates from exponential behavior and is not really in the form of stretched exponential. The average slope, which is a measure of the exponent β in Eq. (4) begin

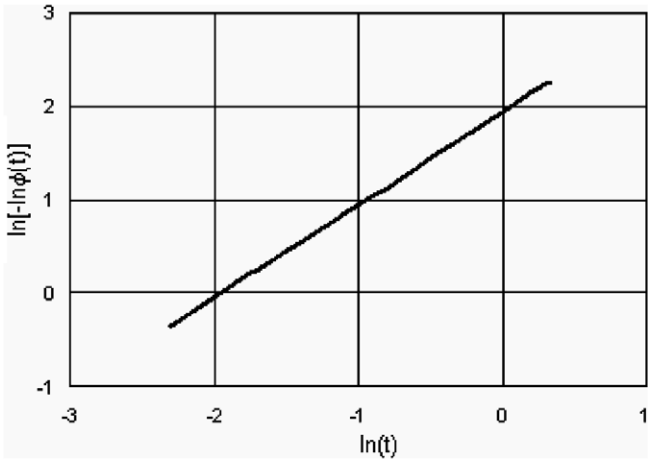

Fig. 4. The decay function of the whole dipolar chain as obtained from MC simulations using Algorithm B mentioned in the text with a parameter value of $K = 0.01$. The axes are arranged to make the degree of the correspondence between Eq. (4) and the results of the simulation visible where the slope gives the value of exponent β in Eq. (4). The behavior is close to exponential in time domain.

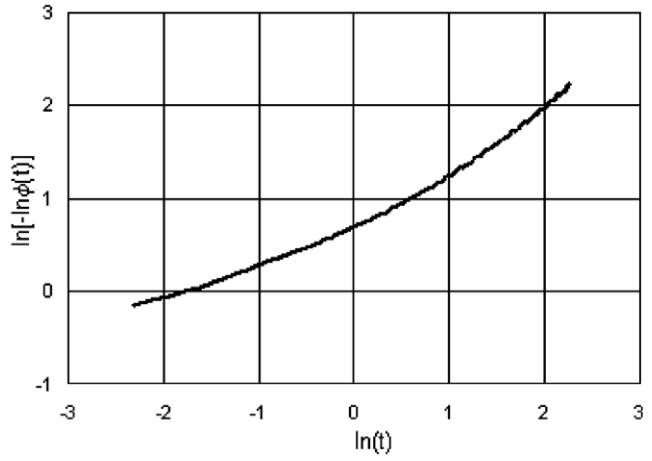

Fig. 5. The same as Fig. 4 but with a parameter value of $K = 1.0$. The behavior is not actually in the form of a stretched exponential. The slope at early times is 0.5 and at late times it is 0.7.

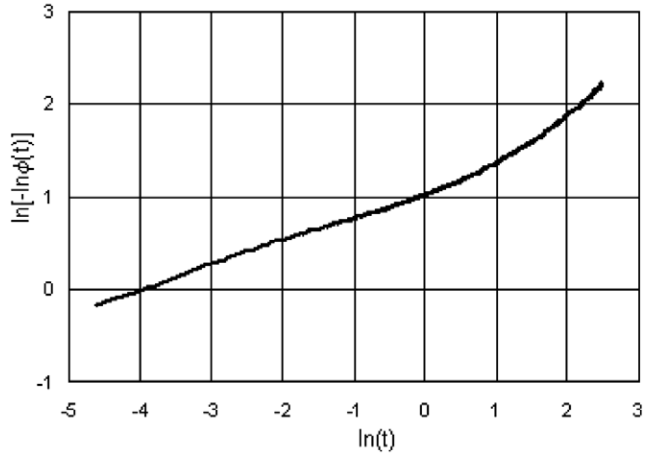

Fig. 6. The same as Fig. 5 but with a parameter value of $K = 1.8$. The slope at early times is 0.3 and at late times it is 0.5.

to decrease as can be seen in Fig. 5 ($K = 1.0$). The slope at early times is approximately 0.5 and at late times it is 0.7 in that figure. When K is increased further, it appears that the dynamics takes place in two different regimes in time domain. The results for $K = 1.8$ are depicted in Fig. 6 where the slope at early times is about 0.3 and it is 0.5 at late times. For this latter case, it appears that there are two regimes of relaxation process in the time domain, one at early times and another at late times but with a larger exponent compared to early times. These results indirectly suggest that β is a temperature dependent exponent.

