

From hydrogen bonding to resonance: A molecular dynamics study of the rose water model in an alternating electric field

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The effects of an alternating electric field on the rose water model were studied. The rose water model is a simple two-dimensional water model consisting of Lennard-Jones disks to which an explicit hydrogen bonding potential has been added. To allow the model to interact with the electric field, partial charges were added to the original model. Changes in the structure, dynamics, and thermodynamics of the water due to fluctuations in the electric field were observed, as the effect of the field on the water depends on the frequency and strength of the electric field as well as on the initial properties of the water, such as the degree of hydrogen bonding. The electric field used is in the frequency and strength range corresponding to the rotational motion of the molecules, so the field affected the system by increasing the rotation of the water molecules. Depending on the frequency of the field, three ranges were observed in which the effects were different. In the low frequency range, the effects of the alternating field were similar to the effects of a constant static electric field, while at high frequencies the field has practically no effect on the water. The frequency range of interest is close to the natural frequency of rotation of the water molecule, where the resonance occurs. We have developed a model that explains both the rotational absorption spectra and the resonance frequency. The model establishes a link between the hydrogen bonding of water molecules and their resonance frequency in electric fields of different strengths.

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I. INTRODUCTION

Water is one of the most abundant molecules in the universe. It was crucial for the development of life on Earth as we know it. Organisms on Earth depend on water because virtually all biochemical reactions occur in water as a solvent, and water is actively involved in some of the reactions. Water is also very important in various industries because it is readily available, a good solvent for many substances, and has other desirable properties that can be utilized. Some of the water properties that make water so useful are anomalous [1], such properties are, for example, the higher density of the liquid state compared to the solid state, which enables the survival of living things in water when it freezes, the high heat capacity, which is useful in industry when it comes to heat transfer, etc. In addition to thermodynamic anomalies, water also exhibits many dynamic [2–7] and also structural anomalies [8–11]. The anomalous properties of water are numerous, but the source of these anomalies lies in the ability of water to form hydrogen bonds. It has been suggested that the structural arrangement of water molecules in a tetrahedral structure may be the reason for many of the anomalous properties [12,13]. There are also other liquids that can form tetrahedral

structures and exhibit similar anomalous behavior to water. Examples of such liquids are: liquid GeO_2 [14], liquid BeF_2 [15,16], liquid silicon [17], and liquid silica [18,19].

Different conditions can have significant effects on the properties of water, which can indirectly affect the properties of the entire aqueous system (e.g., proteins in aqueous solution). Nowadays, we are surrounded by electromagnetic radiation of different wavelengths, both natural and artificial, which can cause potential changes in the system. As far as the electric field is concerned, the static and dynamic electric field have different effects on materials. When the electric field is static, the movement of molecules is generally reduced as their dipole tends to align with the field. The most commonly observed situation in which water molecules tend to align with a static electric field is in the vicinity of polar molecules and ions. Some studies have shown that a static electric field affects the freezing point of water [20–23], where in most cases the electric field causes water to freeze under conditions where it is normally liquid. Freezing is related to the alignment of the dipoles with the external field, which reduces the mobility of the molecules and causes them to freeze. However, the electric field required for freezing was lower than that theoretically predicted for the alignment of the dipoles. A static electric field affects all phases of water, but the effects are most noticeable at the solid-solid and solid-liquid phase transitions [24,25]. The electric field mainly stabilizes the solid phases at the expense of the liquid phase, and the transitions between the solid phases also change. Molecular dynamics (MD) simulations have also shown that an external static electric field reduces the motion of the molecules and freezes them [26]. The response of the system to a static

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electric field depends on the strength of the field. If the field is relatively weak, then the dielectric response is linear until the effect of dielectric saturation becomes significant [27]. Under the conditions where water is normally liquid, a static electric field increases the ordering of water and promotes hydrogen bonding (HB) [28], and also decreases the diffusion of water [29]. *Ab initio* molecular dynamics has shown that the field significantly affects the HB length and molecular orientation and in particular reduces the rotational dynamics, but high electric fields are also able to dissociate the water molecules [30,31].

However, dynamic electric field has different effects on water, which also depends on the frequency of the field. When the electric field oscillates, the dipoles of the water molecules try to follow the field oscillations and align themselves with the direction of the field [29]. Nonequilibrium molecular dynamics simulations have shown that the percentage of molecules that align with the field during the simulation depends on both the temperature and the frequency of the electric field. In general, a higher temperature leads to a higher degree of alignment, as the molecules are more mobile and therefore align more easily with the field. However, increasing field frequency leads to a weaker alignment of the dipoles with the electric field, as the molecules have less time to rotate when the field oscillates [29]. The rotational, librational and translational motion is enhanced by the oscillating electric field, resulting in reduced hydrogen bonding [32,33] and an increased diffusion coefficient of the molecules [29,34,35]. The dynamic properties such as diffusion, the breaking of hydrogen bonds and switching of hydrogen-bonding partners are accelerated with increasing strength of the electric field [36]. In the frequency range of microwaves, the electric field causes the water to heat up, as the energy of the electric field is converted into kinetic and intermolecular energy of the water [37,38]. This type of microwave heating reduces the structuring of the water and the hydrogen bonding [37]. When the frequency of the external electric field matches some of the natural rotational frequencies of the molecules in the system, the absorption of the field increases due to resonance [39]. In this way, rotational spectra of molecules can be measured, which can be used to characterize molecules [40–42]. There are also computational studies in which the rotational spectra have been reproduced with simulations [43,44]. Due to the usefulness of rotational spectroscopy, many more complex techniques such as nonlinear and 2D rotational spectroscopy have been developed [45–47]. Such advanced techniques can also be used to study many-body interactions in water [48].

Water is probably one of the most studied substances, as it has been studied both experimentally and theoretically for a long time. As far as theoretical studies are concerned, the study of water (or any other substance) requires the development of a mathematical model that describes the molecule. The models that have been developed for water are quite diverse, as different models have been developed depending on the properties that researchers were interested in and the environments in which they studied water. The classical models were the first to be developed. The Bernal-Fowler model [49] was the first realistic water model. In this model, water was described with point charges and a repulsion-dispersion term. With the development of computer technology and simula-

tions, further models were developed. There are two groups of models that are widely used in computer simulations, namely TIP models [50–55] and SPC models [56,57]. These models have been used for a long time and are still very common today, especially when water plays a role as a solvent in the system. These models are relatively simple, so that a large number of water molecules can be used as solvents in simulations. These models have a similar design as they all use the Lennard-Jones (LJ) potential with additional point charges. Today, computational resources as well as various algorithms such as machine learning and artificial intelligence are so powerful that even more accurate and complex models can be used. The thermodynamic properties of water can even be calculated using *ab initio* quantum mechanical calculations [58].

Despite the great computational advances that allow us to use ever more complex models, there is also an interest in simple models that can be simplified to the point where they lose atomistic details but still capture the fundamental properties of water as a molecule. Such simple models are Mercedes-Benz [59,60] and the rose water model [61]. Both models are two-dimensional models in which water is modelled with a Lennard-Jones potential and an explicit hydrogen bonding potential. The advantage of such models is that they are ideal for the development of various theories and methods. The reason for this is that they are very simple and therefore the effects of changes at the micro level can be more easily traced to the macro level. In addition, the models are easy to visualise due to their dimensionality. In this paper, we have used the rose water model. The model has been shown to reproduce crucial properties of water and has already been studied using various methods, from simulations [62–65] to statistical-mechanical theories such as integral equation theory and thermodynamic perturbation theory [62,66–69].

An interesting property that is directly related to the effects of the electric field on water is the dielectric constant. The dielectric constant describes how the material—in our case water—attenuates the electric field compared to a vacuum. A large dielectric constant is considered one of the anomalous properties of water and is related to additional correlations of the dipoles of water through hydrogen bonds. The static dielectric constant of water ranges from almost 200 in ice [70] to practically 1.0 in high-temperature low-pressure steam [71]. The most commonly studied and measured dielectric constant is of course at room temperature and pressure, where it is about 78. It would be desirable for the popular water models commonly used in simulations to reproduce this value, at least under normal conditions, but the success of the models is quite limited. The dielectric constant of the SPC model under normal conditions is about 82 [72] and about 70 for the SPC/E model [73]. For the models from the TIP family, the dielectric constants are as follows: TIP3P-94, TIP4P-50, TIP4P/2005-58, TIP5P-91 [74]. The TIP4P and TIP4P/2005 models have a dielectric constant that is quite far from the experimental dielectric constant, while the other models mentioned are in the range of the experimental dielectric constant. The reason for the poor result is the charge distribution, which suggests that placing the charge on the oxygen instead of the dummy atom should give a better dielectric constant. It has been shown that an increased dipole moment increases the

dielectric constant, while an increased quadrupole moment decreases it [75]. The SCP and TIP models have problems in describing the dielectric constant of ice because they predict it too low [24]. The main problem is that the dipole moment of the models in the condensed phase is about 2.3 D, while it should be about 3 D according to first principles. The problem can be solved by scaling the dipole moment of the nonpolarizable model [24]. In simulations, the static dielectric constant can be calculated using different methods [76], with two methods being the most commonly used [77]. In one, the dielectric constant is calculated from the fluctuations of the total dipole moment in the system without an external electric field [78] and in the second, the constant is calculated from the alignment of the total dipole moment with the external electric field [79]. In addition to the static dielectric constant, the complex dielectric constant (permittivity) can also be determined, which is frequency-dependent [80]. The complex dielectric constant can be divided into a real and an imaginary part. In the microwave range, which is the focus of this study, the real part of the dielectric constant of water at low frequencies (about 0.1 GHz) is about 78 under normal conditions. With increasing frequency, the real constant remains practically constant. At frequencies close to 10 GHz, it then suddenly drops to values close to 1 and remains there. The imaginary dielectric constant is practically zero at low frequencies. At frequencies at which the real constant suddenly drops, the imaginary constant reaches a maximum and then falls back to a value close to zero [81]. The maximum of the imaginary dielectric constant corresponds to the Debye relaxation, which has been studied in detail using both experimental and theoretical methods [82–85].

In this work, we investigated how a dynamic electric field with different frequencies and strengths affects the properties of rose water model. The simplicity of the model allowed us to clearly explain the effect of the electric field on the properties of the model. It also allowed us to establish a clear link between hydrogen bonding and resonance. The work is a continuation of our earlier work in which we investigated the effects of a static electric field on the properties of rose water model [65]. Here we first investigated how different structural, thermodynamic and dynamic properties of water are altered by the effects of a dynamic electric field. In the second part of the study, we investigated the resonance effect of the electric field on water molecules. To explain the effect of the electric field on the resonance frequency, we developed a simple model that links the rotational spectra of water to hydrogen bonding. In this way, we have explained the absorption spectra and related the effects of the electric field and hydrogen bonding to the resonance frequency.

II. MODEL AND METHOD

A. Model

Rose water model was used to model water in this study [61]. Two-dimensional LJ disks are used to represent the water molecules in this model. The disks are also equipped with a HB potential, which is used for the formation of hydrogen bonds between the molecules. The total pair interaction energy between two molecules is a sum of the LJ potential term

and the HB potential term:

$$U(\vec{X}_i, \vec{X}_j)_{\text{rose}} = U_{\text{LJ}}(r_{ij}) + U_{\text{HB}}(\vec{X}_i, \vec{X}_j), \quad (1)$$

where r_{ij} is the distance between the molecules i and j , $\vec{X}_i$ and $\vec{X}_j$ are vectors of the positions and orientations of the molecules i and j . The LJ potential term is calculated as usual:

$$U_{\text{LJ}}(r_{ij}) = 4\epsilon_{\text{LJ}} \left(\left(\frac{\sigma_{\text{LJ}}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{\text{LJ}}}{r_{ij}} \right)^6 \right). \quad (2)$$

The energy contribution of hydrogen bonds is considered a little differently than usual, as there is not just one energy term for a pair, but two independent energy contributions for each molecule in a pair:

$$U_{\text{HB}}(\vec{X}_i, \vec{X}_j) = U_{\text{HB}}(\vec{r}_{ij}) + U_{\text{HB}}(\vec{r}_{ji}). \quad (3)$$

Since the contribution of each molecule to HB energy is independent, it is possible for one molecule to form a hydrogen bond while another does not. In other words, this means that while the molecules are in the hydrogen bond distance, one molecule is favourably oriented to form a hydrogen bond while the other does not. This leads to a kind of hydrogen “half-bond.” These “half-bonds” can form in some cases (e.g., when a water molecule is trapped in a hexagonal vacancy in an ice-like structure), but if there is a possibility of a full hydrogen bond forming, then the full bond will virtually always form instead of the half-bond.

