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Modelling Debye Dielectric Relaxation in Monohydroxy Alcohols *

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The Debye relaxation of dielectric spectroscopy exists extensively in monohydroxy alcohols. We model the relaxation based on the infinite-pseudospin-chain Ising model and the Glauber dynamics, and the corresponding complex permittivity is obtained. The model results are in good agreement with the experimental data of 3,7-dimethyl-1-octanol, 2-ethyl-1-hexanol and 5-methyl-2-hexanol in a wide temperature range. Moreover, in the model parameters, the sum of the mean-field interaction energy and two times the orientation is nearly twice the hydrogen bond energy, which further states the rationality of this model.

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Monohydroxy alcohols, which are a class of hydrogen-bonded materials, continue to be studied extensively because they are vital for biophysical processes, of fundamental importance as solvents in industrial processes, and in every-day use.[1] Nevertheless, the way to a microscopic understanding of their properties has been beset with apparently conflicting observations and conceptual difficulties.[1] The Debye relaxation of dielectric spectroscopy exists extensively in monohydroxy alcohol liquids,[1–9] thus the study on its micro-mechanism is of great value to further understand the microscopic structures and interactions in the liquids.

The dielectric strength ($\Delta\varepsilon$) and relaxation time (τ) are the key parameters of the Debye relaxation. The experimental results[1,5,6] of monohydroxy alcohols have shown that $\Delta\varepsilon$ has a crossover from the low temperature (T) Curie–Weiss law to the high temperature one. However, all of the corresponding well-known theories, such as Debye theory,[10] Onsager theory,[11] Kirkwood theory,[12,13] and Stockmayer–Baur theory,[14,15] gave the Curie law of $\Delta\varepsilon$ with T. Recently, according to the existence of the hydrogen-bonded molecular chains[1,2,5,6,16,17] in monohydroxy alcohol liquids confirmed by neutron scattering,[1,18,19] x-ray scattering,[18,20–23] and computer simulation[18,20–22,24,25] as well as the transient chain model[2] proposed by Gainaru *et al.*, Wang *et al.* proposed the infinite-pseudospin-chain Ising model (IPCIM),[26] which can give the crossover of $\Delta\varepsilon$ with T. Although this model does not consider the change of the chain length, its theoretical predictions agree well with the experimental results of $\Delta\varepsilon$ below 250 K. Thus the model provides a theoretical basis for the description of the Debye relaxation in monohydroxy alcohols.

The experimental data[5,6] indicate that τ of Debye relaxation in monohydroxy alcohols satisfies the Vogel–Fulcher–Tammann (VFT) equation at the low temperature, and it approximately satisfies the Arrhenius relation[27,28] in a relatively large range of the high temperature. Although the Debye theory (individual pseudospin orientations in a double potential well, which belongs to the single particle mean-field theory) gives the Arrhenius relation of τ with T, it cannot describe the complicated behavior of $\Delta\varepsilon$ with T as mentioned above. In this study, the Debye relaxation in monohydroxy alcohols is modeled based on the IPCIM and the Glauber dynamics[29] of the pseudospin transition, and the theoretical results are consistent well with the experimental data in a wide temperature range.

For the IPCIM, (1) in the hydrogen-bonded molecular chain, the dipole moment component ($\mu_i^{||}$) of the ith molecule parallel to the chain contour is approximated to the pseudospin, (2) the hydrogen-bonded molecular chains are approximately described as the pseudospin chains with long enough length, and (3) the spatial conformations of the chains are described by the free rotating chains. When the system is in a sufficiently small uniform electrostatic field ($E \to 0$), the Hamiltonian H of the IPCIM is[26]

$$H|_{n\to\infty} = -J\sum_{i=1}^{n-1}\sigma_i\sigma_{i+1} - \mu^{||}E\sum_{i=1}^{n}\sigma_i\cos\alpha_i, \quad (1)$$

where J is the temperature independent constant of the interaction energy between adjacent pseudospins, σ_i expresses the state of the ith pseudospin in the chain, and has two states ($\sigma_i = \pm 1$ ($i = 1,\ldots,n$), and it is appointed that $\sigma_i = 1$ or -1 when the spatial orientation of $\mu_i^{||}$ points to the $(i+1)$th or the

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$(i-1)$th molecule, respectively), $\mu^{||}$ is the amplitude of the molecular dipole moment parallel to the chain contour, and α_i is the angle between $\mu_i^{||}$ and E when $\sigma_i = 1$.

