Hydrogen Bond Distribution of *N,N*-Dimethyl formamide-Water Mixture in Microwave Fields by Molecular Dynamics Simulation

CHEN HAI-CHUAN[1], YANG LI-JUN[1] and GUO-ZHU JIA[2,*]

[1]College of Electrical Engineering and Information Technology, Xihua University, Chengdu 610039, P.R. China
[2]College of Physics and Electronics Engineering, Sichuan Normal University, Chengdu 610066, P.R. China

*Corresponding author: E-mail: jia1689500@126.com

Non-equilibrium molecular dynamics simulations of the aqueous solution of *N,N*-dimethyl formamide have been performed in the canonical ensemble in both the absence and presence of external electromagnetic (E/M) field. The results indicate that as the intensity of the electromagnetic filed increased, the radial distribution functions of the aqueous solution of *N,N*-dimethyl formamide became more pronounced. There appears to be a threshold microwave field intensity below which no tangible field effects are apparent, 10^5 V/m, the lowest field strength used in this study, there was no significant effect on the systems structure. Microwave energy is partly transferred to intermolecular energies of mixture, which induce the change of angle distribution functions of the hydrogen bonding.

Key Words: Non-equilibrium molecular dynamics simulation, Electromagnetic field, Radial distribution function, DMF aqueous solution.

INTRODUCTION

It is well known that microwaves can speed up chemical reactions for the synthesis of organic and inorganic materials and sinter metal oxides with high-energy efficiency[1-3]. The amides represent an important class of organic solvents due to their high polarity, strong solvating power and a large liquid state range[4]. Substitution at the amide nitrogen atom allows control of the extent of intermolecular hydrogen bonding, which is dominating factor for the physical properties exhibited by the liquids. Besides, amides may be used model systems for peptides. A typical example is *N,N*-dimethyl formamide (DMF). Although DMF solutions have been studied with a wide range of experimental techniques, including neutron diffraction[5], NMR[6], electric diffraction[7] and dielectric spectroscopy[8-13], the influence of hydrogen bonding on its aqueous solutions in microwave field were not mentioned in those researches under the varied intensities of external electromagnetic field. Therefore, in this paper the nonequilibrium molecular dynamics study DMF on the hydrogen bond distribution under external electromagnetic field was carried out.

EXPERIMENTAL

In the simulations, the electromagnetic field was taken to be uniform and plane-polarized in z-axis direction, *i.e.* the electric compo-nent is taken to act in the X-axis direction and

the magnetic component in the Y-axis direction, the plane of polarization is then the X-Y plane. The intensities of the electric field and magnetic field are formulated as follows[14]:

$$E(t) = E_{max} \cos(wt)(1\vec{i} + 0\vec{j} + 0\vec{k}) \tag{1}$$

$$B(t) = B_{max} \cos(wt)(0\vec{i} + 1\vec{j} + 0\vec{k}) \tag{2}$$

The two expressions satisfy Maxwell's equations and are related by $E(t)/B(t) = c$, where c is the speed of light. The effects of the applied electromagnetic field on the trajectories of the atoms were modeled using the modified Verlet velocity algorithm[15], in which the half-time step velocity and position are found in the conventional manner and the full-time step velocity is dependent upon the respective intensities of the electric and magnetic fields. The full-time step velocity is given by Chang and Weng[16].

The simulations involved a total of 4000 water molecules contained within an isotropic simulation box and considered 3 M (molality), DMF solution concentration, corresponding 216 DMF molecules. The Nosé-Hoover thermostat was used to maintain the equilibrium temperature at 298 K and periodic boundary conditions were imposed in all three dimensions. The trajectories of the atoms during the equilibration process were calculated using the Verlet velocity algorithm. To make sure the pressure of two systems is the same at 1 bar, the NPT ensemble was carried out in the pre-equilibrium process. The electromagnetic field was applied in the NVT ensemble to

isolate the field effects from the thermal effects and hence the simulations were effectively non-equilibrium NVT (NNVT) simulations. An external electromagnetic fields were applied to those models, all of the fields were of frequency $\nu = 10$ GHz and the root-mean-square (RMS) electric field intensities are $E_{RMS} = 0$-3×10^9 V/m, $(E_{max}/\sqrt{2}E_{RMS})$ respectively. Note that the frequency and intensity of the electromagnetic field are deliberately assigned high values such that the effects of the field on the DMF aqueous solution can be readily determined within a short simulation time.

During the MD simulation, a time step of 1 fs was used in all simulation, a period of 50 ps was allowed for equilibration (NPT ensemble). Following the equilibration process, an electromagnetic field of the specified frequency and intensity were applied for 100 ps. The trajectories generated were stored every 50 fs.