The HB contribution of each molecule is a product of two terms, one of which ($s(r_{ij})$) depends on the distance between the molecules and the other ($U(\theta_{ij})$) on the orientation of the molecule:

$$U_{\text{HB}}(\vec{r}_{ij}) = \frac{\epsilon_{\text{HB}}}{2} * s(r_{ij}) * U(\theta_{ij}), \quad (4)$$

where $\vec{r}_{ij}$ is a vector between molecules i and j oriented in the body frame of molecule i , r_{ij} is the length of the vector and θ_{ij} is the orientation angle of the vector in the body frame of molecule i . ϵ_{HB} is an energy parameter indicating the strength of the hydrogen bond. Since there are two contributions to the total HB interaction, the parameter is divided by 2 so that the total HB interaction is normalized to 1 in reduced units. $U(\theta_{ij})$ governs the energy contribution depending on the orientation of the molecule i with respect to the molecule j (or the line connecting the centres of the molecules). Or from the other perspective, it depends on the position of the molecule j with respect to the body frame of the molecule i . To model the orientation dependence of the potential, a combination of sine functions belonging to the rose functions is used, more precisely, a three-petal rose function is used here for the potential:

$$U(\theta_{ij}) = a_2 \sin^2(3\theta_{ij}) + a_1 \sin(3\theta_{ij}). \quad (5)$$

Here, a_1 and a_2 are coefficients that determine the shape of the orientation-dependent potential by adjusting the contribution of the two terms. The above equation is written in polar coordinates, while in MD simulations it is easier to use it in Cartesian coordinates, where the equation has the

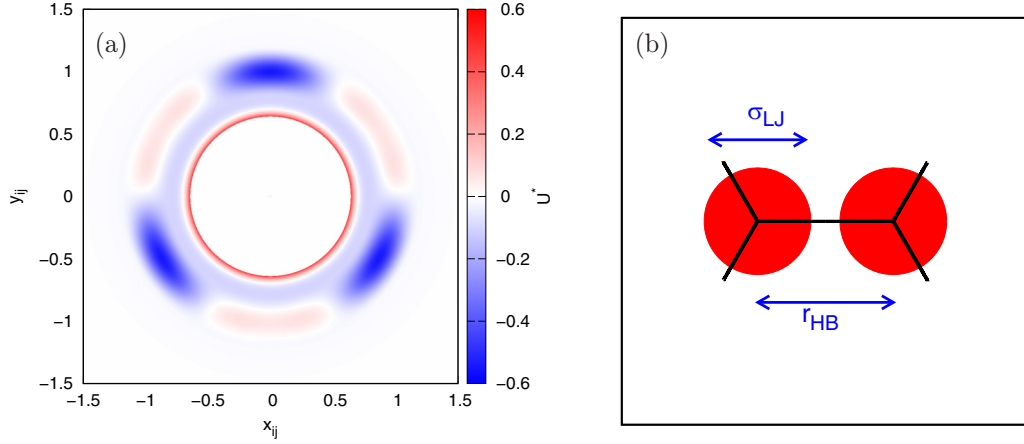


FIG. 1. Potential energy surface of rose water model (a) and schematic representation of two rose model particles forming a hydrogen bond (b).

following form:

$$U_{\text{HB}}(\vec{r}_{ij}) = \frac{\epsilon_{\text{HB}}}{2} s(r_{ij}) \left(a_2 \frac{(3x_{ij}^2 y_{ij} - y_{ij}^3)^2}{r_{ij}^6} + a_1 \frac{3x_{ij}^2 y_{ij} - y_{ij}^3}{r_{ij}^3} \right), \quad (6)$$

where $r_{ij} = \sqrt{x_{ij}^2 + y_{ij}^2}$, while x_{ij} and y_{ij} are Cartesian coordinates of the molecule j in the body frame of the molecule i .

The other term in Eq. (4), which governs the length of the hydrogen bonds, is $s(r_{ij})$, which uses double-sided switching function:

$$s(r_{ij}) = \begin{cases} 0, & r_{ij} < r_l, \\ \frac{(r_l + 2r_{ij} - 3r_{\text{HB}})(r_l - r_{ij})^2}{(r_l - r_{\text{HB}})^3}, & r_l \leq r_{ij} < r_{\text{HB}}, \\ \frac{(r_u + 2r_{ij} - 3r_{\text{HB}})(r_u - r_{ij})^2}{(r_u - r_{\text{HB}})^3}, & r_{\text{HB}} \leq r_{ij} < r_u, \\ 0, & r_u \leq r_{ij}, \end{cases}$$

where r_{HB} is the ideal length of the hydrogen bond, r_l and r_u are the lower and upper limits of the HB length. The switching function is symmetrical about the ideal HB length, since $|r_{\text{HB}} - r_l| = |r_{\text{HB}} - r_u| = r_{\text{FWHM}}$, where r_{FWHM} is the “full width at half maximum” of the peak formed by the function as a function of distance.

The parameters of the rose model were determined in such a way that the properties of the rose model are similar to the properties of the Mercedes-Benz water model [59,60]. The parameters used are the following: $\epsilon_{\text{LJ}} = 0.1$, $\sigma_{\text{LJ}} = 0.7$, $\epsilon_{\text{HB}} = 1$, $r_{\text{HB}} = 1$, $r_{\text{FWHM}} = 0.35$, $a_1 = 0.7$, and $a_2 = -0.3$. The parametrization used here is the same as in our previous article on rose water model in the static electric field [65].

The molecules are also assigned partial charges so that they can interact with the external electric field. The negative charge (with an amplitude of 1.0) is added to the center of the molecule, while the positive charge with the same amplitude is added to one of the HB arms (orientations of maximal HB energy) at a distance of $0.165 r_{\text{HB}}$ from the center of the molecule. The charges on the molecules interact only with the external electric field, because the electrostatic interaction between the molecules, which leads to the formation of hy-

drogen bonds, has already been taken into account in the HB potential (Fig. 1).

B. Molecular dynamics simulations

MD simulations were carried out to calculate the properties of the rose water model. In-house developed MD code [86] was used to carry out the simulations. The code was originally written for the MB model, but due to the similarity between the MB and rose models, it was easily adapted to rose water model. All simulations were performed in the NpT ensemble, also using periodic boundary conditions with minimum image convention to mimic a macroscopic system.

The Verlet algorithm [87] was used to integrate the trajectory velocity, with the size of the integration step set to 0.001 ($t^* = t \sqrt{\frac{\epsilon_{\text{HB}}}{mr_{\text{HB}}^2}}$). The simulations were carried out in two parts. First, the system was equilibrated, for which 100 000 steps were used. Then the sampling phase was performed, which consisted of 20 series, each series being 100 000 steps long. In the sampling phase, all data on the thermodynamic, dynamic and structural properties were collected. At each time point, there were 200 water molecules in the system, which were randomly introduced into the system at the beginning of the simulation without overlapping.

Different thermostats and barostats were used in the study. Initially, we used combinations of a simple velocity scaling with a Berendsen barostat [88] and a stochastic velocity rescaling method [89] with a stochastic cell rescaling approach [90]. Both combinations of thermostat and barostat were relatively successful at low electric field strength and low frequencies. However, at higher frequencies and field strengths, the above-mentioned thermostats and barostats did not work well. Due to the relatively large and sudden forces created by the fluctuation of the electric field, in some cases the system simply froze. This happened because the electric field accelerated the molecule and caused a sudden rise in temperature, which was then drastically reduced by the thermostat, causing the molecule to freeze. In some cases, the system was so unstable that it exploded.

The combination of thermostat and barostat that led to physically meaningful results was the Langevin thermostat with MC barostat [91]. The MC barostat was used in a standard way. At every step, the change in volume was attempted and accepted according to appropriate probability. In the Langevin thermostat, another term representing friction is added to the equations of motion, together with the term describing the random force on a particle

$$m_i \frac{\partial^2 \mathbf{r}_i}{\partial t^2} = \mathbf{F}_i - \gamma m_i \frac{\partial \mathbf{r}_i}{\partial t} + \mathbf{R}_i, \quad (7)$$

where $\mathbf{r}_i$ is the position of the particle i , m_i is the mass, and $\mathbf{F}_i$ is the force of the other particles on the particle i . t is the time, γ is the friction constant, and $\mathbf{R}_i$ is the random force on the particle i . The random force represents the coupling with the heat bath, where $\mathbf{R}_i$ is taken from the Gaussian distribution with mean 0 and variance $2\gamma m_i k_B T$. The Langevin thermostat was implemented by adding the terms for the friction and the random force to the expression for the velocity in the integration algorithm:

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t + \Delta t/2) + \frac{\mathbf{F}(t + \Delta t)}{2m} \Delta t - \gamma \mathbf{v}_i(t + \Delta t/2) \Delta t + \sqrt{\frac{2\gamma k_B T}{m_i}} \mathbf{R}_i \sqrt{\Delta t}, \quad (8)$$

where $\mathbf{R}_i$ is vector from normal distribution.

The friction constant in the Langevin thermostat was set to 1.0 and in the MC barostat the maximum change in box size was 0.3. To verify that the chosen combination of thermostat and barostat provides correct results and does not generate artefacts, we compared the thermodynamic properties calculated with MD simulations with the properties determined with MC simulations. The results of the two methods are in agreement, taking into account the errors of the calculations. The figures showing the comparison of the results of the two methods can be found in the Supplemental Material [92]. Standard relations were used to calculate the thermodynamic, dynamic, and structural properties.

The electric field was applied to the system as a sine function $E_t = E \sin(\omega t)$, where E is the strength (amplitude) of the electric field, ω is the frequency of the field and t is the time. The electric susceptibility was calculated using the method that uses the alignment of the total dipole of the system with the external field [78]. Since the electric field is alternating, the version of the method with Fourier transform was used, in which the alignment between the oscillation of the external field and the total dipole is calculated, also taking into account the phase lag between them. The equation used to calculate the dielectric constant is as follows:

$$\epsilon(\omega) = 1 + \frac{M_z(\omega)}{\epsilon_0 V E(\omega)} = 1 + \frac{\chi(\omega) \epsilon_0}{\epsilon_0}, \quad (9)$$

where ϵ_0 is the electric permittivity of the vacuum, V is the volume of the system, $M_z(\omega)$ is the complex Fourier transform of the total dipole moment of the system as a function of time, and $E(\omega)$ is the complex Fourier transform of the electric field as a function of time. To perform the calculations in reduced units, we have multiplied the susceptibility, which contains essentially the same information as the dielectric constant, by

the permittivity of the vacuum. The dielectric constant in SI units could be calculated from the susceptibility for a given case if the specific energy and length of HB were known/used

C. Resonance model

To explain the resonance response of our water model in the electric field, we have developed a simple model that explains the absorption of the electric field at different frequencies. There are two different regimes of molecular rotation that depend on the strength of the electric field. Both regimes can be approximated by the analogy of a simple harmonic oscillator, where the natural angular frequency of the oscillator is $\omega = \sqrt{k/m}$, where k is the spring constant and m is the mass of the oscillator. At low electric field strength, the electric field does not significantly disturb the hydrogen bonds, but merely amplifies the rotational motion of the molecules, which is already present in the system without an electric field. Using the approximation of a harmonic oscillator, the natural frequency of librations (rotational oscillations) of the molecules is

$$\omega_{\text{HB}} = \sqrt{\frac{k_i}{I}} = \sqrt{\frac{\langle n_{\text{HB}} \rangle k}{I}}, \quad (10)$$

where k_i is the constant of the rotational rigidity of the molecule i due to its bonding to the neighboring molecules, I is the moment of inertia of the molecule, which for our model is $3 * 0.1 * 0.35^2$, k is the rotational rigidity constant of a hydrogen bond, and $\langle n_{\text{HB}} \rangle$ is the average number of hydrogen bonds per molecule.

However, when the electric field is strong, the HB network collapses due to the increased rotational motion of the molecules, so that the molecules behave like free dipoles in the electric field. The natural rotational frequency of the rose water model in a strong electric field is therefore:

$$\omega_E = \sqrt{\frac{C * p * E}{I}}, \quad (11)$$

where $p = q * l = 1 * 0.165$ is the electric dipole moment of the molecule, E is the strength of the electric field and C is the empirical scaling constant, which we have determined to be 2.9. More information and the figure (Fig. S1) that shows how constant C can be determined can be found in the Supplemental Material [92].

The two equations described above are good approximations for the resonant frequency of the rose water model in weak and strong alternating electric fields. However, in a moderate electric field, where the energy of the electric field is of the order of the hydrogen bond energy, there is a competition between the two rotational regimes, which is why the equations must be coupled together.

To explain the absorption of the electric field and the resonance reaction of the water, the model for absorption spectra was also developed. The model assumes two main populations of water molecules in the system, namely the hydrogen bonded molecules and the nonbonded molecules. For bonded molecules we assume that their natural frequency is ω_{HB} and for nonbonded molecules we assume that the natural frequency is ω_E . As the electric field approaches these two frequencies, the intensity of the absorption of the electric field

increases, which is reflected in an increase in kinetic energy (and temperature). Therefore, we used the Gaussian function to model the distribution of the absorption intensity around the resonance frequency:

$$G_i(\omega) = \frac{1}{\sigma_i \sqrt{2\pi}} \exp\left(-\frac{(\omega - \omega_i)^2}{2\sigma_i^2}\right), \quad (12)$$

where ω_i is the natural frequency of the bound or nonbonded population (ω_{HB} and ω_E) and σ_i^2 is the variance of the absorption intensity distribution around the resonant frequency. We measured the absorption of the electric field by the increase in the temperature of the system, which was calculated from the kinetic energy. The increase in temperature is therefore proportional to the square of the electric field frequency ω , since the kinetic rotational energy of the molecules in resonance is $I\omega^2/2$, and the intensity of the absorption is also proportional to the square of the electric field E^2 . The intensity of the energy absorption by the individual molecule populations is also proportional to the number of molecules in each population. The saturation effect of the electric field

has also included in the model, since the rotational energy of the molecules cannot be increased indefinitely by the absorption of the electric field. For example, if we consider an ideal case in which the molecules are in the gas phase, then the absorption of the electric field increases with the square of the electric field strength and more and more molecules in resonance rotate with the frequency of the electric field. If all molecules in the system rotate with the frequency of the electric field, then the increasing strength of the electric field no longer increases the intensity of the field absorption. Therefore, the simple saturation equation was also included in the model:

$$i_i = \frac{i_{i,0}}{1 + (E/E_{i,\text{sat}})^2}, \quad (13)$$

where i_i is the partial absorption intensity of each population (i_{HB} and i_E), $i_{i,0}$ is the absorption intensity without saturation effect and $E_{i,\text{sat}}$ is the strength of the electric field at the saturation point of each population. Combining everything together gives the following equation for the absorption intensity:

$$A(\omega) = A_{\text{ef}} E^2 \left(\frac{\omega_E^2}{1 + (E/E_{E,\text{sat}})^2} x_0 G_E(\omega) + \frac{\omega_{\text{HB}}^2}{1 + (E/E_{\text{HB},\text{sat}})^2} (1 - x_0) G_{\text{HB}}(\omega) \right), \quad (14)$$

where A_{ef} is the effective absorption at each frequency and x_0 is the fraction of nonbonded molecules in the system.

