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# Atomic Understanding of the Swelling and Phase Transition of Polyacrylamide Hydrogel

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A polymer network can imbibe copious amounts of solvent (water) and swell, and the resulting state is known as a hydrogel. In this study, we have made the modification for the all-atom consistent valence force field (CVFF) to investigate the swelling property of polyacrylamide (PAM) hydrogel by molecular dynamics simulation. We have built 21 hydrogel models with different solvent contents and calculate the average chemical potential and diffusion coefficient of solvent molecules in PAM hydrogel. We find that when the mass fraction of solvent is about 90%, PAM hydrogel reaches its free swelling limitation and loses the motivation of absorbing solvent. Furthermore, it is also found that PAM hydrogel has a phase transition phenomenon when the values of solvent chemical potential are between -23.4 kcal/mol and -20.4 kcal/mol. This study will provide insight into the basic parameters which are widely used in continuum mechanics analysis of hydrogels from atomic point of view and help researchers to improve the continuum mechanics model for neutral hydrogel.

 $Keywords\colon$  Diffusion coefficient; molecular dynamics; PAM hydrogel; phase transition; swelling.

## 1. Introduction

Flexible, long-chained polymers can crosslink into a 3D network by covalent bonds. The resulting material, an elastomer, is capable of large and reversible deformation. When contacting with a suitable solvent, e.g., water, the elastomer imbibes the solvent (water) and swells, resulting in an aggregate known as a hydrogel. Meanwhile, when environment stimuli change, the solvent in the hydrogel migrates out and evaporates, making the swelling process reversible. The hydrogel has attributes of both solid and liquid, i.e., elastic deformation results from strong chemical crosslinking between the long-chained polymers, and viscous migration results from weak physical interaction between the solvent molecules and the long-chained polymers.

The combination of the attributes makes hydrogels the great potential materials for various applications, such as medical devices [Peppas *et al.*, 2006; Wichterle and Lim, 1960], tissue engineering [Wong *et al.*, 2008; Lee and Mooney, 2001], actuators responsive to physiological cues [Dong *et al.*, 2006; Beebe *et al.*, 2000; Cho *et al.*, 2008], and packers in oil wells [Kleverlaan *et al.*, 2005]. Mixtures of macromolecular solid networks and solvents also constitute tissues in animals and plants, where the solid networks retain structural support, while the solvents enable the transport of wastes and nutrients. Before we apply the hydrogels to these devices, it is essential for us to understand the mechanics of hydrogel structures, including their swelling/deswelling and instability phenomena. In last few years, many research groups have studied these properties by continuum mechanics approach [Hong *et al.*, 2008; Jia *et al.*, 2014; Liang *et al.*, 2015; Lou and Chester, 2014; Drozdov, 2014; Hong and Wang, 2013; Chester and Anand, 2011; Hamzavi *et al.*, 2016].

Hong et al. [2008, 2009] developed a single-phase theoretical framework for neutral polymeric gels on the basis of a nonlinear field theory of swelling due to Gibbs [1878]. In their research they also developed a finite element subroutine and calculated the swelling property of hydrogel under different boundary conditions. Base on this work, Hong et al. [2010], Ding et al. [2013], Zhang et al. [2012] and Toh et al. [2013, 2014a, 2014b] studied the mechanical and swelling properties of neutral hydrogel, polyelectrolyte hydrogel, temperature sensitive hydrogel, pH sensitive hydrogel and photo-thermal sensitive hydrogel by theoretical approaches and FEM simulations. Liu et al. [2010, 2011, 2013, 2015] and Kang and Huang [2011] studied the buckling of hydrogels and explained the pattern formation in plants by this single-phase theory. Except for the single-phase theory, many other theoretical models were proposed, such as the phase field theory [Hong and Wang, 2013] and thermomechanically coupled theory [Chester and Anand, 2011]. In all these theories, there are many parameters which are hard to be quantified by traditional methods, such as solvent chemical potential, molecule size and diffusion coefficient of solvent. Usually, these parameters were chosen empirically in previous research and that would affect the accuracy and weaken the reliability of their calculations. However, molecular dynamics (MD) simulation is a new approach to solve this problem since it could provide the detailed structures and dynamics information of system at the molecular level [Tamai et al., 1996; Jang et al., 2007; Xu et al., 2015; Lei et al., 2013].