To describe the dielectric relaxation of pseudospins in the IPCIM, we use the Glauber dynamics here, i.e. in addition to the interaction among pseudospins (Eq. (1)), each pseudospin is in a double-potential-well, and the transition probability (w_i) from the initial state (σ_i) to the final one ($-\sigma_i$) is[29]

$$w_i = \frac{1}{2}\nu_0 e^{-U/k_{\rm B}T}\Big[1 - \frac{1}{2}\tanh\Big(\frac{2J}{k_{\rm B}T}\Big) \cdot \sigma_i(\sigma_{i-1} + \sigma_{i+1})\Big], \tag{2}$$

where ν_0 is the vibration frequency in the potential wells, U is the barrier energy between the two potential wells, and $k_{\rm B}$ is the Boltzmann constant.

Based on Eq. (1), the relation between $\Delta\varepsilon$ and T of the IPCIM is gained as[26]

$$\Delta\varepsilon = \frac{N\mu^{||2}}{3\varepsilon_0 k_{\rm B}T}\frac{1+\tanh(J/k_{\rm B}T)\cos\theta}{1-\tanh(J/k_{\rm B}T)\cos\theta}, \tag{3}$$

where θ is the rotation angle in the free rotation chain, N is the molecular number per unit volume, and ε_0 is the dielectric constant of vacuum. To calculate the relaxation time of the IPCIM (Eq. (1)) with the Glauber dynamics (Eq. (2)), let the variation of E with time (t) have the following form

$$E(t) = \begin{cases} E_0, & t < 0, \\ 0, & t \geqslant 0, \end{cases} \tag{4}$$

where E_0 is a constant. Based on Eqs. (1) and (2), for a pseudospin chain with the length of n, the deviation ($\delta_i^n(t)$) of the average value ($\langle\sigma_i\rangle$) of the ith pseudospin from its equilibrium value (1/2), i.e. $\delta_i^n(t) \equiv \langle\sigma_i\rangle - 1/2$ $(i = 1, \ldots, n)$, satisfies the following equation[30–32] for $t > 0$,

$$\frac{\rm d}{{\rm d}t}\begin{bmatrix} \delta_1^n \\ \delta_2^n \\ \vdots \\ \delta_i^n \\ \vdots \\ \vdots \\ \delta_n^n \end{bmatrix} = -\frac{1}{\tau_{\rm w}} M_n \begin{bmatrix} \delta_1^n \\ \delta_2^n \\ \vdots \\ \delta_i^n \\ \vdots \\ \vdots \\ \delta_n^n \end{bmatrix}, \tag{5}$$

where $\tau_{\rm w} = \nu_0^{-1} e^{U/k_{\rm B}T}$, and M_n is the relaxation dynamics matrix of the pseudospins with n lines and n columns. Specifically,

$$M_n = \begin{bmatrix} 1 & u & 0 & & & & \\ v & 1 & v & \cdots & & 0 & \\ 0 & v & 1 & & & & \\ & \vdots & & \vdots & & \vdots & \\ & & & & 1 & v & 0 \\ & 0 & & \cdots & v & 1 & v \\ & & & & 0 & u & 1 \end{bmatrix}, \tag{6}$$

with

$$u = \frac{2}{1+e^{2J/k_{\rm B}T}} - 1,$$
$$v = \frac{1}{1+e^{4J/k_{\rm B}T}} - \frac{1}{2}.$$