The parameters A_{ef} , k , σ_{HB}^2 , and σ_E^2 were obtained by fitting the predicted spectra to the “measured” spectra (calculated temperature minus target temperature), while $E_{i,\text{sat}}$ was obtained from the changes in the shape of the measured spectra with increasing electric field strength. The saturation point was determined as the electric field strength at which the maximum of T_c^*/E^{*2} begins to decrease with increasing electric field strength. The decrease can be seen in Fig. S2 [92]. Here we used $E_{\text{HB},\text{sat}} = 1.0$ and $E_{E,\text{sat}} = 15.0$. The parameter k , which describes the stiffness of a hydrogen bond, was 4.0 in most cases, while the parameters A_{ef} , σ_{HB}^2 and σ_E^2 were different depending on the electric field frequency. The stiffness parameter describes the stiffness of the harmonic potential used to approximate the hydrogen bonds that hold the molecule in place. The parameter k was calculated by applying Eq. (10) to the data at low electric field strength the Fig. S1 [92] showing this can be found in the Supplemental Material [92]). The standard deviations of the populations do not contain information that was further used in the analysis of the resonance effect, so not much attention was paid to them. Nevertheless, in the Supplemental Material [92] you will find figures (Fig. S3) showing how the standard deviations change with the electric field strength. Further information on how the parameters were determined can be found in the Supplemental Material [92] together with the corresponding figures. The total resonant frequency was determined as the maximum of $A(\omega)$.

We also developed a simplified model for the resonant frequency of the system, where it is not necessary to calculate a whole spectrum of absorption. The simplified resonant frequency model predicts only the total resonant frequency.

Again, we assume two populations of bound and nonbonded molecules, where the natural rotational frequencies of the populations are again calculated by Eqs. (10) and (11). The intensity of the absorption is again proportional to the square of the electric field strength and the square of the resonance frequency of each population. The saturation effect of the electric field is again taken into account by Eq. (13). The model equation for the resonant frequency therefore has the following form:

$$\omega_r = g_E * \omega_E + g_{\text{HB}} * \omega_{\text{HB}}, \quad (15)$$

where g_E and g_{HB} are sigmoid switching functions:

$$g_E = \frac{1}{1 + \exp\left(-b \frac{i_E - i_{\text{HB}}}{i_E + i_{\text{HB}}}\right)}, \quad (16)$$

$$g_{\text{HB}} = \frac{1}{1 + \exp\left(-b \frac{i_{\text{HB}} - i_E}{i_E + i_{\text{HB}}}\right)}, \quad (17)$$

where b is a high number that makes the change virtually instantaneous (we used 200), and i_{HB} and i_E are partial intensities of the population's electric field absorption, calculated as

$$i_{\text{HB}} = \frac{\omega_{\text{HB}}^2 (1 - x_0) E^2}{1 + (E/E_{\text{HB},\text{sat}})^2}, \quad (18)$$

$$i_E = \frac{\omega_E^2 x_0 E^2}{1 + (E/E_{E,\text{sat}})^2}. \quad (19)$$

III. RESULTS AND DISCUSSION

All displayed results are expressed in reduced units. For normalization, the HB energy parameter ϵ_{HB} is used as the energy unit ($A^* = \frac{A}{|\epsilon_{\text{HB}}|}$, $T^* = \frac{k_B T}{|\epsilon_{\text{HB}}|}$), the characteristic length of the hydrogen bond r_{HB} is used to normalize the distances

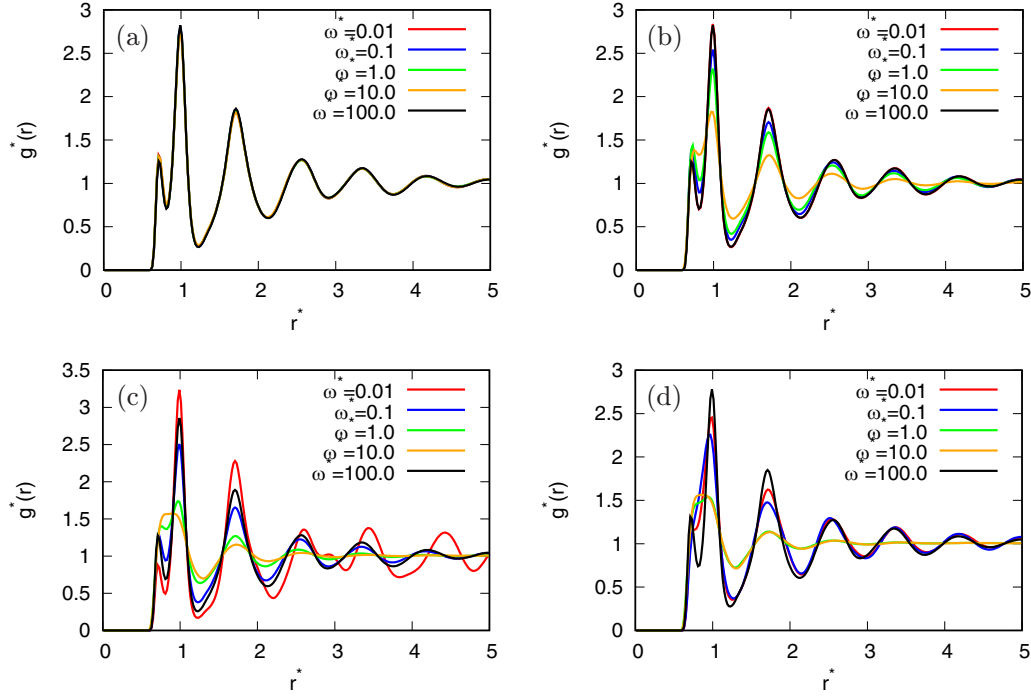


FIG. 2. Radial distribution function at different electric field frequencies and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50. Temperature is 0.15. Errors are in the size range of line width.

($r^* = \frac{r}{r_{\text{HB}}}$). The pressure in reduced units is defined as $p^* = \frac{p r_{\text{HB}}^2}{|\epsilon_{\text{HB}}|}$.

A. Structural properties

Let us begin by analyzing the effect of the alternating electric field by examining how the field affects the structural properties of the water modelled with rose water model. Figures 2(a) and 2(b) shows the radial distribution function (RDF) between water molecules at different electric field amplitudes and frequencies. The peaks in the RDF correspond to different typical structural patterns found in water. The first peak represents two molecules in direct LJ contact, the second peak represents two molecules connected via a direct hydrogen bond and the third peak represents two molecules connected to the third molecule via HB. Further peaks correspond to higher order structures. At a temperature of 0.15 (just above the melting point) and a low field strength of 1.0 [Fig. 2(a)] there is almost no change in the RDF regardless the frequency of the electric field. At a field strength of 5.0 [Fig. 2(a)], however, there is a frequency-dependent effect of the electric field on the RDF. At low frequencies the RDF hardly changes, but at frequency 0.1 the first peak increases, while the second and further peaks decrease. This indicates that the electric field reduces the ordering in the system caused by hydrogen bonding and at the same time increases the proportion of molecules in LJ contact. At a frequency of 10.0, a similar effect occurs, but to a greater extent, as the peaks corresponding to the hydrogen bonds decrease even more. At a high frequency of 100.0, the electric field loses its effect on RDF. If the strength of the electric field is 10.0 [Fig. 2(c)], then the effect of the electric field on the RDF is similar to that of the lower fields, but even

more pronounced. Here too, the electric field with frequencies 1.0 and 10.0 reduces the order in the system, while the high-frequency field has practically no effect. However, a low-frequency field here affects the RDF in such a way that it increases the peak corresponding to the hydrogen bond, which means that the field promotes the formation of hydrogen bonds. A strong electric field has a slightly different effect on the structure of water, as shown in Fig. 2(d), where the RDF is shown in an electric field with an amplitude of 50.0. The effect at high frequencies is the same as before, where there is virtually no change in the RDF. Similar to lower fields, the medium frequency field disturbs the hydrogen bonding of the water molecules, with this disturbance increasing with field strength. However, there is a difference in the effect of the low frequency field as its strength is increased. At a frequency of 0.01 and a field strength of 50, the field reduces the order of the water in the system. The effect of the field on the system is similar to that of a strong static electric field, in which the dipoles of the molecule align themselves with the direction of the electric field and thus break the structure of the hydrogen bonds.

At a temperature of 0.20 (Fig. 3), the effects of the electric field on RDF are similar to those at the lower temperature. This means that the moderate frequency field disrupts the structure and the high frequency field simply passes through it. The only major difference is that at a frequency of 0.01 and a field strength of 10.0, the structuring does not increase when a field is applied, as was the case at a temperature of 0.15. The likely reason for this difference is that in both cases the electric field immobilizes the molecules a little, but at temperature 0.15 the system is so close to the freezing point that the field reduces the motion of the molecules just enough to freeze them, whereas at temperature 0.20 the

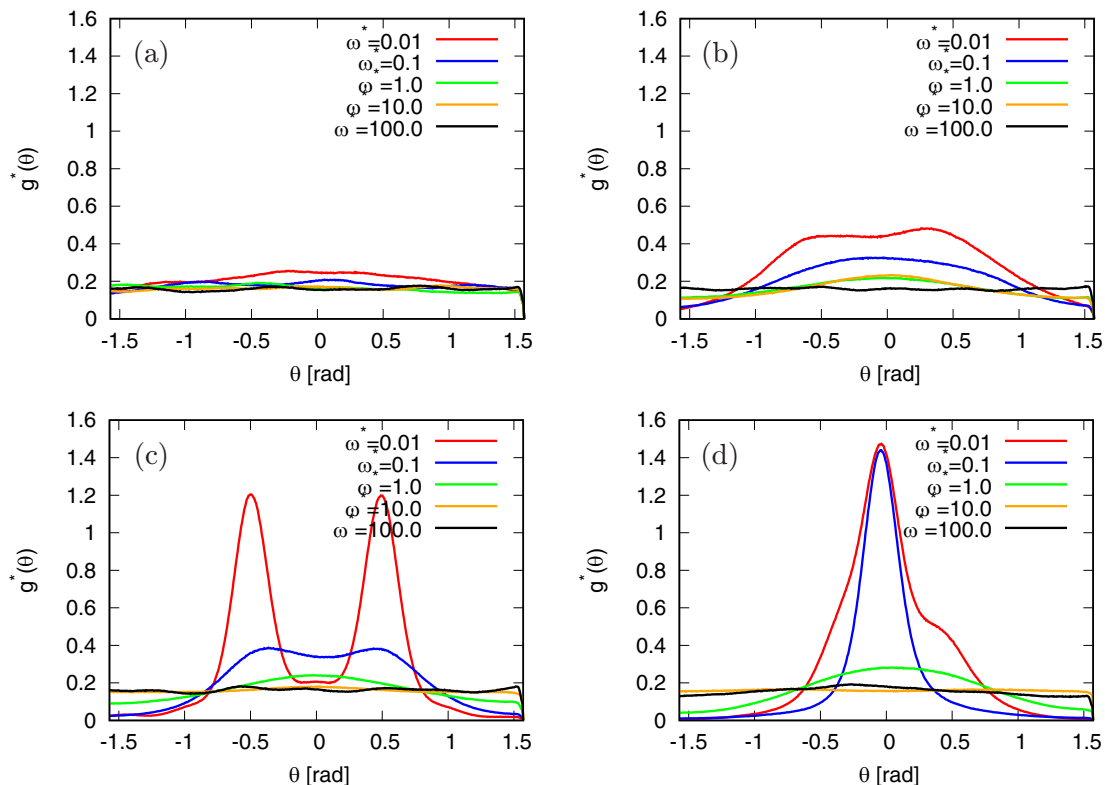


FIG. 3. Angular distribution function at different electric field frequencies and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50. Temperature is 0.15. Errors are in the size range of line width.

thermal motion is large enough that the effect of the field is not so visible.

Angular distribution functions were also calculated. Figures 3(a) and 3(b) shows angular distribution functions at different electric field frequencies and amplitudes at temperatures of 0.15 and 0.20. The angle on the figures represents the angle between the dipole and the direction of the electric field. At a temperature of 0.15 and an electric field strength of 1.0 [Fig. 3(a)], the electric field has a minimal effect on the orientation of the molecules, which is to be expected since it also has a minimal effect on the RDF. The function appears to be more or less uniform across the angle. However, at the lowest frequency shown, there is a broad maximum around angle zero, suggesting that there is a small tendency for dipoles to orient in the direction of the electric field, but due to the low field strength, this orientation is limited by the structuring of the water molecules. When the strength of the electric field is 5.0, the orientation of the dipoles in the direction of the electric field is more pronounced. At low frequencies, the peak is highest around the zero angle and as the frequency increases, the height of the peak decreases. This trend of decreasing peak height with increasing frequency also occurs at stronger fields (10.0 and 50.0). In addition, the peaks at low frequencies become narrower as the strength of the electric field increases, because the stronger the field, the easier it is to force the molecules into a certain orientation. At a field strength of 10.0, the peak splits around the zero point. This splitting occurs under the same conditions as the freezing of RDF that we discussed above. Under these conditions, the electric field restricts the movement of the molecules to a

certain extent. However, the strength of the electric field is still so low that the strength of hydrogen bonding predominates, i.e., the field actually enhances the formation of hydrogen bonds as the molecules approximately align with it while still adopting the preferred orientation that allows hydrogen bonding. In the presence of a strong electric field [Fig. 3(d)], the low-frequency field causes the majority of molecules to align with the electric field, with the alignment with the field being so extreme that a hydrogen bonding network can no longer be formed. At moderate frequencies there is some alignment to the field, but the peak value of the radial distribution function is much lower than at low frequencies. This is because the molecules rotate according to the fluctuations of the electric field. However, there is no preferential alignment at high frequencies either, but here the reason is that the field simply does not affect the molecules as it fluctuates too quickly.

At a temperature of 0.20 (Fig. 4), the angular distribution functions are influenced by the electric field in a similar way as at lower temperatures. The difference to lower temperatures is that the structure of the water at temperature 0.20 is already less ordered, so we do not observe such a splitting of the peak around angle zero as we saw at temperature 0.15. Here, increasing frequency lowers the height of the peak at angle zero, while increasing field strength increases the height of the peak and reduces its width.