RESULTS AND DISCUSSION

Fig. 1 presents the RDFs of O-O, O-H, H-H and C-C in the DMF aqueous solution with a concentration of 3 M both with and without an electromagnetic field. In those figures, the intensity of the external electromagnetic field was applied. It was also found that the positions of the first peak of $g_{oo}(r)$ and second peaks of $g_{oh}(r)$ shifted to the distances bigger than 0.04 angstrom. In presence of microwave, we found that DMF aqueous solution preserves the structure characteristics, such as there appears to be a threshold microwave field intensity
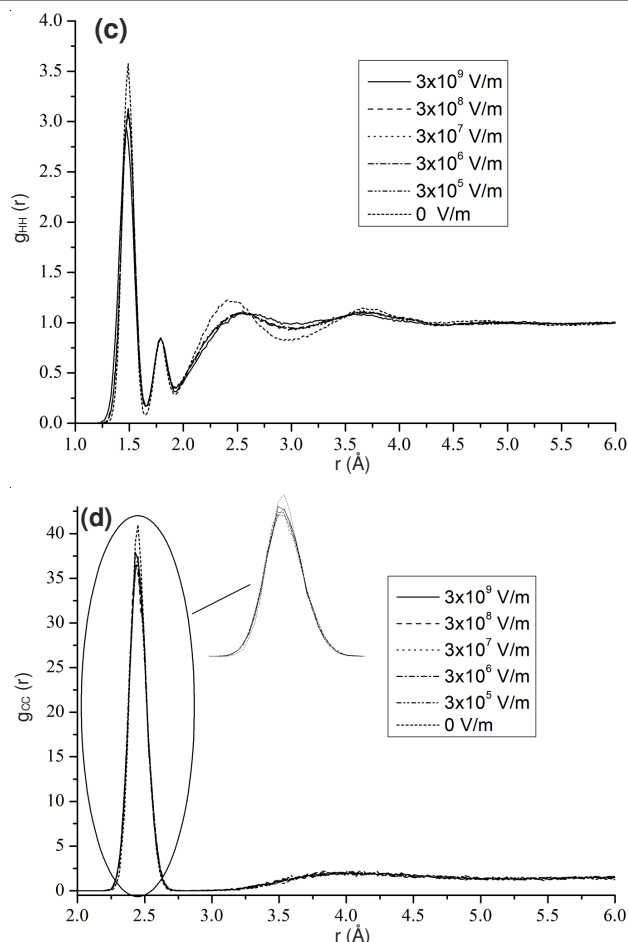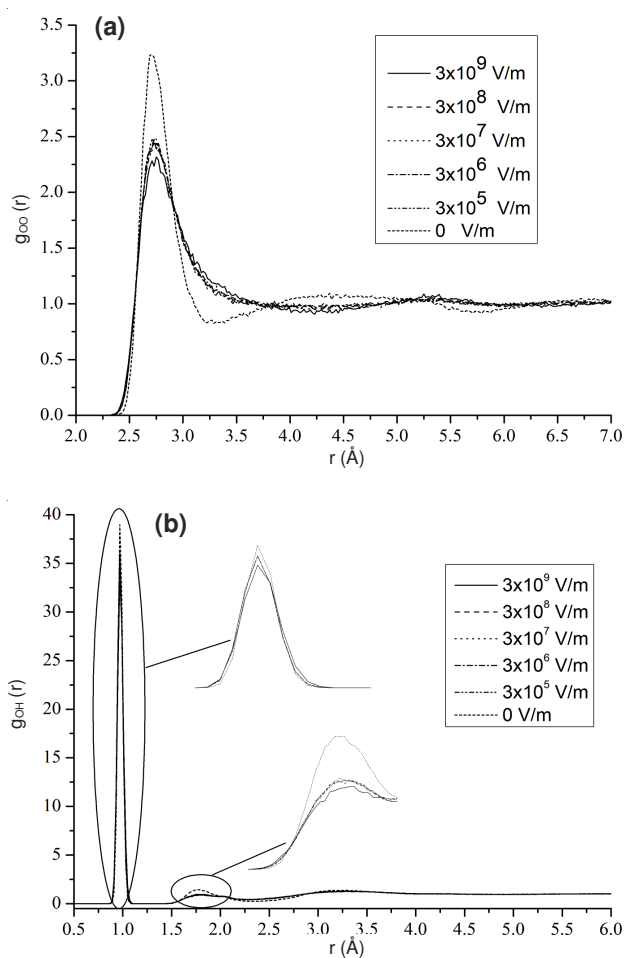
Fig. 1. Radial distribution functions of 3 M DMF aqueous solution with and without applied E/M field. (a) O-O, (b) O-H, (c) H-H and (d) C-C

below, which no tangible field effects are apparent, 10^5 V/m, the lowest field strength used in this study, there was no significant effect on the RDFs.