4. Dielectric relaxation in frequency domain

This section is devoted to the numerical calculation of the components of the dielectric permittivity and forms the main results of this study. The frequency domain response of dielectric relaxation is the normalized dynamic permittivity as a function of frequency $\chi(\omega)$ which is derived from the Fourier transform of the corresponding time domain response $\phi(t)$. Using Eq. (1) and the definition $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$, we can find the real and complex components of the normalized complex dielectric permittivity, respectively, as

$$\chi'(\omega) = 1 - \omega \int_0^\infty \phi(t)\cos(\omega t)\mathrm{d}t,$$
$$\chi''(\omega) = \omega \int_0^\infty \phi(t)\cos(\omega t)\mathrm{d}t. \tag{6}$$

The method we have used in the calculation of the component of the normalized dielectric function is as follows: To be able to obtain the Fourier transforms in Eq. (6), one needs to know the decay function $\phi(t)$. We have used the decay function obtained for the whole chain whose behavior for different values of K is shown in Figs. 4–6. The decay function for a single dipole is not used in the calculation of the components of the normalized dielectric function. The decay function depends on the parameters β and τ as given in Eq. (4). The β values are obtained from the slope of $\ln[-\ln[\phi(t)]]$ vs $\ln(t)$ curve and the τ values are determined from the intercepts of the slopes with the vertical axis. Fig. 1 shows that the decay function is exponential with $\beta = 1$ for small values of the parameter K. The integrations in Eq. (6) are performed numerically using the trapezoidal technique [20]. When the Fourier transforms of Eq. (6) are carried out with $\beta = 1$, the result obtained for this case is shown in Fig. 7 where the dielectric loss factor $\chi''(\omega)$ values are plotted as a function $\log(\omega t)$. Since the decay function is a perfect exponential, the behavior in frequency domain is of Debye-type.

When it comes to large values of parameter K, the situation is different since for these cases there are different regimes of the evolution and therefore there are various values for β. For the case of $K = 1.0$, the value of β was found to be 0.5 at early times and 0.7 at late times. We have performed the Fourier transforms in (6) using these two

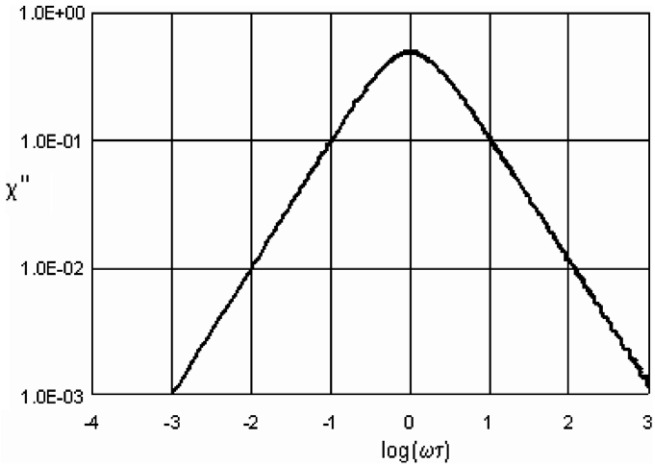

Fig. 7. Frequency domain transformation of the decay function as obtained from MC simulations given in the text with a parameter value of $K = 0.01$ as a function of $\log(\omega\tau)$. The behavior is in the form of Debye-type.

values separately. The results for this case are depicted in Fig. 8. As one can see in that figure there are two loss curves corresponding to the two values of β. When $K = 1.8$, again there are two regimes of the decay function with parameter values of $\beta = 0.3$ at early times and $\beta = 0.5$ at late times. When the Fourier transforms in (6) are taken using the decay functions corresponding to each of these values of β (=0.3 and 0.5) separately, the curves shown in Fig. 9 are obtained for the dielectric loss factor in frequency domain. Note that the single curve shown in Fig. 7 is now split into two separate curves for large values of K as shown in Figs. 8 and 9. One can easily see that one of the curves in Figs. 8 or 9 is broader than the other. The broadening increases as K increases (compare Figs. 8 and 9). Furthermore, as K increases the amplitude of the broader curve decreases while amplitude of the other curve increases.