The statistics of the hydrogen bonding were also examined during the simulations. The proportion of molecules with a different number of hydrogen bonds was calculated. The interaction between two molecules was considered as hydrogen bond if the energy contribution of the hydrogen bonding

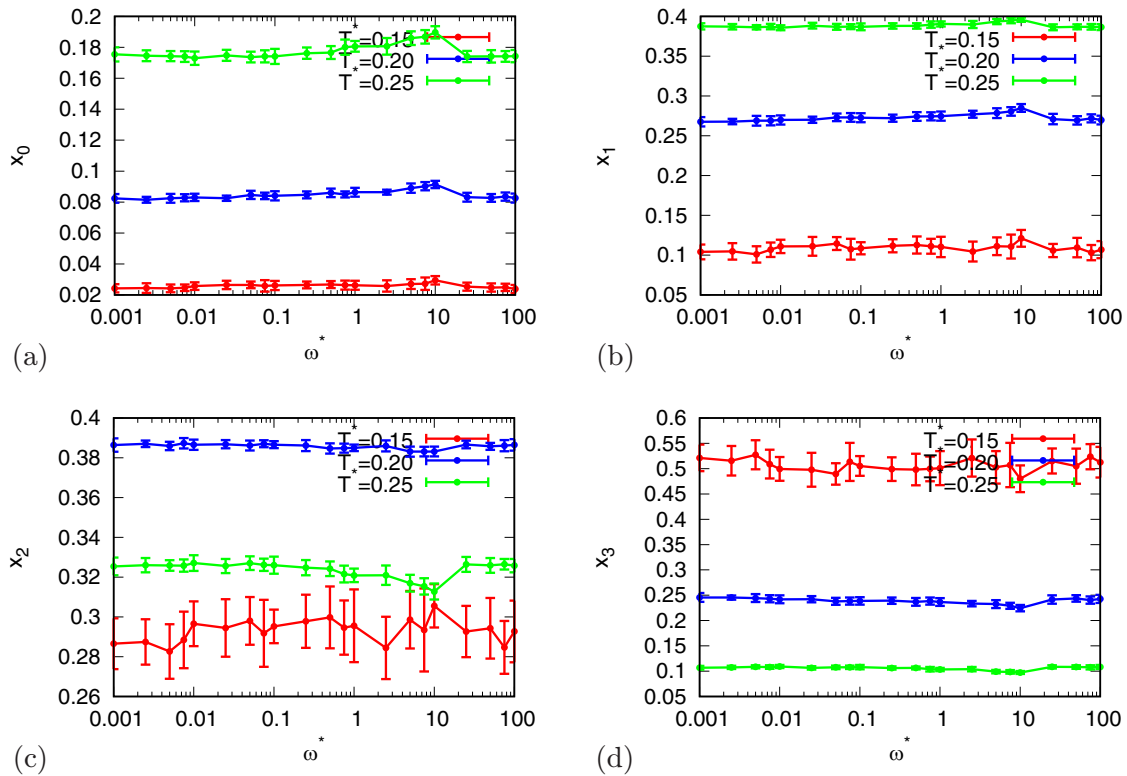


FIG. 4. Fraction of molecules with different number of HB [(a) 0, (b) 1, (c) 2, (d) 3] as function of electric field frequency at different temperatures and electric field amplitude 1.0.

potential between them was -0.4 or less. Figure 4 shows the ratios of differently bonded molecules as functions of electric field frequency at different temperatures and electric field strength 1.0. As seen from the radial and angular distribution functions, it is expected that the field of this strength has no significant influence on the properties of the system. The ratios of differently bound molecules as functions of field frequency are more or less flat lines at a field strength of 1.0, with a slight extremum at frequencies close to 10. The extrema here occur at frequencies that coincide with the resonance frequency of the molecules at this field amplitude. Why the resonance occurs at these frequencies is explained in more detail in later sections of the article. The electric field at the resonance frequency causes a change in the proportions of differently bound molecules. Although the change is not drastic, it is still noticeable. At this frequency, the proportion of molecules with zero or one bond increases, while the proportion of molecules with two or three bonds usually decreases. An exception here is the proportion of molecules with two bonds at temperature 0.15, which increases at the resonance frequency. Overall, the changes in the proportions indicate that the number of hydrogen bonds in the system is reduced by the effect of the electric field. However, this change is minimal and has no influence on the overall properties on a larger scale. At other frequencies, the electric field has virtually no effect on the fraction of differently bonded molecules, as the field is too weak to have any noticeable effect.

Figure 5 shows the same proportions of differently bound molecules as Fig. 4, except that the strength of the electric field is now 5.0. Such an electric field is already strong enough to cause some significant changes in the hydrogen

bonding of the molecules. Again, there are very pronounced extremes at field frequencies around 10, again these are resonant frequencies of the molecules at which the absorption of the field is most effective, but these frequencies are not the same as at lower field strengths. The dependence of the resonance frequency on the field strength and other properties will be discussed later. Overall, the general effect of the electric field on the bonding of the molecules is similar to that at lower field strengths, i.e., the field reduces the number of hydrogen bonds in the system. Thus, the fraction of molecules with zero and one HB increases near the resonance frequency, while the fraction of molecules with two or three bonds usually decreases. The effect of the electric field on the structure and the bonding is now significant and not just barely noticeable as at field strength 1.0. There is also a further maximum/minimum in the fraction of molecules with different bonding at a temperature of 0.15 and a frequency around 0.02. At this temperature and frequency, the fraction of molecules with zero bonds appears to remain unchanged, while the proportion of molecules with one and two bonds decreases in favour of an increasing fraction of molecules with three HB. Under these conditions, the electric field therefore causes an increase in the bonding between the molecules and thus a stronger structuring of the system.

At an electric field strength of 10.0 (Fig. 6), the effects of the electric field on the hydrogen bonding are more drastic, but qualitatively similar to those at lower field strengths. Here too, the electric field with a frequency close to the resonance frequency of the molecules increases the fraction of molecules with zero and one HB, while at the same time reducing the proportion of molecules with two and three HB. The width

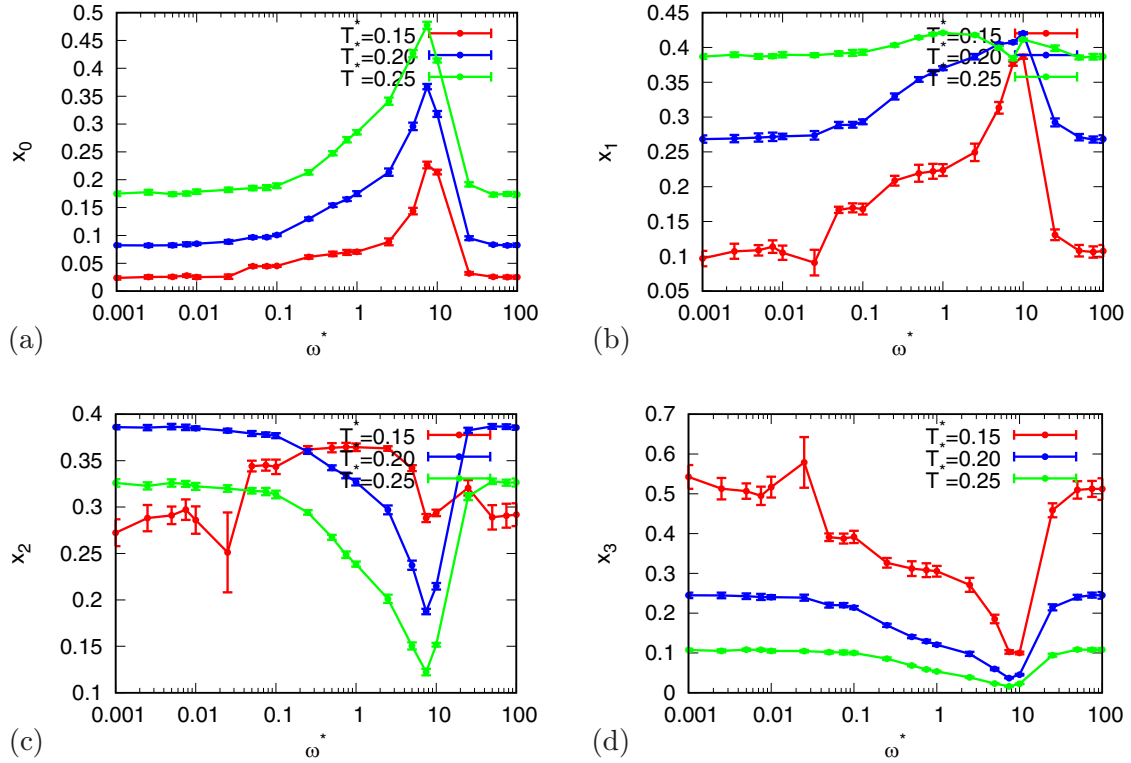


FIG. 5. Fraction of molecules with different number of HB [(a) 0, (b) 1, (c) 2, (d) 3] as function of electric field frequency at different temperatures and electric field amplitude 5.0.

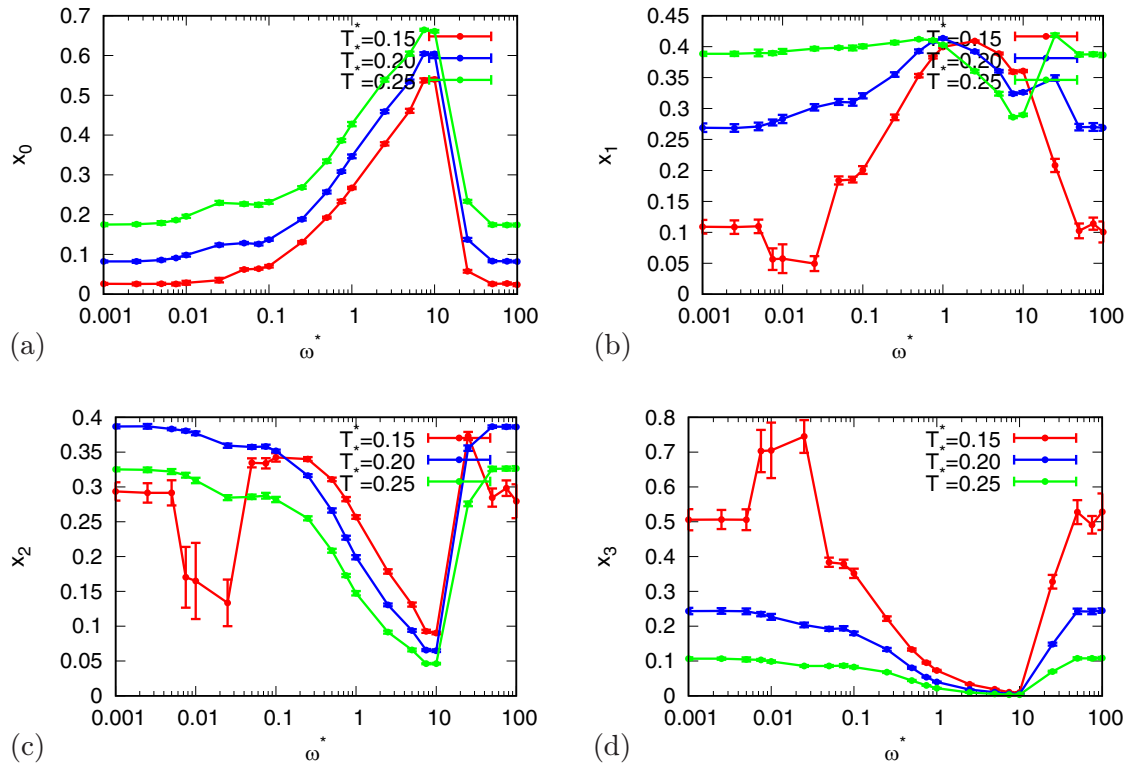


FIG. 6. Fraction of molecules with different number of HB [(a) 0, (b) 1, (c) 2, (d) 3] as function of electric field frequency at different temperatures and electric field amplitude 10.0.

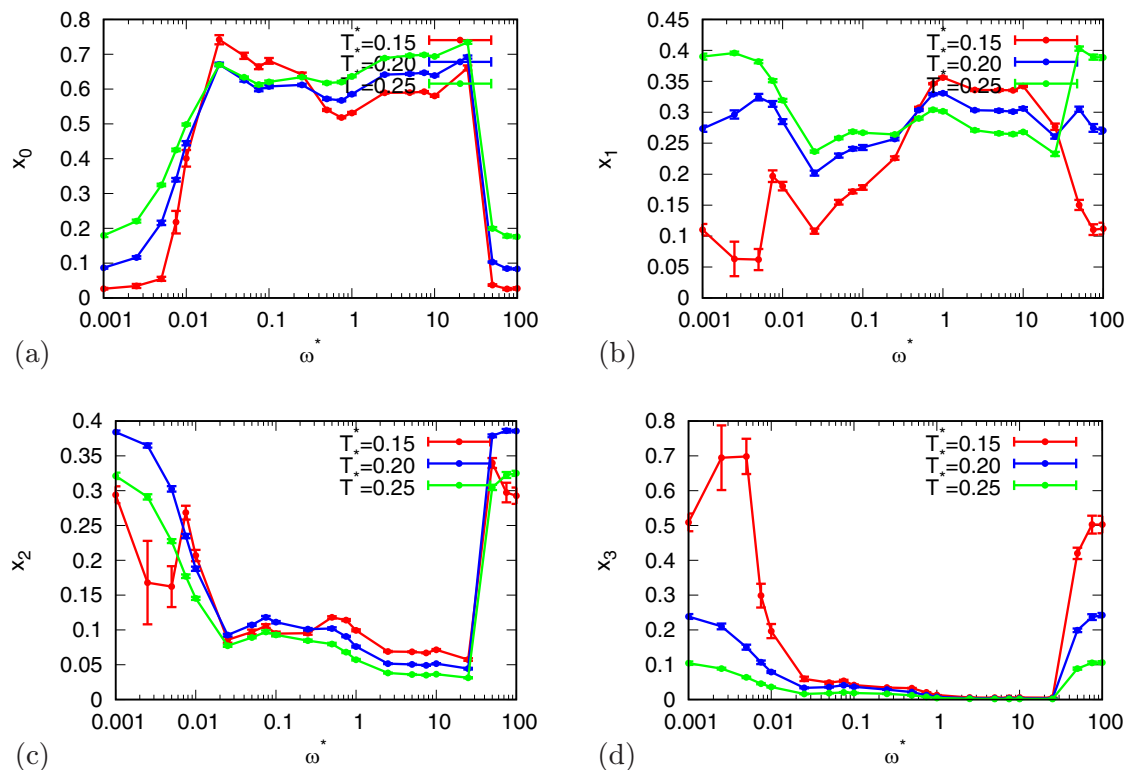


FIG. 7. Fraction of molecules with different number of HB [(a) 0, (b) 1, (c) 2, (d) 3] as function of electric field frequency at different temperatures and electric field amplitude 50.0.

of the peaks representing these extremes is now wider than at a lower field strength, which means that the frequency of the field does not need to be as close to the resonance frequency to cause the changes due to the increased strength of the electric field. The effect of increasing binding at frequencies around 0.01 and a temperature of 0.15 is now clearly visible, as the fraction of molecules with three HB increases dramatically under these conditions. The reason for this behavior is that a low-frequency electric field has a similar effect on water as a static electric field, as it is almost static on the molecular time scale. This low-frequency field therefore increases the orientation of the molecules in one direction, while at the same time the field is not so strong that it would break the hydrogen bonds. This leads to increased hydrogen bonding at low temperatures, as the field slightly immobilises the molecules, allowing for more efficient hydrogen bonding formation. The reason why we do not observe this at even lower frequencies is due to the way the simulation was performed. The electric field fluctuates as a sinusoidal function, so that the field strength is zero at the beginning. If the frequency is very low, then the simulation ends before the maximum field amplitude is reached.

