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Molecular Dynamics Study on Configuration Energy and Radial Distribution Functions of Ammonium Dihydrogen Phosphates Solution

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Molecular dynamics simulations were carried out to study the configuration energy and radial distribution functions of ammonium dihydrogen phosphate solution at different temperatures. The dihydrogen phosphate ion was treated as a seven-site model and the ammonium ion was regarded as a five-site model, while a simple-point-charge model for water molecule. An unusually local particle number density fluctuation was observed in the system at saturation temperature. It can be found that the potential energy increases slowly with the temperature from 373 K to 404 K, which indicates that the ammonium dihydrogen phosphate has partly decomposed. The radial distribution function between the hydrogen atom of ammonium cation and the oxygen atom of dihydrogen phosphate ion at three different temperatures shows obvious difference, which indicates that the average H-bond number changes obviously with the temperature. The temperature has an influence on the combination between hydrogen atoms and phosphorus atoms of dihydrogen phosphate ion and there are much more growth units at saturated solutions.

Key words: Ammonium dihydrogen phosphates solution, Configuration energy, Radial distribution function, Molecular dynamics simulation

I. INTRODUCTION

As a type of nonlinear optical crystal like the potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP) crystal is well known for its piezo-electric, non-linear optical and electro-optical properties and widely used in X-ray monochromators [1]. Despite some differences in the chemical composition, ADP and KDP have a number of important properties in common. In particular, they are characterized by low symmetry of crystal lattice and possess complex unit cells. A common distinctive feature is the contrast between strong covalent chemical bonds inside these anionic groups and relatively weak ionic bonds between a cation and the corresponding anionic group.

ADP crystal has usually grown in an aqueous solution by the temperature reduction method, since growth from an aqueous solution is particularly amenable to optical visualization. Recently, ADP has been given considerable interest among the researchers to grow this important crystal from solutions with faster rates by adopting cooling rates [2]. A lot of work has been done to study how to control the growth rates and growth habits of the ADP crystal. The surface micromorphol-

ogy, defect substructure, defect concentration, surface conductivity and microhardness have been studied by Ramakrishna [3]. The effect of EDTA on the growth kinetics, structure, optical and mechanical properties of ADP crystal has been discussed by Rahman *et al.* [4]. The kinetics of electron tunneling transfer under the conditions of thermostimulated mobility of recombining reactants in nonlinear KDP and ADP crystals has been investigated by Ogorodnikov *et al.* [5] using the method of mathematical modeling. Structural characterization at the atomistic level of ADP solution is crucial for the quantification and prediction of crystal growth rate, growth morphology, and their physical, chemical and mechanical properties. Study on microstructure of ADP solution is an important step for exploring the stabilization of crystal growth solution and growth mechanism of ADP crystal. However, the structure of mother liquid and the structural characterization at the atomistic level now face challenges. We have investigated thermodynamic properties and solutions micro-structure of KDP [6]. In this work, the solutions micro-structure of ADP and the effect of temperature on configuration energy and structural characterization at the atomistic level were studied in detail.

II. SIMULATION METHODS

Molecular dynamics simulations were carried out to study the configuration energy and the micro-structure

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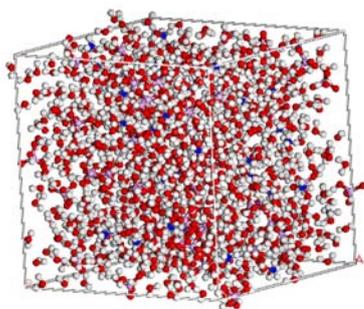


FIG. 1 Atomic structure model of saturated solution of ammonium dihydrogen phosphate at 293 K after 200 ps relaxation.

of ADP solution at different temperatures. All calculations were performed in the framework of the MD, using the Material Studio 4.0 from Accelrys Inc. (formerly Molecular Simulation, Inc.) [7]. In both energy optimization and MD simulations, the Discover package included in MS software was adopted and the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) [8–10] forcefield were used for all the components of the system. COMPASS which is based on the earlier class IICFF9X and PCFF forcefield is able to make accurate predictions of structural, conformation, vibrational, cohesive and thermophysical properties for a broad range of compounds both in isolation and in condensed phase.

The system size of the simulated solution is $2.69 \text{ nm} \times 2.69 \text{ nm} \times 2.69 \text{ nm}$. In order to allow the system to exchange heat with the environment at a controlled temperature, the canonical ensemble (NVT) molecular dynamics simulations were adopted while applying the periodic condition. The ammonium ion and dihydrogen phosphate ion were treated as a five-site and seven-site model, while the water molecule was treated as simple-point-charge (SPC) model respectively. The system contains 854 water molecules, 50 ammonium cations and 50 dihydrogen phosphate anions, which corresponds to the solubility 37.4% of ADP saturated solution at 293 K. Both molecular species, water and ammonium dihydrogen phosphate, were kept rigid throughout the simulations, and equations of motions were solved using leapfrog scheme with a timestep of 1 fs. The pre-equilibrium period was performed for 200 ps. The atomic structure model of saturated solution of ADP at 293 K after 200 ps relaxation is shown in Fig.1.