A suitable force field is the assurance for the computational accuracy of MD simulation. As for hydrogel, being able to achieve the swelling phenomenon is the basic requirement for the chosen force field. Nevertheless the traditional force field ignores the fact that the hydrophilic group in hydrogel has stronger interaction with water molecules, so the swelling process of hydrogel by MD simulation is rarely observed in previous studies. In present work, we modify the parameters of the all-atom Consistent Valence Force Field (CVFF) [Dauberosguthorpe *et al.*, 1988] and successfully perform the swelling process of both polyacrylamide (PAM) chain and cross-linked PAM. Besides, we also investigate the solvent absorbing

capacity and phase transition phenomenon of PAM hydrogel by calculating the solvent chemical potential and solvent diffusion coefficient. In what follows, Sec. 2 will provide the brief description of our simulation works, such as the methodology and modified force field. Section 3 gives the modeling details and discussion of swelling processes of PAM chain and cross-linked PAMgel. In Sec. 4, we build 21 hydrogel models with different solvent content and calculate the chemical potential and diffusion coefficient of solvent to investigate the water absorbing capacity of PAM hydrogel. Section 5 investigates the phase transition phenomenon of PAM hydrogel. Finally, the concluding remarks will be provided in Sec. 6.

## 2. Brief Description of Our Simulations

PAM hydrogel is composed of PAM polymer and water. Figure 1 shows the chemical formulas of PAM and water. The chemical group shown in the cycle is hydrophilic, which means that this group has stronger interaction with water molecules. That is why PAM can absorb water molecules and generate PAM hydrogel.

In present study, both commercial software Material Studio and open-source software Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) are used. Material Studio is mainly adopted to build MD models because of its powerful graphical operation interface. For the purpose of high computational efficiency, we use LAMMPS to run the MD simulation process. The simulation results are analyzed with the aid of atomistic configuration viewer (AtomEye). In our simulations, we use CVFF force field to describe the interactions between atoms, which has been used in many previous studies about hydrogel or other aggregate of polymer and inorganic matter [He *et al.*, 2011; Awasthi *et al.*, 2009; Wu *et al.*, 2011]. The energy formula of CVFF is described as Eq. (1),

$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{improper}} + E_{lj} + E_{\text{coul}}.$$
 (1)

The total energy consists of bond energy, angle energy, dihedral energy, improper energy, LJ energy and coulomb energy. The first four items are the energy contributed by bond interaction while the last two items are that contributed by non-bond interaction. Most of our CVFF parameters are output from Material Studio directly. In the force field output from Material Studio, for LJ item, only the



Fig. 1. (a) The chemical formula of PAM. (b) The chemical formula of water.

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LJ pairs $(E = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6])$	$\epsilon (\rm kcal/mol)$	$\sigma(\text{\AA})$
$N_{acylamino} - H_{water}$	3.0	3.0
U <sub>acylamino</sub> -H <sub>water</sub>	2.0	3.0

Table 1. LJ parameters we modified.

parameters between same atom types are defined. The parameters between different atom types are calculated as the geometric average value of the two atom types in LAMMPS. However, by using these parameter values, the interaction between hydrophilic group and water is quite weak; as a result, it fails to catch the swelling phenomenon of hydrogel. So we modify the parameters of LJ item between the hydrophilic group and water molecules (as shown in Table 1) to reinforce their interaction. In our MD simulations, we make use of NPT ensemble to keep the temperature and pressure at 298 K and atmosphere pressure, respectively. To study the swelling property and the water absorbing capacity of PAM hydrogel, we build two different kinds of MD models. More details are discussed in Secs. 3 and 4.

 $N_{acylamino}$ ,  $O_{acylamino}$  and  $H_{water}$  mean nitrogen atom in acylamino group, oxygen atom in acylamino group and hydrogen atom in water, respectively.