Let us now examine the effect of a strong alternating electric field on the hydrogen bonding. Figure 7 shows the proportions of differently bonded molecules as functions of frequency in a strong electric field with a maximum amplitude of 50.0. Here, the effect of the field on hydrogen bonding is different than at lower field strengths. The strong field reduces hydrogen bonding over a much wider frequency range than a weaker field, as can be seen from the sharp increase in the fraction of unbonded molecules at frequency 0.01, which

then becomes constant up to frequency 30 and then decreases again, while the trend in the proportion of molecules with three HB is reversed. This means that the frequency selectivity of the strong alternating electric field is low when it comes to its effect on the hydrogen bonding. At the extreme ends of the frequency, however, the effect of the electric field is different. At high frequencies, the fluctuations of the electric field are too fast for the molecules to follow, so the field simply passes through. However, at extremely low frequencies, the alternating electric field acts in a similar way to a static electric field. In this case, the electric field forces the dipoles to align themselves in the same direction. The network of hydrogen bonding is more or less broken because the electric field is much stronger than the tendency of the molecules to form hydrogen bonds. The molecules tend to form a hexagonal, dense packing, while all dipoles are aligned in the same direction. In Fig. 7(d), a large fraction of molecules with three HB can be seen, partly because there are many hydrogen bonds when the dipoles change direction as the direction of the electric field changes. Furthermore, when the amplitude of the electric field is maximal and the molecules form a hexagonal dense packing with aligned dipoles, the structure also allows the formation of “half” hydrogen bonds, which also fall under the cutoff energy we set for the HB count. This description of the structural changes is also supported by the visualization of the trajectory of the molecules in the system.

The effect of the alternating electric field on the proportion of molecules with a different number of hydrogen bonds can be summarized by calculating the average number of hydrogen bonds per molecule, as shown in Fig. 8. For a weak field with a maximum amplitude of 1.0, the average number of

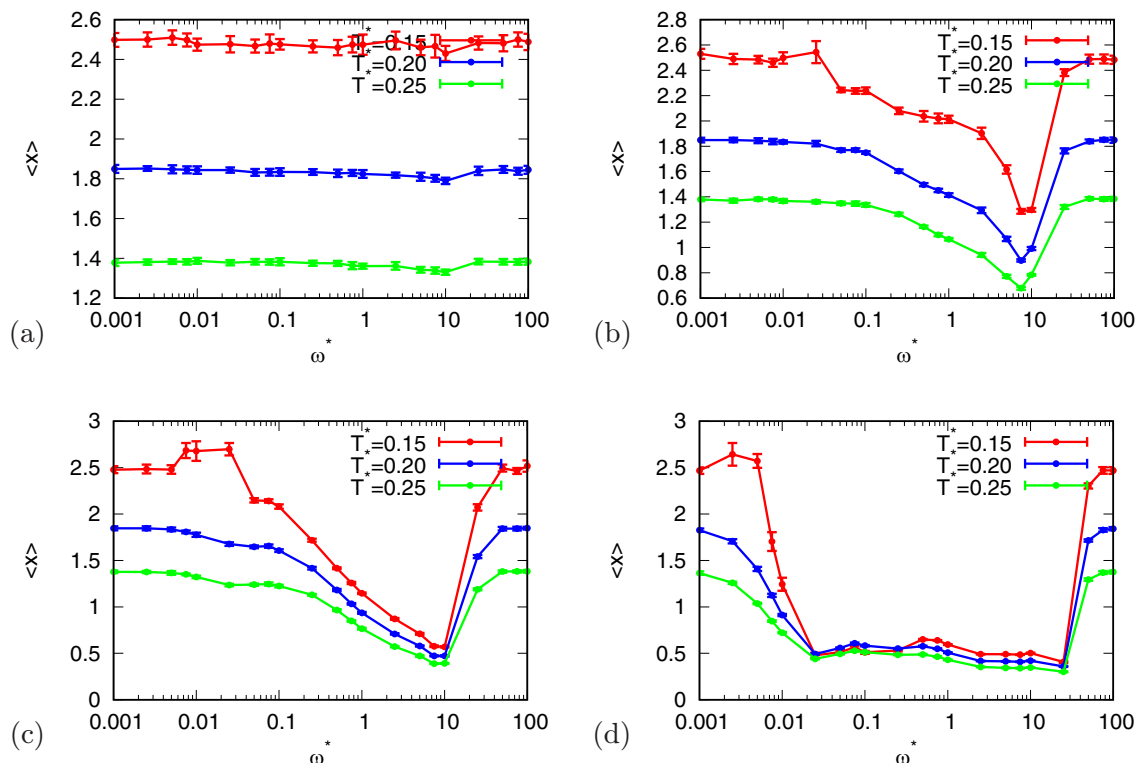


FIG. 8. Average number of HB per molecule as function of electric field frequency at different temperatures and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50.

HBs is practically constant with a small minimum around the resonance frequency. For stronger fields, this minimum becomes deeper and wider until it spreads over most of the investigated frequencies for strong fields with a maximum amplitude of 50.0. At high frequencies, the effect of the electric field on the average number of hydrogen bonds is minimal and the field simply passes through. However, at extremely low frequencies, the field has similar effects to a static electric field.

B. Thermodynamic and dynamic properties

When water molecules are exposed to an electric field, the field influences the orientation of the dipole moment of the water in such a way that the dipole is ideally aligned with the field. With a strong static field, this alignment can be achieved, but with a weaker or dynamic field, the dipoles of the molecules cannot always follow the direction of the field. The effect of the field therefore depends on its strength and frequency. But in all cases, the field influences the movement of the molecules. To understand how the field influences the movement of the water molecules, the diffusion coefficient was therefore calculated. Figure 9 shows the diffusion coefficient as a function of the field frequency at different field strengths and temperatures. Overall, the diffusion coefficient appears to be relatively constant in all cases, without any drastic changes. As usual, the diffusion coefficient is larger at higher temperatures, but here the temperatures at which the diffusion coefficient is shown are quite close together. At moderate and high field amplitudes, there is a slight increase in the diffusion coefficient at frequencies around 10.

The rotational diffusion coefficient was also calculated alongside the standard translational diffusion coefficient and is shown in Fig. 9. Here it can be seen that the rotational diffusion coefficient does not change significantly at low field amplitudes, but at moderate and high field amplitudes there is a sharp increase in the rotational diffusion coefficient at frequencies close to 10—which are resonant frequencies. The magnitude of this increased rotational diffusion is higher when the electric field is stronger. This means that when the frequency of the field is close to a natural rotational frequency of the molecule, a rotational resonance occurs, causing a strong increase in the rotational motion of the molecules. This increase in the rotation of the molecules also leads to the breaking of the hydrogen bonds, as we have already discussed above in the effects of the electric field on the hydrogen bonding. As the hydrogen bonds are broken, translational diffusion also increases, as shown in Fig. 9 at moderate and stronger fields near frequency 10.

The energy of the electric field, which is absorbed by the molecules, is converted into kinetic energy of the molecules, from which the average temperature of the system can be calculated. Figure 10 shows the temperature calculated from the kinetic energy of the molecules as a function of the frequency of the electric field at different field amplitudes and target temperatures. With a weak electric field, the kinetic temperature is constant over most of the frequency range, but there is a slight increase in temperature at the resonance frequency. This increase becomes greater when the strength of the electric field is greater. Also, the peak becomes wider because the field frequency does not need to be as close to the resonant frequency to trigger a response when the field is

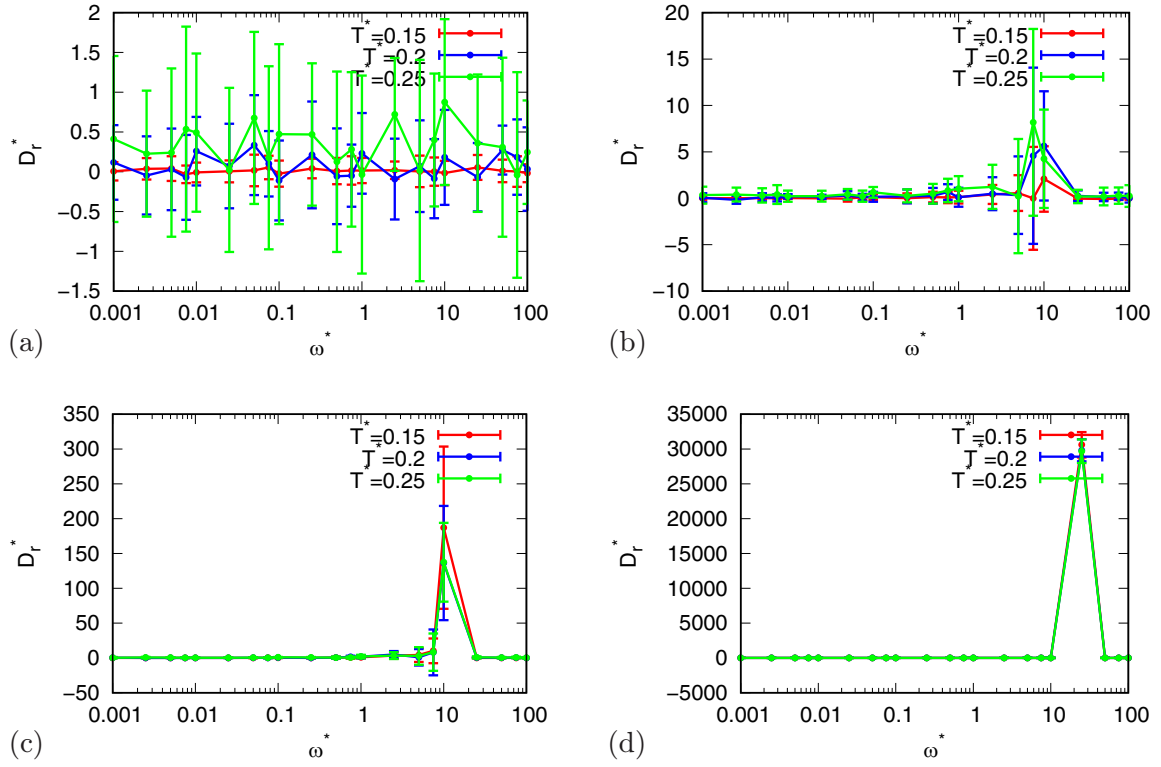


FIG. 9. Rotational diffusion coefficient as function of electric field frequency at different temperatures and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50.

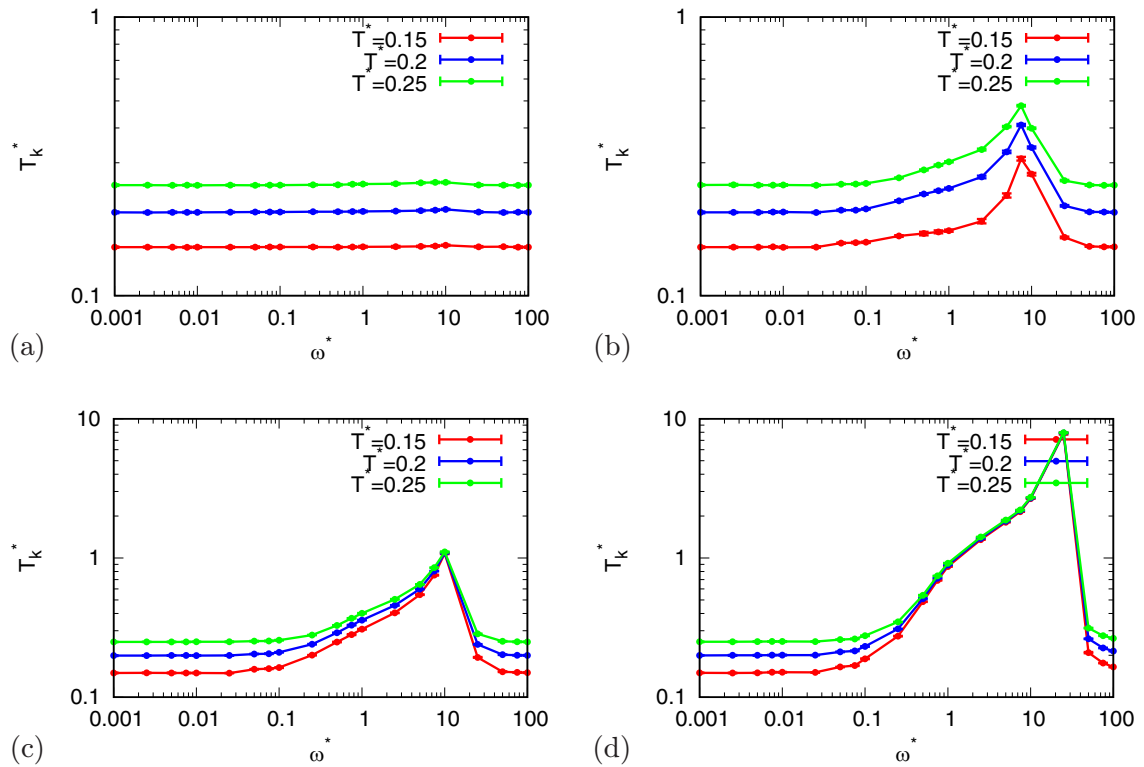


FIG. 10. Kinetic temperature as function of electric field frequency at different temperatures and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50.