The computational results[30] show that matrix M_n has n independent eigenvalues ($\lambda_j^n, j = 1, \ldots, n$, arranged in the ascending order), and it is obtained that

$$\delta_i^n(t) = \sum_{j=1}^{n} c_{i,j}^n e^{-\lambda_j^n t/\tau_{\rm w}}, \tag{7}$$

where $c_{i,j}^n$ $(i = 1, \ldots, n)$ is the ith matrix element corresponding to the reduced eigenvector of λ_j^n that satisfies $\delta_i^n(0) = \sum_{j=1}^{n} c_{i,j}^n$. Equation (7) shows that the coupled relaxation of n pseudospins is equivalent to the relaxation of n independent spatial relaxation modes with a certain relaxation time ($\tau_j^n = \tau_{\rm w}/\lambda_j^n$) and intensity ($\Delta_j^n = \sum_{i=1}^{n} c_{i,j}^n$, $c_{i,j}^n$ denotes the spatial distribution of relaxation intensity in the chain).[33]

Here Δ_1^n of the relaxation mode with the longest relaxation time (i.e., τ_1^n) is the largest among all relaxation modes,[30] and the others ($\Delta_j^n, j = 2, \ldots, n$) can be neglected in comparison with Δ_1^n. Therefore, the relaxation of the whole chain can be described by the first relaxation mode approximately, that is, the relaxation time (τ_n) of the chain can be expressed as

$$\tau_n \approx \tau_{\rm w}/\lambda_1^n. \tag{8}$$

At present, the analytic expression of λ_1^n versus T of M_n has not been obtained. Moreover, the numerical solution of λ_1^n cannot be solved when $n \to \infty$. In this work, by analyzing the evolution tendency of τ_n with finite n and T, the relaxation time (τ) of the chain with infinite length ($n \to \infty$) as a function of T is obtained.

The eigenvalues of M_n matrix are solved by MATLAB, and the results of $\tau_n/\tau_{\rm w}$ versus $J/k_{\rm B}T$ calculated according to Eq. (8) are shown in Fig. 1. It can be seen that: (1) the relationship between $\tau_n/\tau_{\rm w}$ and $J/k_{\rm B}T$ conforms to an Arrhenius relation when $J/k_{\rm B}T$

is small, and crosses over to another Arrhenius relation with the increase of $J/k_{\rm B}T$, presenting a crossover temperature ($T_{\rm co}$) as shown in Fig. 1, (2) as n goes up, $T_{\rm co}$ decreases gradually, i.e. the range satisfied the high temperature Arrhenius relation extends to the low temperature. Moreover, (3) in the high temperature range above $T_{\rm co}$, the same Arrhenius relation is satisfied between $\tau_n/\tau_{\rm w}$ and $J/k_{\rm B}T$ for different n, and by fitting the data, it is gained that

$$\frac{\tau_n}{\tau_{\rm w}} = \frac{1}{2}e^{4J/k_{\rm B}T}. \tag{9}$$

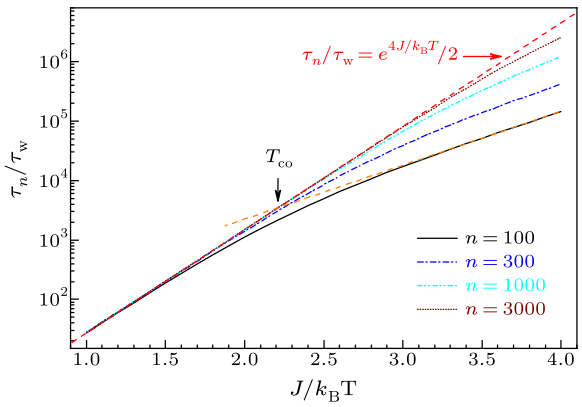

Fig. 1. The value of $\tau_n/\tau_{\rm w}$ versus $J/k_{\rm B}T$ for a series of n.

The results of Eq. (9) are exhibited by the dashed line in Fig. 1, and it could be expected that, when $T \neq 0$, τ of the infinite pseudospin chain is

$$\tau = \frac{\tau_{\rm w}}{2}e^{4J/k_{\rm B}T} = \frac{1}{2\nu_0}e^{(U+4J)/k_{\rm B}T}. \tag{10}$$