## 3. Swelling of PAM Chain and Cross-linked PAM

Since the traditional force field ignores the fact that the hydrophilic group has stronger interaction with water molecules, the swelling process of hydrogel by MD simulation is rarely observed in previous research. In the present work, we modify the parameters of CVFF force field and simulate the swelling process of both PAM chain and cross-linked PAM.

First, the swelling property of PAM chain is studied. We build a PAM chain which contains 50 repeat units in Material Studio as shown in Fig. 2(a). Then the model is imported into LAMMPS and relaxed at 298K and atmosphere pressure, after which the polymer chain shrinks and becomes a cluster as shown in Fig. 2(b). Figure 2(c) shows the water model we build in Material Studio which contains 2700 water molecules. By using mathematical software MATLAB, we dig a hole in water which has the same shape of polymer cluster as shown in Fig. 2(d). Figure 2(e) displays the MD model for swelling simulation (polymer cluster surrounded by water molecules). The final model contains 7477 atoms (502 polymer atoms and 2325 water molecules).

Usually, polymer chains are cross-linked into 3D polymer networks by chemical cross linker. Under suitable conditions, cross linkers can react with polymer chain. As a result, polymer chains are connected to cross-linker by covalent bonds. In our simulations, we use 2,4,6-trimethylolphenol as the chemical cross-linker. Before the cross-linking reaction, polymer chain also needs a modification at the amidogen. The raw materials for cross-linking reaction are PAM, formaldehyde and phenol and the reaction process [Moradi-Araghi, 2000] is displayed in Fig. 3.



Fig. 2. Modeling process of polymer immersed in water. (a) Polymer chain contains 50 repeat units. (b) Polymer cluster after relaxing. (c) Water model contains 2700 water molecules. (d) Water with a hole. (e) MD model for swelling simulation.



Fig. 3. The cross-linking reaction process. Formaldehyde and phenol react with water and generate the cross-linker 2,4,6-trimethylolphenol. At the same time, some amidogens in PAM chain are modified and the cross-linker reacts with these varietal amidogens.



Fig. 4. Swelling model of cross-linked PAM. (a) Unit cell of cross-linked PAM. (b) Cross-linked PAM contains 8 unit cells. (c) Cross-linked PAM cluster immersed in water, the brown atoms are water atoms and the atoms in the central part are polymer atoms.

From Fig. 3, we can see that three polymer chains are connected together by one cross-linker. Using Material Studio, we build the MD model of cross-linked PAM. Figure 4(a) shows the unit cell of cross-linked PAM. The two ends on one direction are bonded together at the boundary, which means when periodic boundary conditions are adopted, Fig. 4(a) could be regarded as an infinite 3D polymer network. Then we build a model contains 8 unit cross-linked cells, after which the polymers are imported to LAMMPS for simulation. Like dealing with the PAM chain, we relax the cross-linked PAM and imbed the shrunk polymer into water as shown in



Fig. 5. Swelling process of PAM. (a)–(d) Snapshots of PAM chain during simulation, water molecules are hidden. (e)–(g) Snapshots of cross-linked PAM during simulation. The brown atoms are water molecules.

Fig. 4(c). The final swelling model contains 285,794 atoms, including 12,248 polymer atoms and 91,182 water molecules.

During the MD simulations, we do nothing but let the systems relax themselves at 298 K and the atmosphere pressure. The results are shown in Fig. 5. In order to display the swelling process more clearly, water molecules in Figs. 5(a)-5(d) are hidden. Before simulation, the polymer chain is a cluster as shown in Fig. 5(a). During the simulation, because of the interaction between hydrophilic group and water molecules, polymer cluster swells and stretch to linear chain gradually as shown in Figs. 5(b)-5(d). For cross-linked PAM, the polymer is also a cluster before calculation as displayed in Fig. 5(e). Figures 5(f) and 5(g) show the snapshots of cross-linked PAM when calculation times are 3000 ps and 20,000 ps, respectively. We can see that the cross-linked PAM swells as water molecules diffuse into polymer. With the continuous diffusion of water molecules, the properties of water molecules inside and outside PAM show less and less difference. At some point, water molecules will lose the motivation of diffusion and the PAM reaches its equilibrium state of swelling. It has a significant meaning to determine the free swelling limitation of hydrogel and we will discuss it in next section.