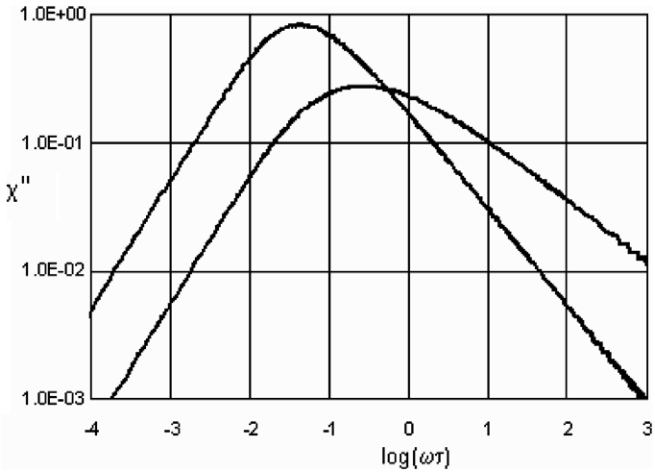

Fig. 8. The same as Fig. 7 but decay function obtained from MC simulations with a parameter value of $K = 1.0$ is used. Note that the single curve shown in Fig. 7 is now split in to two separate curves for large values of K where there are two loss curves corresponding to the two values of β.

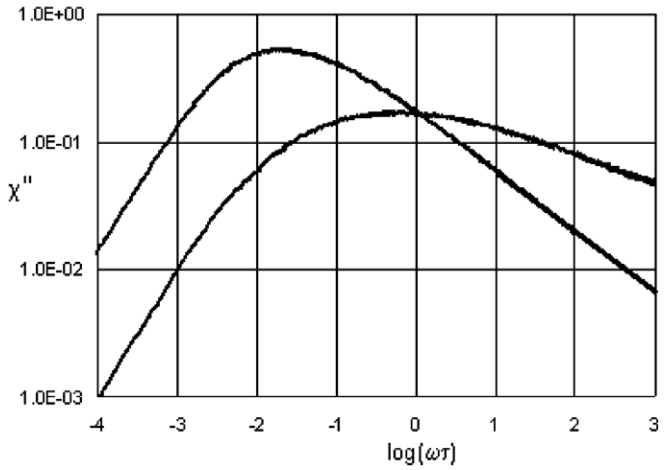

Fig. 9. The same as Fig. 8 but the decay function obtained from MC simulations with a parameter value of $K = 1.8$ is used. For large values of K (low temperatures), the loss curves show two peaks, one with a lower frequency but higher amplitude that corresponds to higher values of exponent β and another at higher frequencies which is broader with a smaller amplitude.

Our parameter K is temperature dependent through $J/k_B T$. Therefore a large values of K correspond to low temperatures and small values of it to high temperatures. This aspect of K and the loss curves we have shown in Figs. 8 and 9 – appear to be in full agreement with experimental results for glass-forming materials [14–16,21–23]. The so called α peak in frequency domain in these materials in fact corresponds to low frequency peaks in Figs. 8 and 9. The other observed relaxation process, called β process, corresponds to high frequency broader peaks in Figs. 8 and 9.

5. Conclusions

In this study, we have determined the relaxation behavior of one dimensional dipolar chain with Glauber dynamics using Monte Carlo simulation both in time and frequency domains. The decay function of a single dipole and the whole chain are obtained with suitably constructed algorithms. The decay functions for a single and also for the whole dipolar chain are always exponential for small values of parameter K. For the same parameter values, the decay function for the whole dipolar chain resembles more that of a KWW behavior. For the latter case, it appears that there are two regimes of relaxation process in the time domain, one at early times and another at late times but with a larger exponent compared to early times.

We have also presented the results of numerical calculations of the normalized dynamic permittivity as a function of frequency which is derived from the Fourier transform of the dipole correlation functions. For large values of K (low temperatures), the loss curves show two peaks: one with a lower frequency but higher amplitude that corresponds to higher values of exponent β and another at higher frequencies which is broader with a smaller amplitude (see

Figs. 8 and 9). As the temperature increases (small values of K) this split of loss curves begin to merge to a single curve. This observed behavior of loss curves are in full agreement with experiments performed on glass-forming materials in which two loss curves – called α- and β-relaxation processes – are observed.

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