Based on the Debye equation,[10] as well as Eqs. (3) and (10), the complex permittivity (ε^*) of the infinite pseudospin chain system is

$$\begin{aligned}\varepsilon^* &= \varepsilon' - i_{\rm c}\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+i_{\rm c}\omega\tau} \\ &= \varepsilon_\infty + \frac{N\mu^{||2}}{3\varepsilon_0 k_{\rm B}T}\frac{1+\tanh(J/k_{\rm B}T)\cos\theta}{1-\tanh(J/k_{\rm B}T)\cos\theta} \\ &\quad\cdot\frac{1}{1+i_{\rm c}\omega\nu_0^{-1}e^{(U+4J)/k_{\rm B}T}/2},\end{aligned} \tag{11}$$

where ε' and ε'' are the real and the imaginary parts of ε^*, ε_∞ is the dielectric constant at the high frequency, $i_{\rm c}$ is the imaginary unit, $i_{\rm c} = \sqrt{-1}$, and ω is the angular frequency of sine alternating external electric field ($\omega = 2\pi f$ and f is the frequency).

For 3,7-dimethyl-1-octanol(3,7D1O), 2-ethyl-1-hexanol(2E1H) and 5-methyl-2-hexanol(5M2H), the comparisons of the present model results (Eqs. (10) and (11)) to the experimental data[6] of τ versus T and ε'' versus f at a series of temperatures are shown in Figs. 2 and 3. We would like to point out that, (1) above 250 K, the molecular chains formed by hydrogen bonds in monohydroxy alcohols will be shortened due to thermal motion, resulting in the deviation from that of infinite long chains, and (2) as can be seen from Fig. 2, there is an obvious deviation from the Arrhenius relation below 180 K (the reasons of the deviation will be discussed later). Therefore, the model results are compared with the experimental data only in the temperature range of 180–250 K. The fitting parameters used are listed in Table 1.

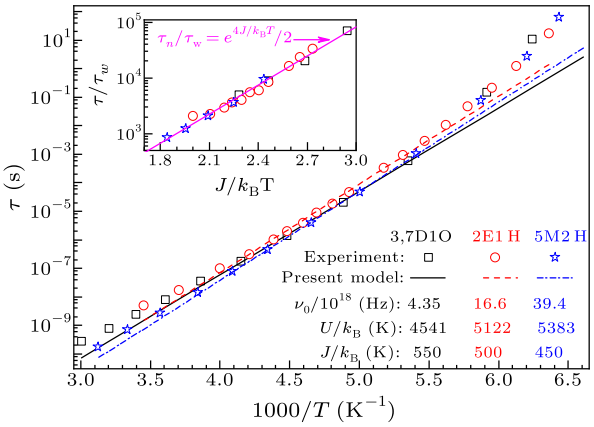

Fig. 2. The value of τ versus T of 3,7D1O, 2E1H and 5M2H obtained from the experiments[6] and the model results.

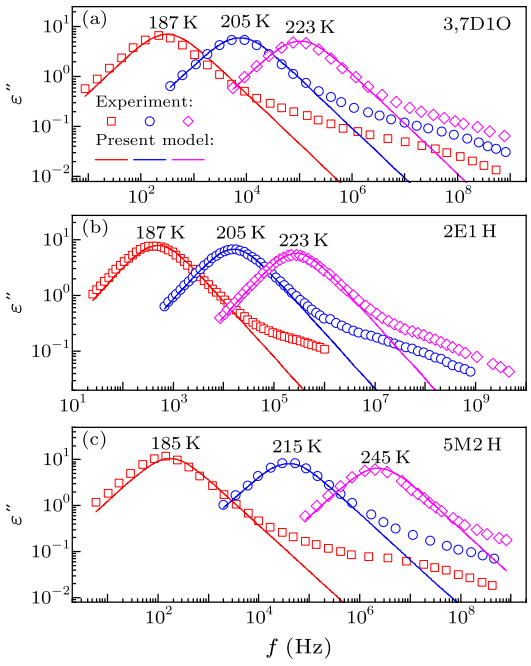

Fig. 3. The value of ε'' versus f of 3,7D1O, 2E1H and 5M2H obtained from the experiments[6] and the model results.