## 4. Water Absorbing Capacity of PAM

When absorbing water, the volume of hydrogel can have a significant change. Hydrogel with different water contents can show different mechanical and chemical properties, which could be regarded as the measurement of activity of water molecules. Compared with pure water, the water molecules in hydrogel usually have lower chemical potential and diffusion coefficient because of the entanglement by hydrophilic groups in PAM, and that is why hydrogel can absorb water. In present work, we calculate the chemical potential and diffusion coefficient of water molecules in hydrogel and pure water to determine the water absorbing capacity of PAM hydrogel. In our simulations, we build 21 hydrogel models with water mass fraction  $M_{\text{water}}$  changing from 3.39% to 90.02%. Figure 6 shows several hydrogel models with different water contents. In each model, it contains only one unit cell of cross-linked PAM as shown in Fig. 4(a). So with higher water content, the model contains more water molecules and has larger size. Some details of our models (mass fraction of water  $M_{\text{water}}$ , number of water molecules N and the size of our model L) are listed in Table 2.

Figure 7 shows the average chemical potential of water molecules at different water contents. Basically, the average potential increases with the increasing of water content. However, when mass fraction of water is around 35%, the average potential has a sudden drop. We think this strange relation between potential and water content has a significant relationship with the configuration of hydrogel. When the water content is quite low, for example the configuration showed in Fig. 7(a), polymer chain is shrunk. So in the interaction zone of water molecules, it contains many polymer atoms. With the increase of water content, polymer swells as shown



Fig. 6. Hydrogel model with different water contents. (a)  $M_{\text{water}} = 23.79\%$ . (b)  $M_{\text{water}} = 42.90\%$ . (c)  $M_{\text{water}} = 65.32\%$ . (d)  $M_{\text{water}} = 81.11\%$ .

$M_{\rm water}$ (%)	N	L(Å)	$M_{\rm water}$ (%)	N	L(Å)
3.39	21	25.718	45.40	498	31.065
13.94	97	26.717	48.85	572	32.764
23.79	187	27.817	50.17	603	33.049
34.90	321	29.297	53.43	687	33.806
35.66	332	29.419	65.32	1128	37.278
36.12	339	29.485	70.32	1419	39.258
36.82	349	29.549	73.58	1668	40.810
37.22	355	29.658	76.02	1899	42.151
37.93	366	29.764	81.11	2572	44.206
39.07	384	29.949	90.02	5401	55.593
42.90	450	30.603			

Table 2. Details of our hydrogel models.

in Fig. 7(b). As a result, water molecules interact with less polymer atoms and it makes water molecules at a higher chemical potential state. When mass fraction of water increases to about 35%, polymer chains continuously swell. However, unlike the configurations showed in Figs. 7(a) and 7(b), water molecules come to interact with each other as shown in Fig. 7(c) and that makes the chemical potential decrease suddenly. As hydrogels reach higher water content state as shown in Fig. 7(d), PAM



Fig. 7. Average chemical potential of water molecules at different water contents. (a)–(d) The schematics of hydrogel configuration of different water contents.

chains further swell and polymer atoms in the interaction zone of water molecules further decrease, so the average chemical potential of water increases continuously.

We wonder when the PAM hydrogel would reach its equilibrium swelling state. Based on Fig. 7, we can get the relationship between total chemical potential of



Fig. 8. The relationship between total chemical potential and molecules number of water in PAM hydrogel.