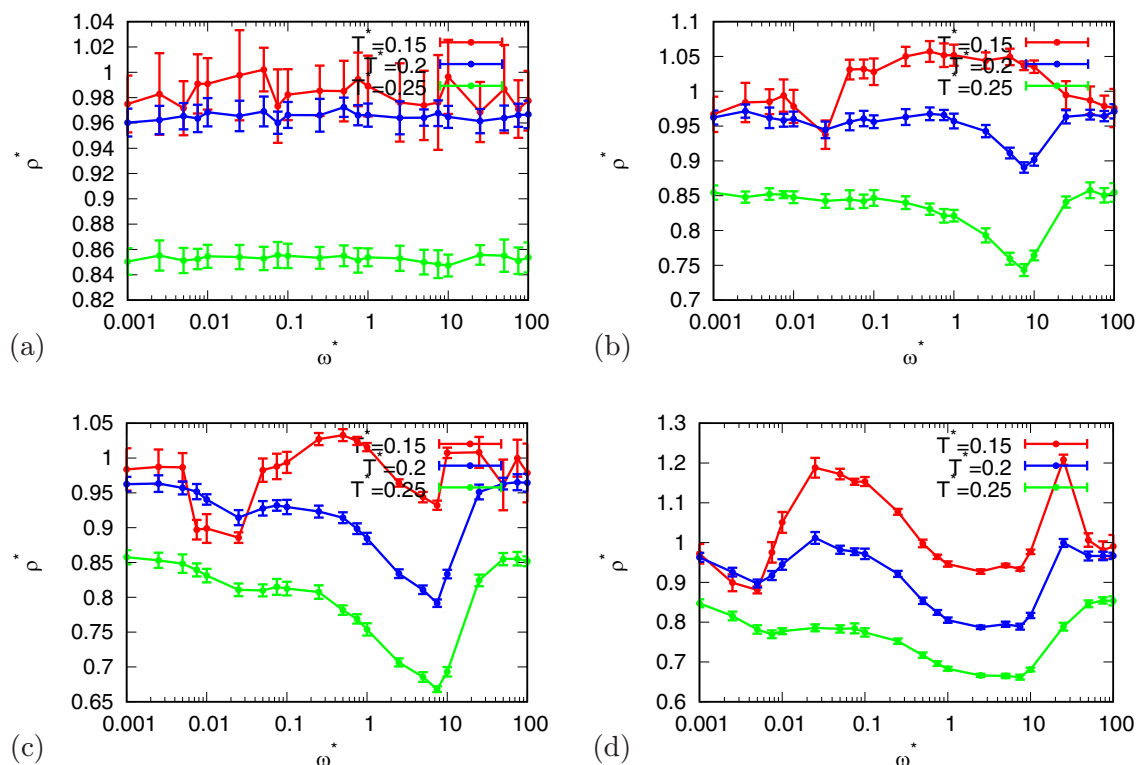


FIG. 11. Density as function of electric field frequency at different temperatures and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50.

stronger. In our simulations, we used a thermostat to keep the temperature constant. However, if the frequency of the electric field is close to the resonance frequency of the molecules, then energy is constantly supplied to the molecules and the thermostat is not able to dissipate all the excess kinetic energy. Therefore, the temperature rise calculated from the kinetic energy is observed. In this work, the calculated temperature will serve as a spectrum of the absorption of the electric field in the water and will therefore be discussed in more detail later.

Figure 11 shows the density as a function of the electric field frequency at different field amplitudes. The changes in density correspond to the changes in the other quantities just discussed. At a low field strength of 1.0, the field has no major effect on the density, while at moderate and high field strengths changes occur, especially in the frequency range close to the resonance frequency. The electric field causes a reduction in density as it approaches the resonant frequency at moderate field amplitudes (5, 10). This occurs because the rotations of the molecules caused by the field break down the hydrogen bonding structure, allowing the molecules to expand to a larger volume. With strong electric fields, however, the effect of the field on density is somewhat different. In virtually all cases, the alternating electric field increases the rotation of the molecules (if the field has a suitable frequency and amplitude), which breaks the hydrogen bonds and usually reduces the density. With a strong electric field [Fig. 11(d)] we can observe a similar effect as with a lower field strength, but here the resonance frequencies of the bound and unbound molecules are so far apart that we observe two density minima. The first is in the frequency range from 1.0 to 10.0, i.e.,

the resonance frequency of the bound molecules, while the second minimum is at frequency 25 and corresponds to the rotation of the unbound molecules in the electric field. In both cases the effect is similar—increased rotational motion of the molecules. In a strong electric field, there is also a density maximum at frequencies between 0.01 and 0.1. This increase in density is the result of the alignment of the dipoles of the molecules with the strong field, which leads to the formation of hexagonal dense packing.

The next thermodynamic quantity that was investigated is the excess enthalpy (Fig. 12). The information that can be obtained from the excess enthalpy is practically the same as when studying the effect of the electric field on the hydrogen bonding, since the trends in enthalpy are practically opposite to the trends in the average number of hydrogen bonds (if we flip the enthalpy plots over the x axis, they become very similar to the plots of the average number of hydrogen bonds). To summarize again briefly: The electric field leads to a decrease in the number of hydrogen bonds as it approaches the resonant frequency of the molecules, and thus to an increase in enthalpy. If the frequency is low and the maximum amplitude of the field is so large that it does not destroy the HB network, then the hydrogen bonding are strengthened (at a temperature of 0.15), which leads to a decrease in enthalpy.

Figure 12 shows how the heat capacity changes with the frequency of the electric field at different field amplitudes. At low field strength (1.0), the changes in heat capacity due to the electric field are small, practically on the size scale of the error. When the strength of the electric field is increased, relatively large maxima appear. At a field strength of 5.0, there are two maxima of heat capacity as a function

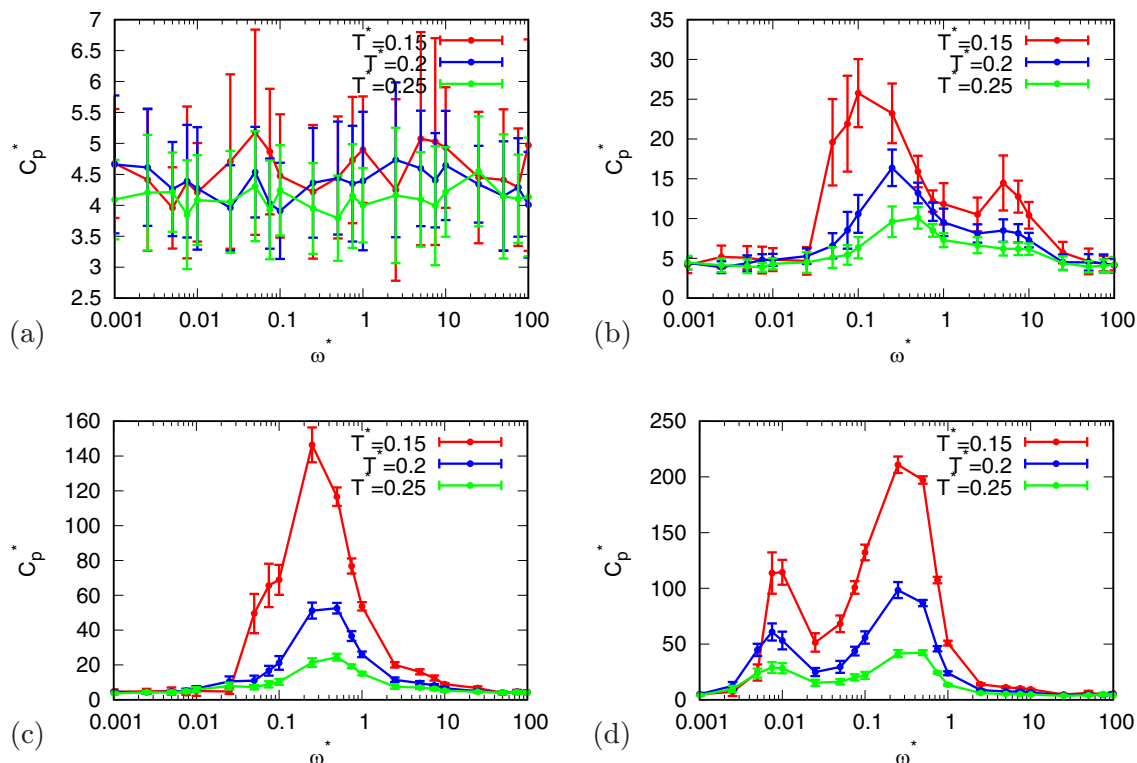


FIG. 12. Heat capacity as function of electric field frequency at different temperatures and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50.

of temperature at all three specified temperatures. The first, larger maximum is at frequencies around 0.1 and the second at 7. As the field strength increases, the first peak shifts to slightly higher frequencies [Figs. 12(c) and 12(d)], while the second peak disappears. The highest peak of the heat capacity in Figs. 12(b)–12(d) is probably due to the same mechanism. The high heat capacity here is the result of many energy states that are accessible and between which the system switches as the electric field fluctuates. The frequency here is so low that it appears that the system is in different states depending on the time during the simulation, while at higher frequencies we have a state where the molecules are constantly rotating. To further explain what we mean by different states. Let us assume that the electric field fluctuates from $+E_0$ to $-E_0$. So for a large electric field, the dipoles will be aligned in the $+x$ direction when the field strength is $+E_0$ and in the $-x$ direction, and between these two final states there is a transition state that the molecules go through when the field fluctuates over zero. If the field is very strong, then the molecules are in the final states most of the time and the transition from one final state to the other is fast. However, if the field is weaker, then the molecules may spend less time in the final states and more time in the transition state, where they can also form hydrogen bonds because the field is not strong enough to break them. If the field is even weaker [this is shown in Fig. 12(b)], then the molecules also form hydrogen bonds in the final state, but there is a preferred orientation of the dipoles in one direction, which shifts from one direction to the other when the electric field fluctuates. At a strong electric field (50.0), there is another maximum of heat capacity at a

frequency of about 0.01. Again, there is a constant transition of molecules from one final state to another, but the transition is a little different than at the frequency 0.1. At the frequency 0.1, the transition from one final state to another is fast, the dipoles practically change from one direction to another. However, the frequency of the field fluctuations is low enough to allow a gradual realignment of the system. During this gradual realignment, the molecules tend to form hydrogen bonds as they have time to adopt the positions that allow this to happen. This observation is supported by films of the trajectories of the molecules during the simulation.

The coefficient of thermal expansion as a function of the frequency of the electric field is shown in Fig. 13. Similar to the other quantities, the weak electric field (1.0) has no noticeable influence on the coefficient. With an electric field amplitude of 5.0 [Fig. 13(b)] the effect of the electric field on the expansion coefficient becomes clearer. At all temperatures, there appears to be a maximum at frequencies around 10, which corresponds approximately to the resonance frequency of the molecule. This maximum is caused by an increased rotational motion of the molecules, which destabilizes the hydrogen bonds in the system. At this point, increasing the temperature would further destabilize the hydrogen bonds, so the expansion coefficient is positive and quite large. There is also a relatively large minimum of the expansion coefficient in Fig. 13(b) at frequency 0.1 and temperature 0.15. This minimum could be due to the change of the system from a less dense and more ordered system to a denser and less ordered system with less HB at higher frequencies. This point is similar to the density maximum of real water at 4°C . At a higher electric field strength (10.0), this minimum becomes lower.

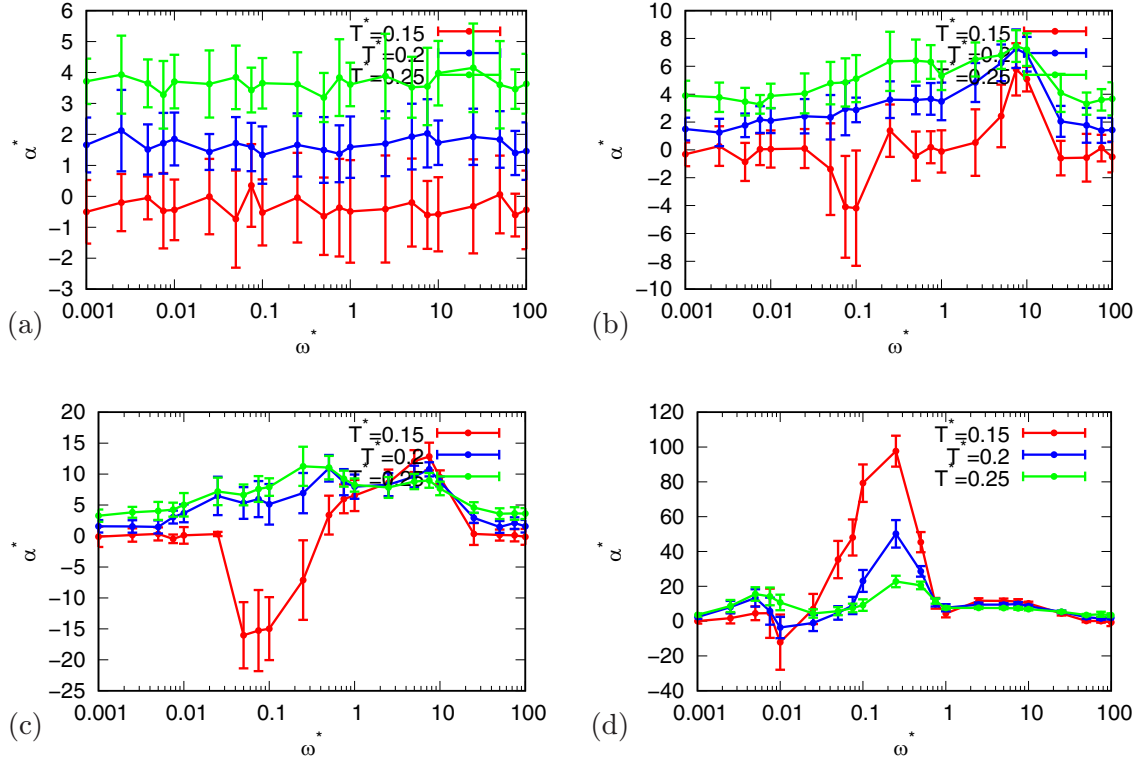


FIG. 13. Thermal expansion coefficient as function of electric field frequency at different temperatures and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50.

