Size-change induced electrofreezing transition point shift of confined water

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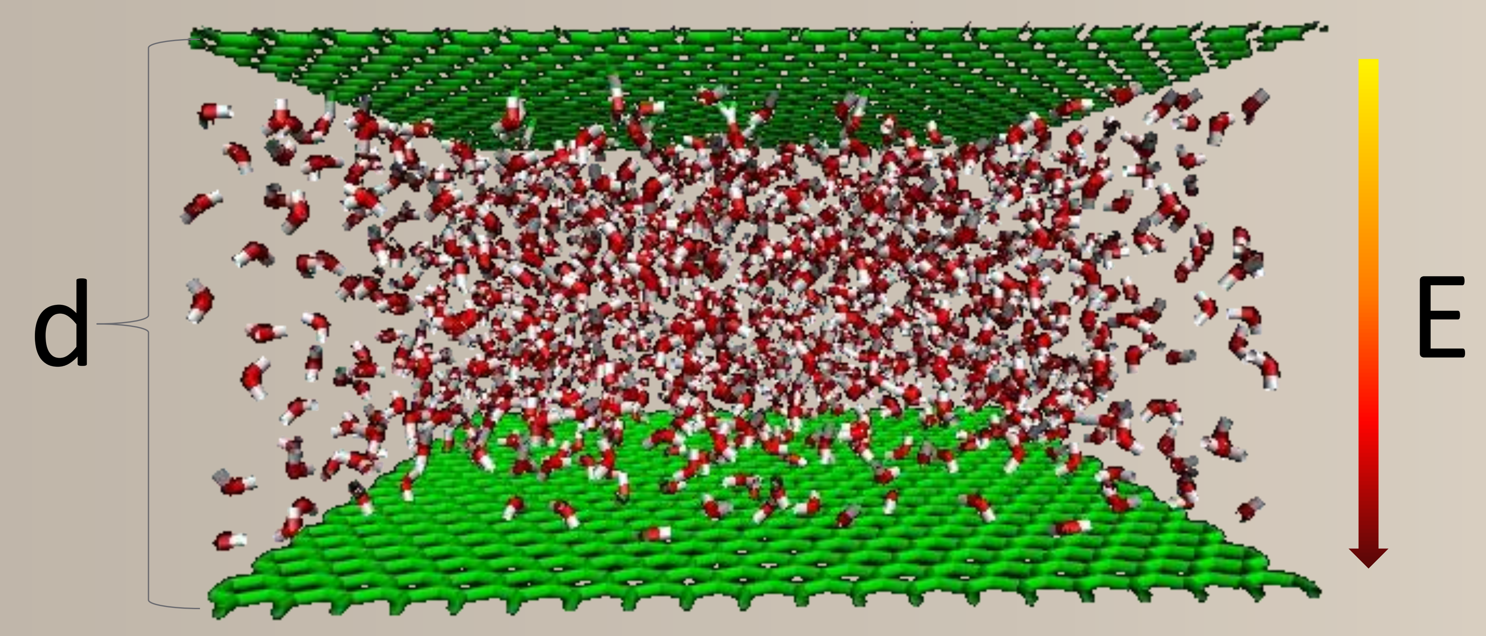
Introduction

Water is a kind of fantastic matter because of its many anomalous behaviors. Investigation on water in macro, micro and even nano scale appeals plenty of interests in the past several decades. Molecular dynamics simulation helps us figure out water behavior in nanoscale, which is different from bulk water. And the research on water in confined system has important meaning on biological, agricultural and industrial field, since it can imitate the real scene in the mentioned field.

In confined system, there have been many novel findings in phase transitions. Zangi et al. found that water can be changed into monolayer ice with the increase of distance between plates [1]. They also suggested that under electric field water can be freezing [2]. Qiu et al. found that besides electric freezing, there also exists electric melting [3]. In our work, we achieve electric freezing in a relative larger scale and find that with the increase of distances between plates, the transition point decreases.