Fig. 9. (a) Chemical potential of last absorbed water molecule at different water contents. (b) Water diffusion coefficient at different water contents.

water in PAM hydrogel and water molecules number which is plotted in Fig. 8. Since it is far away from reaching the hydrogel's saturated state at low water content, we only consider the last few points in Fig. 8. A smooth fit result is displayed as the red dash line and the slope of red line means the chemical potential of the last absorbed



Fig. 10. Relationship between free swelling stretch and solvent potential.

water molecule at a specific water content. From Fig. 9(a), we can see that there is a proportional relationship between chemical potential of last absorbed water molecule and water content. We also calculate the potential of pure water and it has almost the same value with that when water content is about 90%. With no chemical potential difference, there would be no motivation for water molecules diffusing into hydrogel.

We also calculate the diffusion coefficient of water molecules in hydrogel at different water contents as shown in Fig. 9(b). The diffusion coefficient D is calculated according to Eq. (2),

$$D = \frac{1}{6} \frac{d\left(\frac{1}{N} \sum_{1}^{N} \operatorname{dis}_{n}^{2}\right)}{dt}.$$
 (2)

dis<sub>n</sub> means the displacement of the *n*th water molecule in hydrogel. We can see that D is also proportional to water content. The diffusion coefficient at about 90% water content is almost equal to that of pure water, which also indicates that PAM hydrogel loses the motivation of absorbing water here. Base on the chemical potential and diffusion coefficient of water molecules, we can say that when the mass fraction of water is about 90% PAM hydrogel reaches its swelling limitation.

### 5. A Phase Transition Phenomenon of PAM Hydrogel

Since chemical potential of solvent is an important measurement of the swelling ability of hydrogel, we determine the relationship between free swelling stretch  $\lambda$  and average potential of solvent molecules. Free swelling stretch is defined as the ratio between the hydrogel length after and before swelling if no mechanical load is applied. The result is plotted in Fig. 10. Basically,  $\lambda$  increases with the increase

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of solvent potential. It is easy to understand because a higher potential difference between hydrogel and solvent corresponds to a greater driving force for solvent diffusion, i.e., a greater swelling ability for hydrogel. However, there is a sudden drawing back when chemical potential is between -23.6 kcal/mol and -20.4 kcal/mol. This phenomenon indicates that the swelling state can jump from state 'a' to state 'b' when solvent potential increase to -20.4 kcal/mol, and it can jump from state 'c' to state 'd' when solvent potential decrease to -23.6 kcal/mol as shown in Fig. 10. If we regard the configurations in Figs. 7(b) and 7(c) as two different phases, we may conclude that phase transition happens in PAM hydrogel when solvent potential is between -23.4 kcal/mol and -20.4 kcal/mol. We have studied the swelling property of hydrogel under different types of stimulations by theoretical approach [Ding et al., 2013; Toh et al., 2014a,b]. In these studies, both temperature sensitive and photo-thermal sensitive show phase transition phenomena when changing the surrounding stimulations. However, different with present work, our previous theoretical model for neutral hydrogel fails to catch this fantastic phenomenon of a sudden drawing back when chemical potential is between -23.6 kcal/mol and -20.4 kcal/mol, instead, it shows a proportional relationship between free swelling stretch and solvent potential. Usually, chemical potential is normalized by kT in our previous continuum mechanics and FEM studies of hydrogels, in which k represents the Boltzmann constant. At room temperature, kT = 0.592 kcal/mol. So we can use the chemical potential calculated in this work to our previous theoretical studies by dividing 0.592. The present research gives us a better understanding of hydrogel and inspires researchers to improve the theoretical model for neutral hydrogel.

## 6. Concluding Remarks

In present work, the swelling property of PAM hydrogel is studied by MD simulations. By making a modification to the traditional CVFF force field, both the swelling process of PAM chain and cross-linked PAM are observed in our simulations. On the other hand, according to the solvent chemical potential and diffusion coefficient we calculated, the solvent absorbing capacity of PAM hydrogel is investigated. The result shows that when mass fraction of solvent is about 90%, PAM hydrogel reaches its free swelling limitation. Besides, a phase transition phenomenon is observed when solvent potential is between -23.4 kcal/mol and -20.4 kcal/mol. This work may help researcher have a better understanding of hydrogel that were proposed before.

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