With a strong electric field [Fig. 13(d)], a large maximum appears at frequencies around 0.2. The most likely reason for this maximum is that the increase in temperature causes additional movement of the molecules with aligned dipoles, thus increasing the volume of the system.

The last thermodynamic quantity discussed in this section is the isothermal compressibility (Fig. 14). At low electric field strength, the electric field has no appreciable influence on the compressibility, while at a slightly stronger field with an amplitude of 5.0, the compressibility increases with frequency until the resonance frequency is reached and then decreases drastically. The explanation for this is that the electric field destabilizes the HB more strongly as it approaches the resonance frequency, thus increasing the compressibility coefficient. At higher field strength, the compressibility increases and the frequency range in which the compressibility increases becomes wider. An interesting phenomenon is a large maximum in compressibility at an electric field strength of 50.0, a frequency of 0.01 and a temperature of 0.15 [Fig. 14(d)]. This maximum occurs because at this frequency the fluctuations of the field from one end point to the other are relatively slow, so that the system can transition gradually. This transition makes the system quite compressible, while at higher frequencies this transition occurs faster and the system spends more time in endpoint (final) structures that are more compact and less compressible. At frequencies lower than 0.01, the compressibility is lower because the frequency is so low that the field does not go through the entire fluctuation during the simulation. If the simulation lasted indefinitely, then the compressibility at these low frequencies would also be high.

C. Electric susceptibility

The electrical susceptibility of the system containing rose water particles was also calculated at different frequencies and amplitudes of the electric field. The electrical susceptibility basically contains the same information as the dielectric constant. Here we have used the susceptibility (multiplied by the permittivity of the vacuum) instead of the dielectric constant for two reasons. The first reason is that we want to keep all results in reduced units—this means that they are independent of specific values of the energy and length of the hydrogen bond. The second reason is that the value of the dielectric constant for rose model would not give us any useful information because the system is two-dimensional and there are no useful references to compare the value with.

Figure 15 shows the real part and Fig. 16 shows the imaginary part of the electric susceptibility multiplied by the permittivity of the vacuum as a function of the electric field frequency at different electric field strengths and temperatures. First of all, it is noticeable that the amplitude of both the real and imaginary parts of the susceptibility decreases with increasing field strength, which indicates nonlinear polarization effects where a stronger field disturbs the efficiency of the dipole alignment. In addition, saturation effects are noticeable, especially at strong fields (50), where the response is significantly damped. Let us first concentrate on the real part of the susceptibility. The real part of the susceptibility shows a dispersive behavior, which is typical for the Debye relaxation. At low frequencies, the dipoles can follow the oscillation of the field, while at higher frequencies the alignment between dipoles and field becomes less effective as the dipoles cannot reorient fast enough, leading to a decreasing susceptibility.

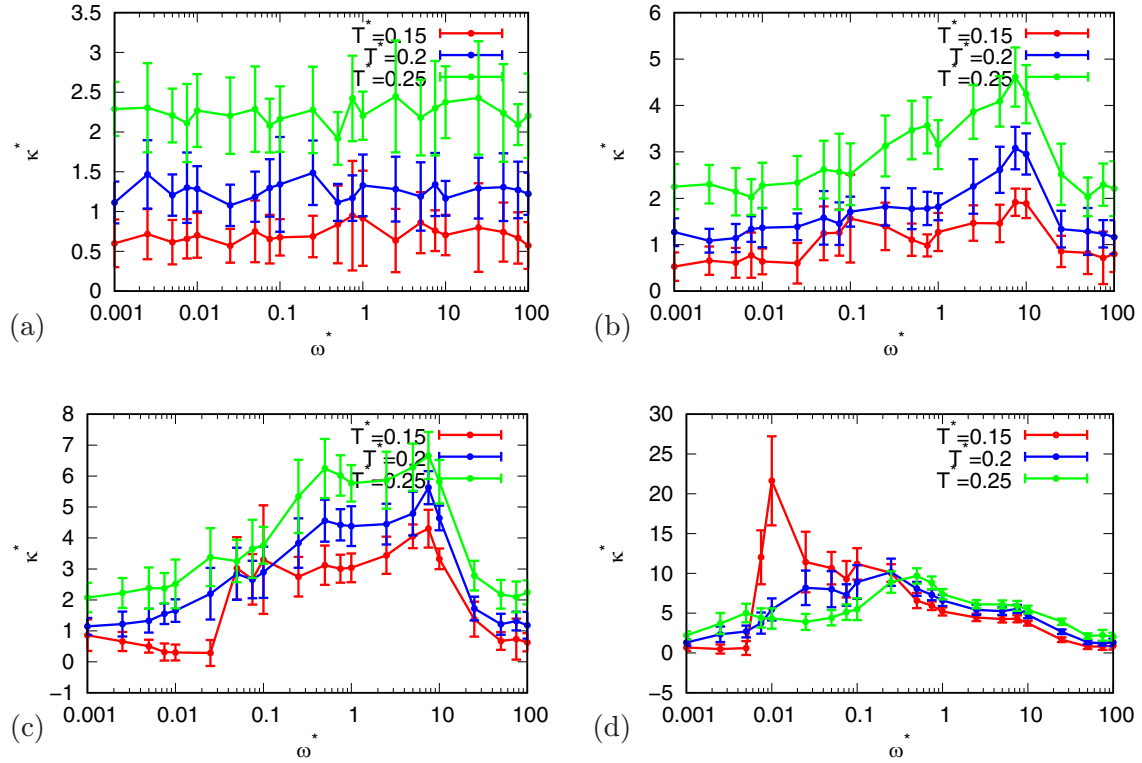


FIG. 14. Isothermal compressibility as function of electric field frequency at different temperatures and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50.

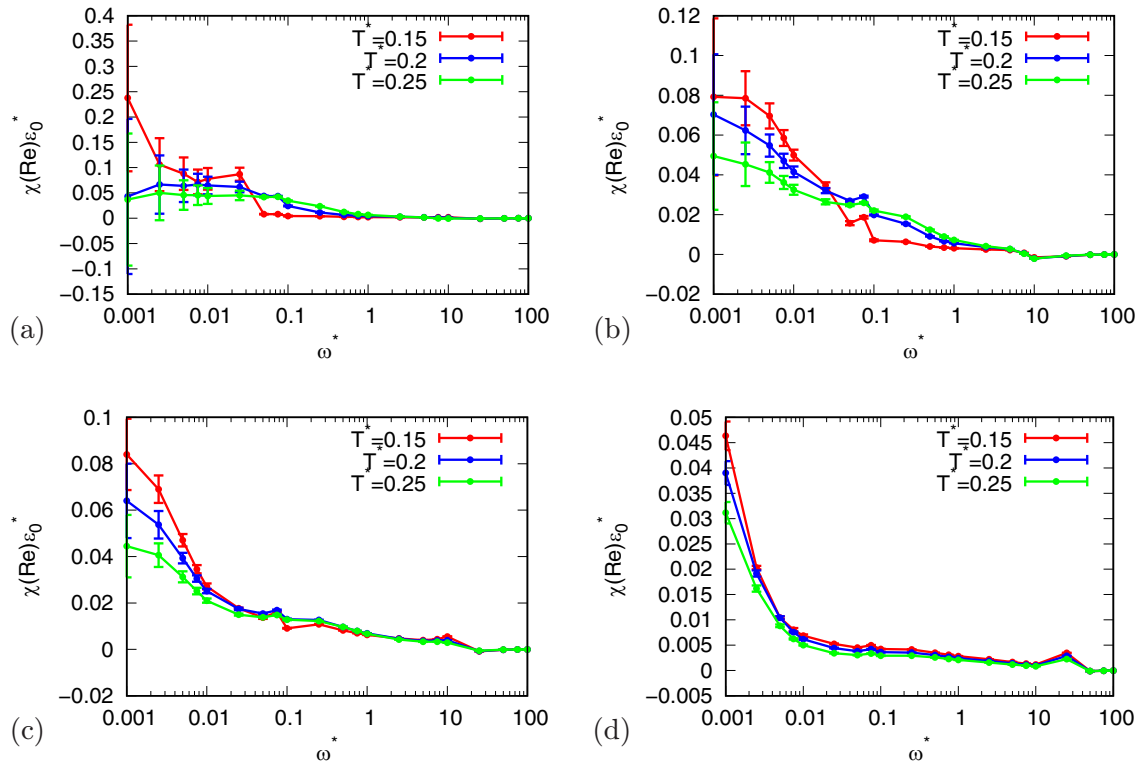


FIG. 15. Real part of electric susceptibility as function of electric field frequency at different temperatures and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50.

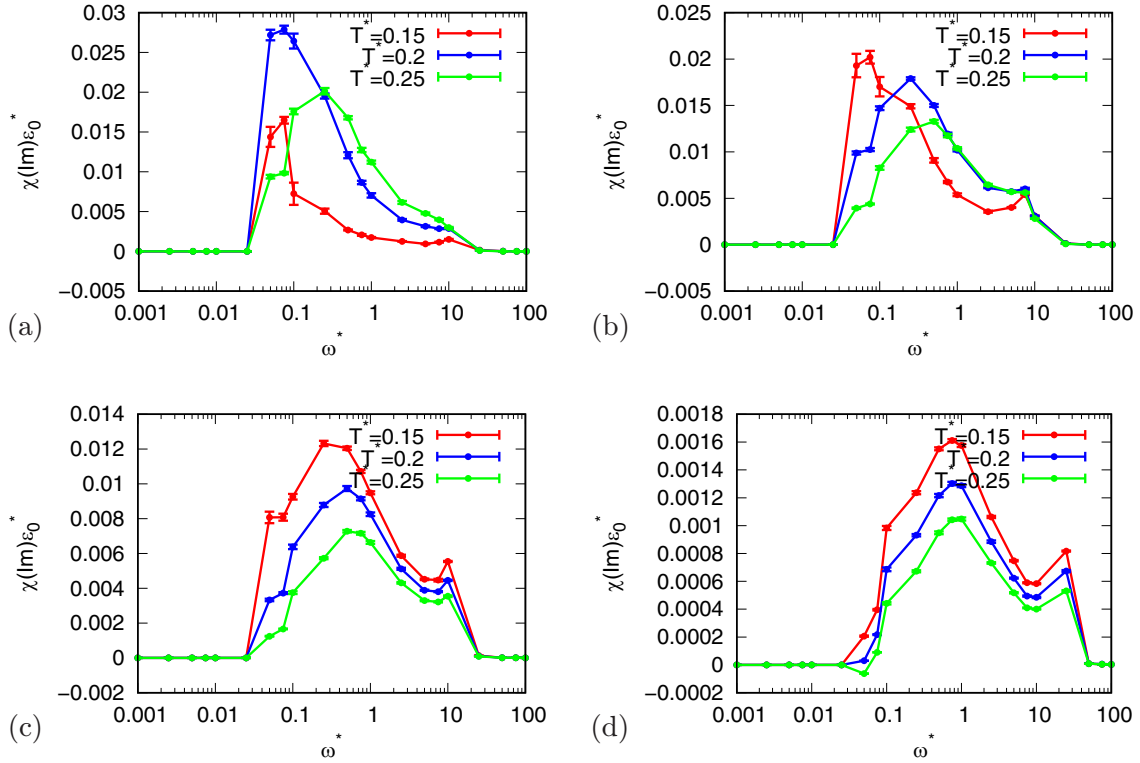


FIG. 16. Imaginary part of electric susceptibility as function of electric field frequency at different temperatures and electric field amplitudes: (a) 1, (b) 5, (c) 10, (d) 50.

As the electric field strength increases, the dispersion region becomes narrower, which is due to increased suppression of the dipole orientation by the electric field. With stronger fields, the dipoles are more rigidly aligned with the field. The dispersion region also shifts toward lower frequencies which indicates that a stronger field causes a stronger field-induced ordering of the molecules and thus slows down the molecular reorientation. At a low electric field, the dispersion range shifts to higher frequencies due to the increased temperature, as the number of hydrogen bonds decreases, which accelerates molecular reorientation. However, an opposite trend is observed at strong fields, where increased temperature shifts the dispersion region toward lower frequencies, as field-induced structuring dominates over the thermal motion of the molecules. At low frequencies, the susceptibility is higher at low temperature, suggesting that a more ordered structure (due to hydrogen bonding) increases the susceptibility of water, which has also been observed experimentally in water.

The imaginary part of the susceptibility as a function of frequency (Fig. 16) also has the same qualitative form, which is typical for water. The peaks of the imaginary susceptibility represent the frequency at which the energy dissipation is maximized. The higher temperature shifts the maximum of the imaginary susceptibility to a higher frequency since there are fewer hydrogen bonds in the system and thus the mobility of the dipoles increases, which is why the polarization cycles of the molecules are faster. The stronger electric field also shifts the maximum to higher frequencies, which is also a consequence of the faster polarization cycles. At the strongest field strength, the values of the imaginary susceptibility are an order of magnitude smaller than at weaker fields, which

indicates a more rigid alignment of the molecules to the strong electric field, which is reflected in a lower energy loss.

Both the real and imaginary part of the electric susceptibility also exhibit a resonance effect, but it is not as pronounced as for the other quantities already discussed. In Fig. 15(c) (at a frequency around 10) and 15(d) (at a frequency around 20), a slight increase can be seen at the frequencies at which resonance occurs, while the prominence of the peak increases with the field strength. This means that at this frequency the entire dipole of the system is more strongly aligned with the field. The peak at the resonance frequency can also be seen in the imaginary susceptibility (Fig. 16), indicating increased energy dissipation.