Method

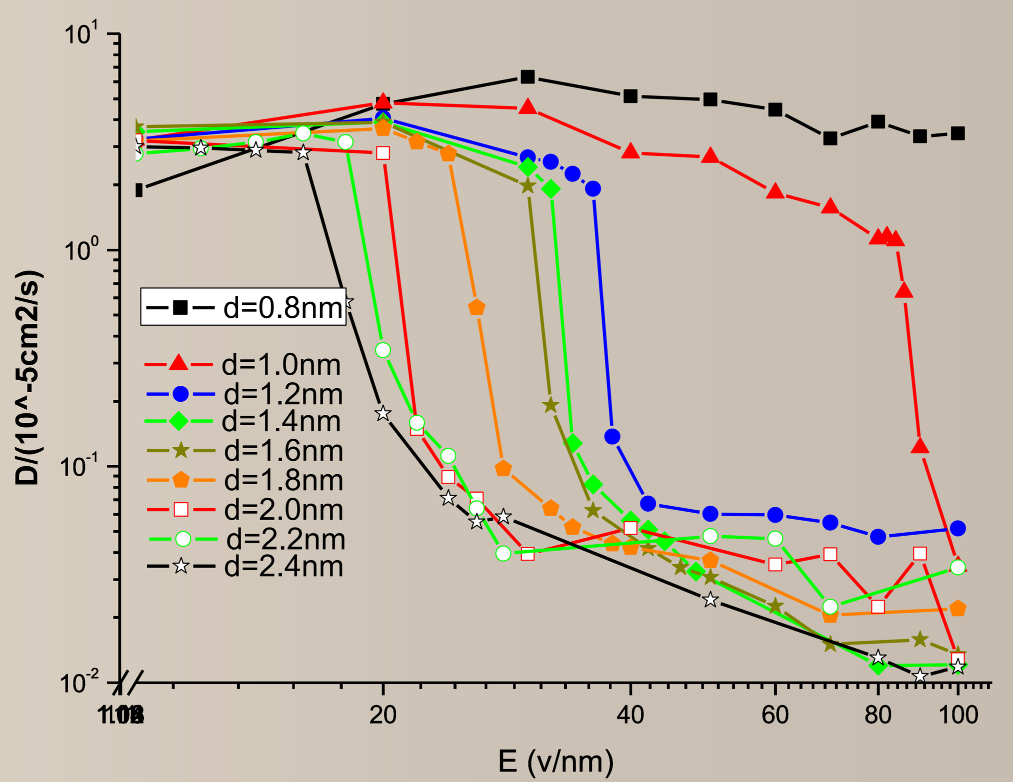
We set two graphene plates in the box which is $4.762nm \times 5.006nm$ in X and Y direction respectively, and leave enough space in Z direction to avoid non-physical phenomena. The distance between the plates is increased by $0.2nm$ starting from $0.8nm$. In each system, we make the density of water same. The external electric field is along Z axis, and is set to be from $0v/nm$ to $100v/nm$. All of the simulations are under Gromacs 4.0.7, SPCE water model and NVT ensemble (T=300K) are used. We first run $2ns$ to equilibrate the system, and another $3ns$ are used to calculate physical quantities. Besides, 0.9-1.4 cut-off pair are used in our work. The system is shown in the below picture.

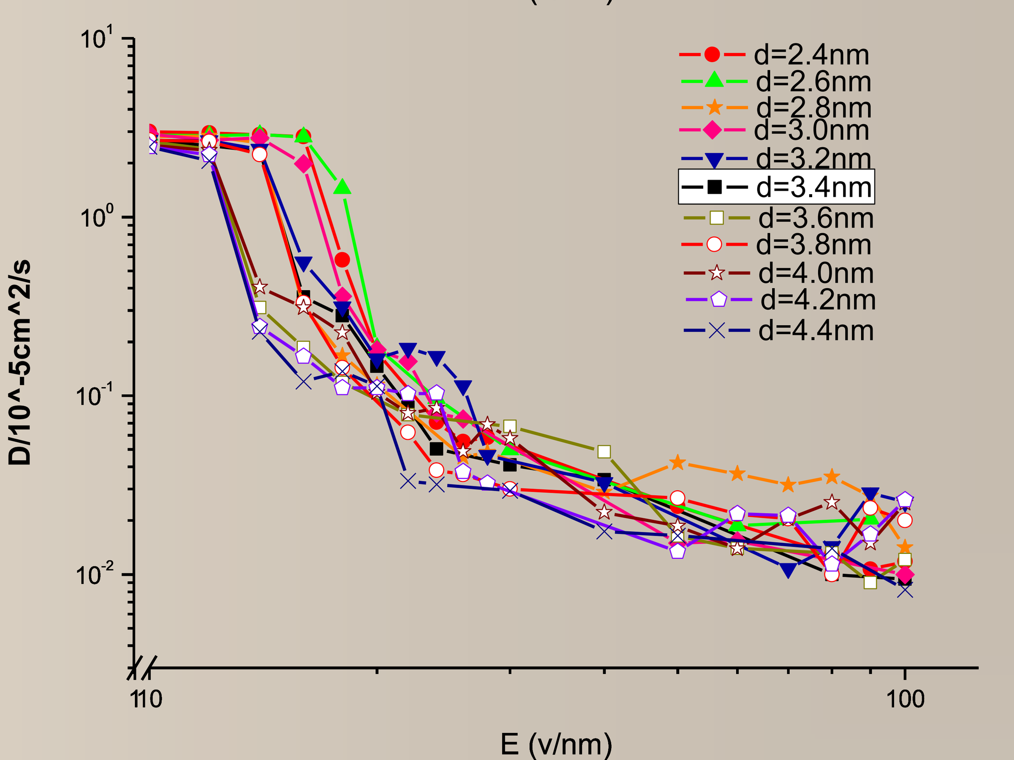


The design of our system, SPCE water model are used. E is electric field which is perpendicular to the plates, and d represents the distance between the two plates. In our work d=0.8-4.4nm, increased by 0.2nm, and E is from 0 to 100 v/nm.