Fig. 2 presents microwave energy is partly transferred to intermolecular energies of mixture, which induce the change of distribution functions of the hydrogen bonding. The strongly nonlinear change can be categorized as one of microwave nonthermal effects.
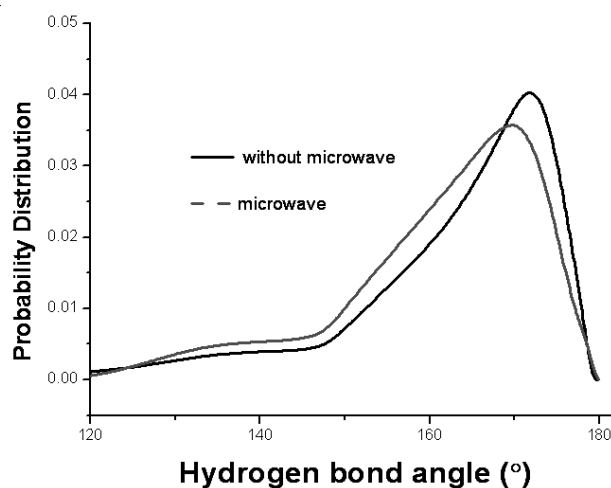
Fig. 2. Distribution functions of the hydrogen bonding

Conclusion

In this paper, non-equilibrium molecular dynamics simulations of the DMF aqueous were performed at 298 K under different strengths of external electromagnetic field, ranging from 0 to 3×10^9 V/m, to investigate the influence of an external field on structural and the distribution functions of the hydrogen bonding properties of DMF solution.

The results indicate DMF aqueous solution preserves the structure characteristics, such as there appears to be a threshold microwave field intensity below, which no tangible field effects are apparent, 10^5 V/m, the lowest field strength used in this study, there was no significant effect on the RDFs. Microwave energy is partly transferred to intermolecular energies of mixture, which induce the change of angle distribution functions of the hydrogen bonding. The strongly nonlinear change can be categorized as one of microwave nonthermal effects.

REFERENCES

1. J. Gao, J.J. Pavelites and D. Habibollazadeh, *J. Phys. Chem.*, **100**, 2689 (1996).
2. C. Desfrançois, V. Périquet, S. Carles, J.P. Schermann and L. Adamowicz, *Chem. Phys.*, **239**, 475 (1998).
3. R. Vargas, J. Garza, D.A. Dixon and B.P. Hay, *J. Am. Chem. Soc.*, **122**, 4750 (2000).
4. G.Z. Jia, K.M. Huang, X.Q. Yang, J.P. Song and L.J. Yang, *Acta Phys. Chim. Sin.*, **25**, 1906 (2009).
5. M. Yamagami, H. Wakita and T. Yamaguchi, *J. Chem. Phys.*, **103**, 8174 (1995).
6. D. Wallach, T. Wesley and J. Huntress, *J. Chem. Phys.*, **50**, 1219 (1969).
7. G. Schultzl and I. Hargittai, *J. Phys. Chem.*, **97**, 4966 (1993).
8. A.K. Sharma, D.R. Sharma, K.C. Sharma and D.S. Gill, *Z. Phys. Chem.*, **F141**, 15 (1984).
9. A.K. Sharma and D.R. Sharma, *Indian J. Pure Appl. Phys.*, **23**, 418 (1985).
10. S.J. Bass, W.I. Nathan, R.M. Meighan and R.H. Cole, *J. Phys. Chem.*, **68**, 509 (1964).
11. J. Barthel, K. Bachhuber, R. Buchner, J.B. Gill and M. Kleebaur, *Chem. Phys. Lett.*, **67**, 62 (1990).
12. Y. Lei, H.R. Li, H.H. Pan and S.J. Han, *J. Phys. Chem. A*, **107**, 1575 (2003).
13. G.Z. Jia, K.M. Huang, L.J. Yang and X.Q. Yang, *Int. J. Mol. Sci.*, **10**, 1590 (2009).
14. N.J. English and J.M.D. MacElroy, *J. Chem. Phys.*, **118**, 1589 (2003).
15. M.P. Allen and D.J. Tildesley, Computer Simulation of Liquids (Clarendon Oxford, 1987).
16. K.T. Chang and C.I. Weng, *Mol. Phys.*, **106**, 2515 (2008).