D. Rotational resonance and its origins

In the previous section, an overview was given of the various structural, thermodynamic and dynamic properties of water modelled with rose water model in an alternating electric field. As mentioned before, the system undergoes the most significant changes when the electric field matches the natural frequency of the molecules and causes resonance. In this work, we focus on the energy and frequency range that corresponds to the rotations of the molecules and thus increases the rotation of the molecules. Of the quantities discussed in the previous section, the temperature, which is calculated from the kinetic energy of the molecules, reflects the effect of the electric field most clearly. We have used the kinetic temperature as the absorption spectra of our system. At first glance, one might think that the maxima in

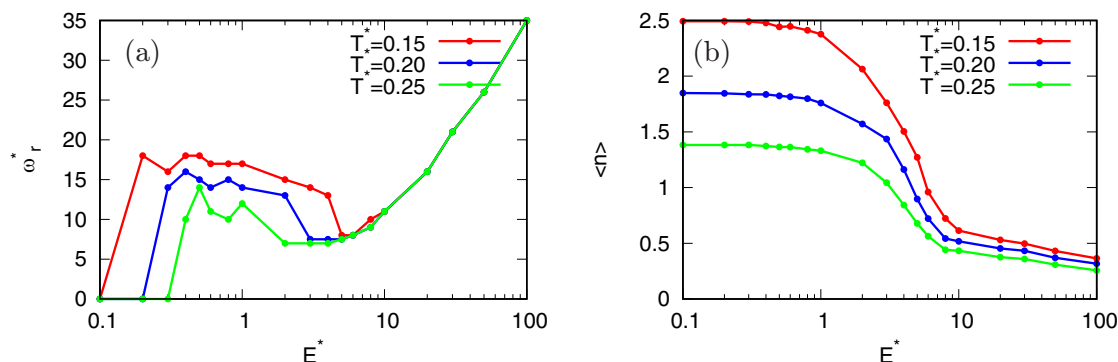


FIG. 17. (a) Resonance frequency as function of electric field strength. (b) Average number of HB per molecule at resonance frequency as function of electric field strength.

Fig. 10 are all at the same frequency, but this is not true. They depend on the electric field strength and also on the temperature.

In Fig. 17 the resonance frequency is shown as a function of the electric field strength together with the average number of bonds per molecule at the same resonance frequency. It is clear that there is a correlation between the resonance frequency and the average number of hydrogen bonds. Here, the resonance frequency was determined as the maximum of the kinetic temperature as a function of frequency at each electric field amplitude (functions like the one in Fig. 10). From Fig. 17(a) it can be seen that there are two regimes of rotational resonance. The regimes depend on the ratio between the strength of the intermolecular interactions and the strength of the electric field, which essentially counteracts these interactions. With a weak electric field around the value 1.0, the resonance frequency has a relatively constant value, as the resonance frequency as a function of the electric field has a kind of plateau here. In this region, the resonant frequency is relatively independent of the strength of the electric field, as the strength of the electric field is small enough not to cause any disruption of the hydrogen bonds, but at the same time the electric field is strong enough to enhance the rotational motion of the molecules, which can be measured as an increase in kinetic temperature. Thus, if we assume that each molecule is a classical rotator in an orientation-dependent potential, then the stiffer the potential, the higher the natural frequency of the molecule's rotation. The stronger the hydrogen bonds of the molecule, the higher the natural frequency of the molecule. Furthermore, in this range of electric field strength, the electric absorption of the electric field is highest when its frequency matches the natural frequency of the molecules, which librate (rotationally vibrate) around the position determined by the hydrogen bonds. For this reason, there is a direct correlation between the average number of hydrogen bonds and the resonant frequency. As there are more hydrogen bonds at lower temperatures, the resonance frequency decreases as the temperature rises. With a weaker electric field, the resonant frequency determined from the simulation is zero, as the increase in kinetic energy caused by the electric field is in the range that can be suppressed by the thermostat, so that the resonant frequency cannot be derived from the simulations. Theoretically, however, the resonance frequency here still corresponds to the natural frequency of the hydrogen bond

librations. At an electric field strength between 1.0 and 10.0, the electric field becomes strong enough that the rotational motion of the molecules induced by the electric field causes the disruption of the hydrogen bonds. In Fig. 17(b) you can see how the average number of HBs decreases in this range and in Fig. 17 a corresponding decrease in the resonant frequency can be observed. At this point, the system enters the second rotational regime in which the resonant frequency corresponds to the natural frequency of the electric dipole rotation. In a strong electric field, the average number of HBs is relatively constant as the HB network is mostly broken down. The resonance frequency thus becomes independent of the temperature and depends only on the strength of the electric field, as a stronger electric field increases the resonance frequency.

To explain why the resonant frequency changes in the manner shown in Fig. 17, we developed a model that allowed us to replicate the absorption spectra based on the information about the hydrogen bonds in the system. The model is described in section and uses a partition of the molecules in the system into two populations—one of bonded and one of nonbonded molecules. The model function was fitted to the excess temperature (temperature calculated from kinetic energy minus target temperature). As can be seen in the Fig. 18, the resonance model is very successful in explaining the absorption spectra of the model. The figure shows a rotational absorption spectrum of the electric field at a temperature of 0.20 and different electric field strengths. The maximum of the spectrum in Fig. 18 increases with increasing electric field, as more energy is absorbed with a stronger field. At a low electric field (1.0), the entire absorption spectrum practically corresponds to the absorption spectrum of bound molecules, since the majority of molecules are bound by hydrogen bonds under these conditions. However, there is also a small peak corresponding to nonbonded molecules at low frequencies. As the strength of the electric field increases, the relative height of the bound spectrum decreases, while the height of the unbound peak increases. The peaks of the bound and unbound absorption spectra also shift in position. With increasing electric field strength, the natural frequency of nonbonded molecules increases, as described in Eq. (11), while however the natural frequency of the bound molecules decreases according to Eq. (10), which is due to the fact that the average number of hydrogen bonds per molecule decreases. At first glance, the Fig. 18(c) appears to be an exception to the movement

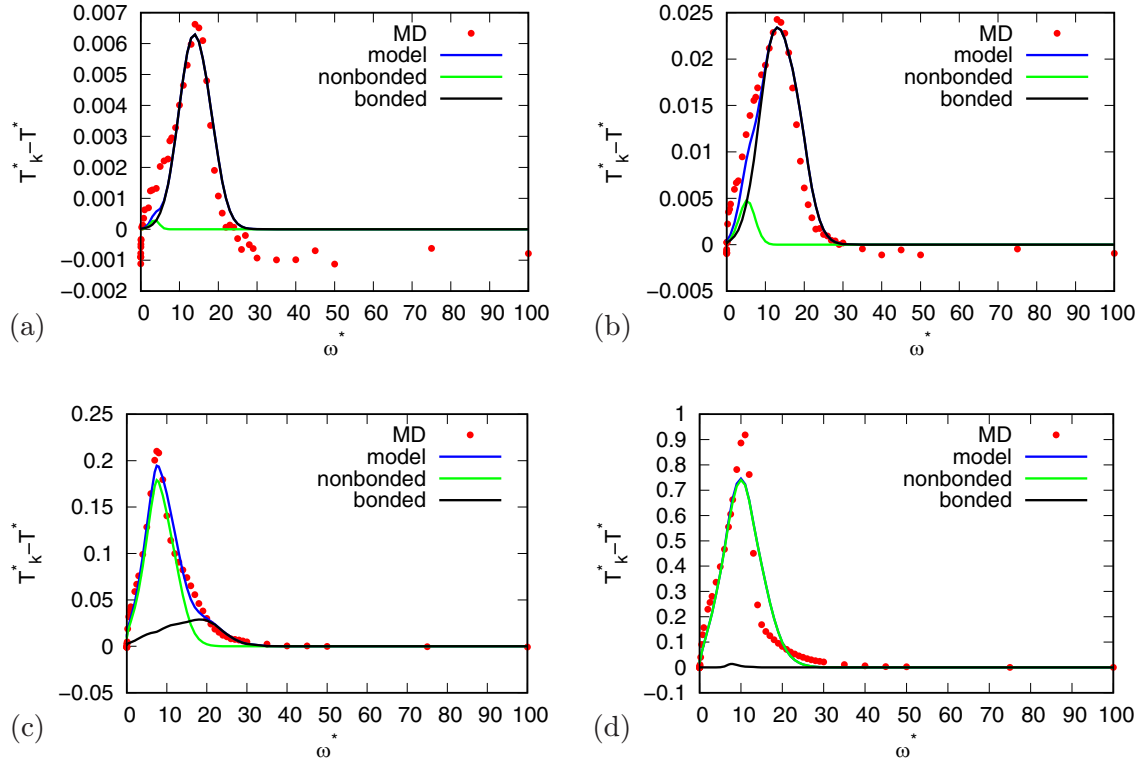


FIG. 18. Rotational spectrum of the system at temperature 0.20 and different electric field amplitudes: (a) 1.0, (b) 2.0, (c) 5.0, (d) 10.0. With red change in temperature of simulation is shown, with blue lines the predicted spectrum is shown, and with green and black lines nonbonded and bonded component of predicted spectrum are labeled.

of the resonance frequency just described. However, here the peak of the absorption spectra of the bound molecules does not match the resonance frequency of the population. The absorption peak of the bound molecules is shifted toward higher frequencies because there is a resonance of nonbonded molecules at lower frequencies, which reduces the fraction of bound molecules in the system.

The maximum of the spectra shown in Fig. 18, which were obtained directly from simulations or calculated from hydrogen bonding statistics, agree very well. The maximum of the absorption spectra is considered as the total resonance frequency of the system. Figure 19(a) shows the comparison

of the resonance frequency as a function of the electric field for the simulations and the model function used to describe the spectra. The agreement between the simulation results and the model result is very good at all temperatures shown. The model correctly predicts that the resonant frequency is higher for a weak electric field when the temperature is lower. In addition, the transition from one resonance region to another is successfully predicted. As expected, the model also predicts the correct resonant frequency of the system in a strong electric field. The resonant frequency of the model and the resonant frequency of the simulation differ for a very weak electric field. As already mentioned, the simulation cannot

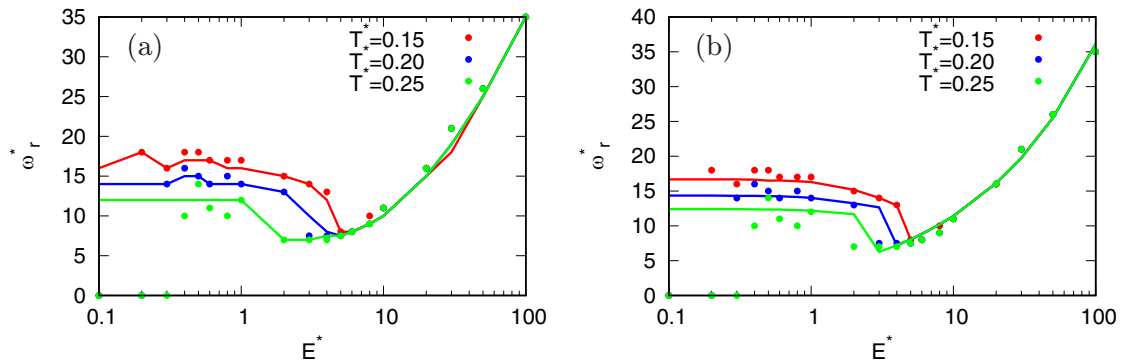


FIG. 19. Model function of resonance frequency as function of electric field strength: (a) version with Gaussian distributions, (b) simplified version with only peak frequency. The direct results from simulations are shown with points, while the results of the models are shown with lines.

detect the temperature rise in such weak fields, so the resonant frequency cannot be determined. However, the model correctly predicts that the frequency remains practically constant when the field becomes weaker.

In Fig. 19 a similar comparison is made, but here we have the simplified model that predicts only the peak resonant frequency and not the entire absorption spectrum. Again, the agreement between the model and the simulation results is very good. The main difference is that the model predicts the transition from one resonance region to the other at a slightly higher electric field strength at temperature 0.25 and 0.20. However, the advantage of this simplified model is that it has fewer parameters that need to be adjusted.

IV. CONCLUSION

To conclude, in this paper we have studied how a dynamic electric field influences the properties of the rose water model. The energy and frequency of the electric field were in a range corresponding to the rotational motion of the molecules, so that the electric field was absorbed into the system via increased rotations and librations of the water molecules. The effects of the electric field on the structural, dynamic and thermodynamic properties of water were observed. Depending on the frequency and strength of the electric field, the electric field has different effects on the properties. If the frequency of the electric field is high, then there is practically no effect of the field on the properties of the water, as the fluctuations of the field are too fast for the molecules to follow, so the field simply passes through. Low frequency fields tend to reinforce the structuring of the water molecules as they act in a similar way to a static electric field. When the low-frequency field is weaker than the hydrogen bonds, the electric field increases the ordering of the molecules in the system in such a way that the molecules are more aligned with the field, while the molecules can continue to form hydrogen bonds. In addition, such increased alignment of the electric field also increases the hydrogen bonds in the system. However, if the low-frequency electric field is stronger than the hydrogen bonds, then the tendency of the molecules to align with the field outweighs the

tendency to form hydrogen bond, leading to the breakdown of the hydrogen bonding network. The most interesting phenomena occur in the medium frequency range of the electric field, where the frequency of the electric field is close to the natural rotational frequency of the molecules. When the frequency of the external field matches the natural rotational frequency of the molecules, the electric field is absorbed and thus the rotational motion of the molecules is significantly enhanced. If the energy (and strength) of the electric field is lower than the energy of the hydrogen bonds, then the network of hydrogen bonds remains undisturbed, but the librational motion of the molecules within the network is enhanced. However, if the energy/strength of the electric field exceeds the energy of the hydrogen bonds, then the rotational movement of the molecules leads to the breaking of the hydrogen bonds, which reduces the structuring of the system and thus also change its thermodynamic properties. If the electric field is very strong, then practically no hydrogen bonds remain in the system and the molecules behave like rigid rotators in a fluctuating electric field. To quantitatively explain the effect of the electric field on the resonance frequency of the water model and to establish the link between electric field, hydrogen bonds and resonance, we have developed a model that can explain the rotational absorption spectra of the electric field. The model uses the statistics of hydrogen bonding to predict the populations of bonded and nonbonded molecules and their corresponding rotational absorption spectra. The spectra can be used to determine the resonance frequencies. In addition to the model that describes the entire spectra, we have also developed a simpler model that predicts the resonance frequency of water in an electric field of varying strength. The model establishes a link between hydrogen bonds, electric field strength and resonance frequency. The principle used in this model could potentially be extended to other systems where resonance in electric fields could be used to study the local environment of the molecules.

DATA AVAILABILITY

The data that support the findings of this article are openly available [93].

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