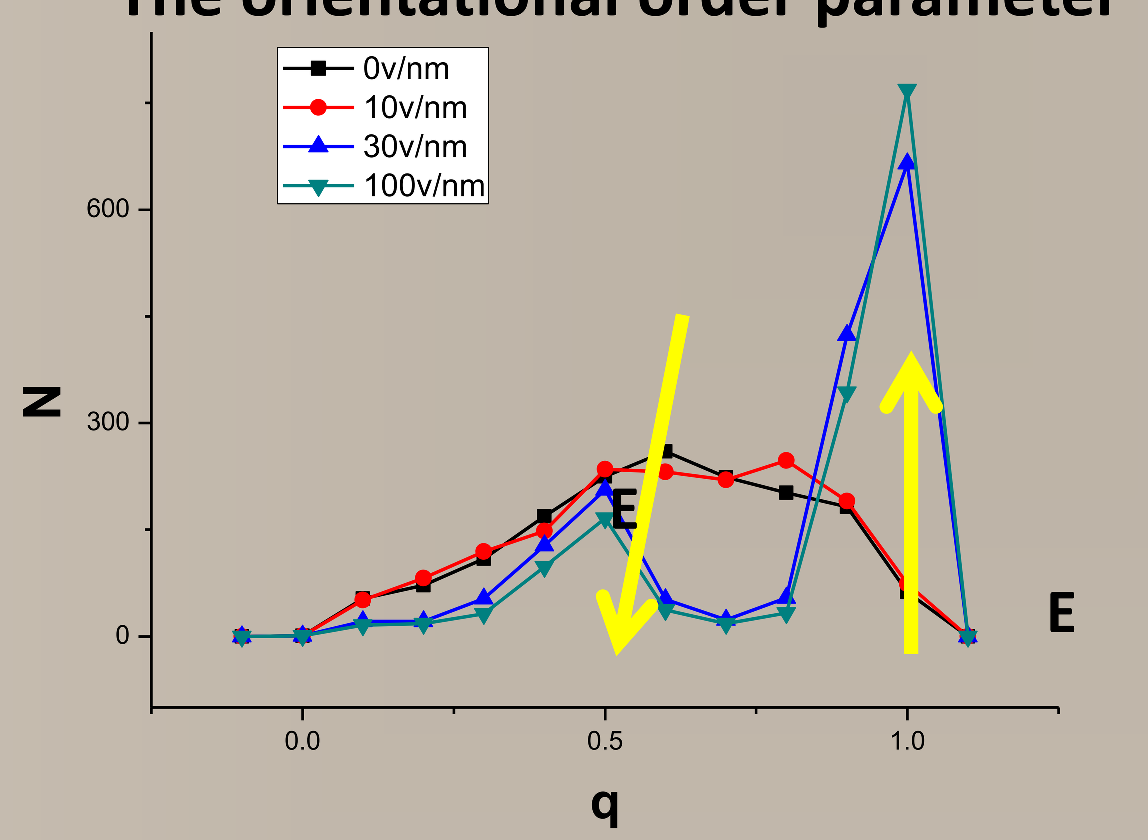
Results

Diffusion coefficient





The orientational order parameter



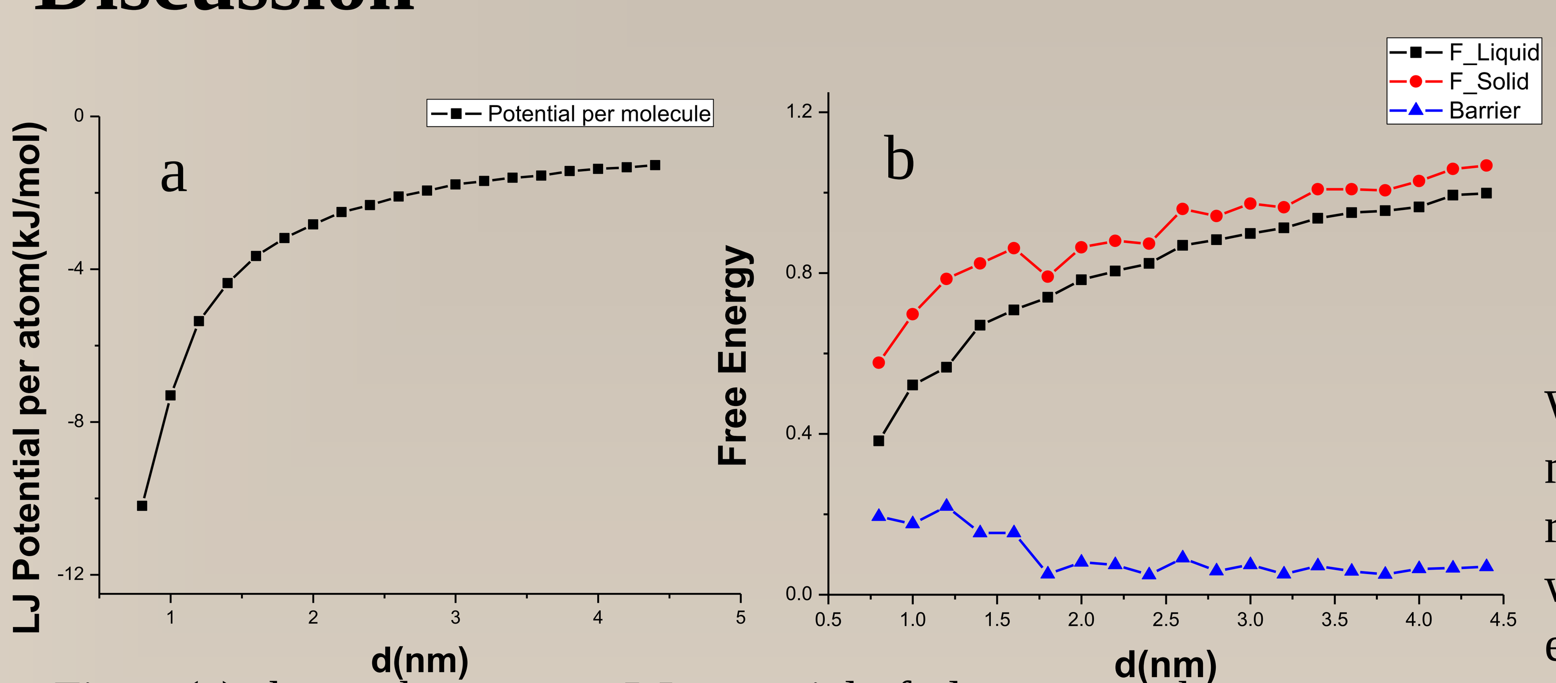
$$D_{xy} = \lim_{t\to\infty} \frac{1}{4}\frac{d}{dt} < [x_i(t) - x_i(0)]^2 + [y_i(t) - y_i(0)]^2 >$$

$$q = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}(cos\psi_{jk} + \frac{1}{3})^2$$

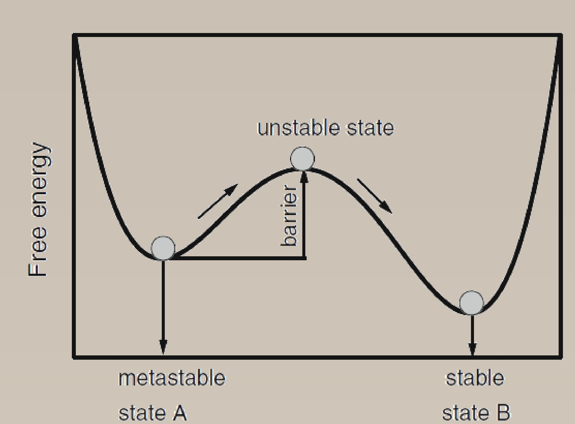
Summary

We have realized electric freezing in larger scale than previous work, and find that, in nanoscale systems, the electric freezing transition point decreases with increasing plates' distances. However, the tendency is weaken and even vanishes when the scale goes beyond the confined scale.

Discussion



Figure(a) shows the average LJ potential of plates on each water molecule. Figure(b) shows the free energy of water in liquid, solid state, as well as the free energy barrier for water to transit into ice.



We use the average LJ potential of plates on each water molecule to measure the level of how water is constrained by plates. And the result is that the level decreases with d increaseing, which leads that water in smaller system is more difficult to be activated by external electric field and predicts a higher barrier for water in smaller system to transit. The direct estimate of free energy barrier for each system also proves our result, because the barrier decreases with distance increasing.

References

1.R. Zangi et al. Physical Review Letters, 91,2(2003)
2.R. Zangi et al. J. Chem. Phys. 120, 7123 (2004)
3.H. Qiu et al. Physical Review Letters, 110, 19(2013)
4.J. R. Errington et all. Nature, 409(2001)
5.E. B. Moore et al. Phys. Chem. Chem. Phys., 12(2010)