From Figs. 2 and 3, it can be seen that in the range of 180–250 K, the model predictions are in good agreement with the experimental results (in the high frequency range of Fig. 3, the deviations of the experiments from the theory are generally believed to orig-

inate from α relaxation, not belonging to the Debye relaxation). According to the theoretical prediction (Eq. (10)), the change of $\tau/\tau_{\rm w}$ with $J/k_{\rm B}T$ is independent of materials. The reduced experimental τ values ($\tau/\tau_{\rm w}$) with $J/k_{\rm B}T$ of 3,7D1O, 2E1H and 5M2H shown in the inset of Fig. 2 are consistent with the theoretical predictions.

It should be pointed out that only the intra-chain interaction, corresponding to the hydrogen bond in monohydroxy alcohol liquids, are considered in this study, and the van der Waals interaction are neglected between neighboring molecules. The deviation of the experimental data of τ below 180 K from the model results may be due to this neglecting. This is because: (1) at high temperature, the thermal motion energy of the molecules is larger than the van der Waals interaction (much smaller than the hydrogen bond energy), thus the interaction has less influence on the motion of the hydrogen-bonded chains, and the Debye relaxation originates from the nearly individual motion of the chains, leading to the relationship between τ and T being the Arrhenius relation, and (2) at low temperature, the thermal motion energy becomes smaller, and the van der Waals interaction can no longer be neglected, which results in the Debye relaxation stemming from the coupled motion of the chains by the interaction. It could be imagined that the couple will lead to the deviation of the relation between τ and T from the Arrhenius relation, i.e. it satisfies the VFT equation, which is one of the problems that need further theoretical study. In addition, the deviation of τ and ε'' above 250 K from theoretical predictions may originate from the shortening of chain length, being another problem to be studied.

Table 1. Fitting parameters of the model.

Liquid	N	$\mu^{\parallel}$ (C·m)[26]	θ (deg)[26]	J (eV)[26]	U (eV)	ν_0 (Hz)
3,7D1O	3.15×10^{27}	1.29×10^{-30}	20	0.047	0.391	4.35×10^{18}
2E1H	3.86×10^{27}	1.57×10^{-30}	25	0.043	0.441	1.66×10^{19}
5M2H	4.24×10^{27}	2.07×10^{-30}	30	0.039	0.464	3.94×10^{19}

Among the fitting parameters used, $\mu^{\parallel}$, θ and J are taken from Ref. [26] and N is calculated based on the density at room temperature and the molecular weight. Here, we mainly discuss J, U and ν_0. From Table 1, we can see that $U+2J$ is about two times the hydrogen bond energy (about 0.22 eV) in the monohydroxy alcohol liquids, that is, each molecule has two hydrogen bonds approximately, which means that the IPCIM is reasonable to some extent in the range of 180–250 K. The increase of U and decrease of J with carbon atom number decreasing in the molecules indicate that the mean-field interaction part of the single pseudospin double-well becomes stronger, while the orientation correlation interaction part between pseudospins becomes weaker. The value of U is much larger than that of J, which indicates that, under the effect of thermal fluctuations, hydrogen bond energy mainly contributes to the mean field of single molecule, while its contribution to spatial orientation correlation, such as the molecular chain bonding, is very small.

Table 1 also lists that ν_0 increases with carbon atom number decreasing. Moreover, ν_0 gained here is around 10^{19} Hz, much larger than vibration frequency (about 10^{15} Hz) of the general molecular orientation. We consider that the molecular orientation in monohydroxy alcohol liquids mainly comes from the proton (i.e., the nucleus of hydrogen) in the hydroxyl, and it has the quantum effect, resulting in larger ν_0.

In conclusion, we have modeled the Debye relaxation based on the IPCIM and the Glauber dynamics, and the corresponding complex permittivity is obtained. The model results are in good agreement with the experimental data of monohydroxy alcohols of 3,7D1O, 2E1H and 5M2H in the range of 180–250 K. Moreover, in the model parameters, $U+2J$ is nearly two times the hydrogen bond energy, which further states the rationality of the present model. It can be expected that the model will provide an important theoretical basis for the study of Debye relaxation in monohydroxy alcohols below 180 K and above 250 K, and it also plays an important role in understanding hydrogen bonding, supramolecular structures and their effects on liquid properties.

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