III. RESULTS AND DISCUSSION

A. Configuration energy

The configuration energy corresponding to different temperatures is shown in Table I. The relationship of ADP solution between kinetic, potential, total energy and temperature is shown in Fig.2, respectively. It is seen from Table I that the potential and total energy

TABLE I Kinetic energy E_k , potential energy E_p , total energy E_t at different temperature T .

T/K	$E_k/(\text{MJ/mol})$	$E_p/(\text{MJ/mol})$	$E_t/(\text{MJ/mol})$
273	10.775	-67.425	-56.650
283	11.353	-67.155	-55.802
288	11.671	-66.817	-55.146
290	11.398	-66.409	-55.011
291	11.446	-66.452	-55.006
292	11.472	-66.315	-54.843
293	11.562	-66.302	-54.740
294	11.743	-66.377	-54.634
295	11.958	-66.400	-54.442
296	11.515	-66.052	-54.537
298	11.785	-66.207	-54.422
303	11.764	-65.787	-54.023
313	12.242	-65.457	-53.215
323	12.937	-64.530	-51.593
333	13.119	-64.050	-50.931
343	13.433	-63.060	-49.627
353	14.238	-62.968	-48.730
363	14.269	-62.081	-47.812
373	14.803	-61.896	-47.093
383	15.350	-61.530	-46.180
393	15.498	-61.224	-45.726
403	15.693	-60.553	-44.860

of ADP solution basically increase with temperature, which indicates that the long-range attractive interaction dominates. The kinetic energy increases with the temperature, which is in agreement with tradition thermodynamic theory.

At saturation temperature 293 K, it can be seen from Fig.2 that the kinetic, potential and total energy have an obvious fluctuation, which indicates an unusually local particle number density fluctuation in the system. Thus we can conclude that the solution experience a crystallization process below saturation temperature. From Fig.2(b), it can be observed that the potential energy increases slowly with the temperature from 373 K to 404 K, which means that the ammonium dihydrogen phosphate has partly decomposed.

B. Structure of ADP solution

The most important information about the structure of ADP solution is calculated in the form of atom-atom radial distribution functions, $g_{i-j}(r)$. These functions give the probability of finding a pair of atom i and j with a distance r apart, relative to the probability expected for a completely random distribution of atoms at the same temperature [11].

Symbols Ow, Hw, and Op, Hp, hereafter, represent oxygen atoms and hydrogen atoms of water and dihydrogen phosphate.

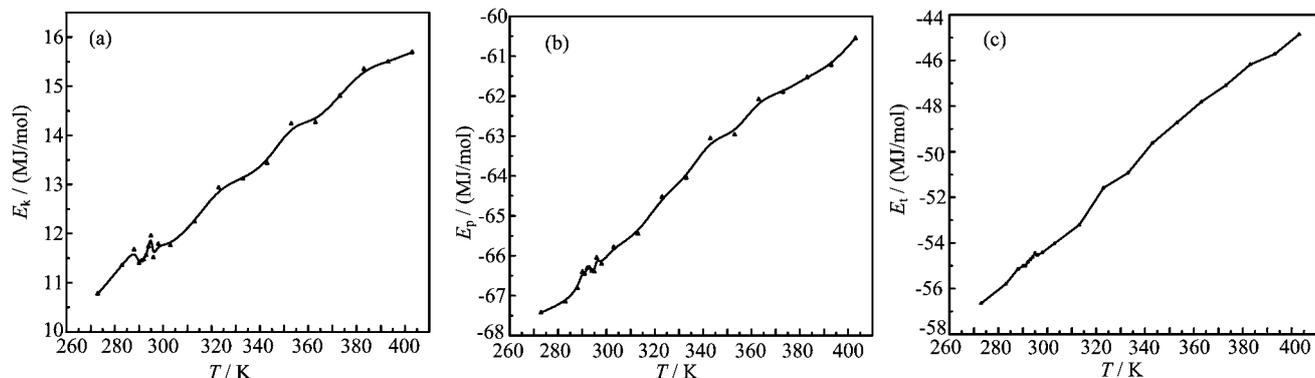


FIG. 2 The relationship of ADP solution between (a) kinetic energy E_k , (b) potential energy E_p , (c) total energy E_t and temperature.

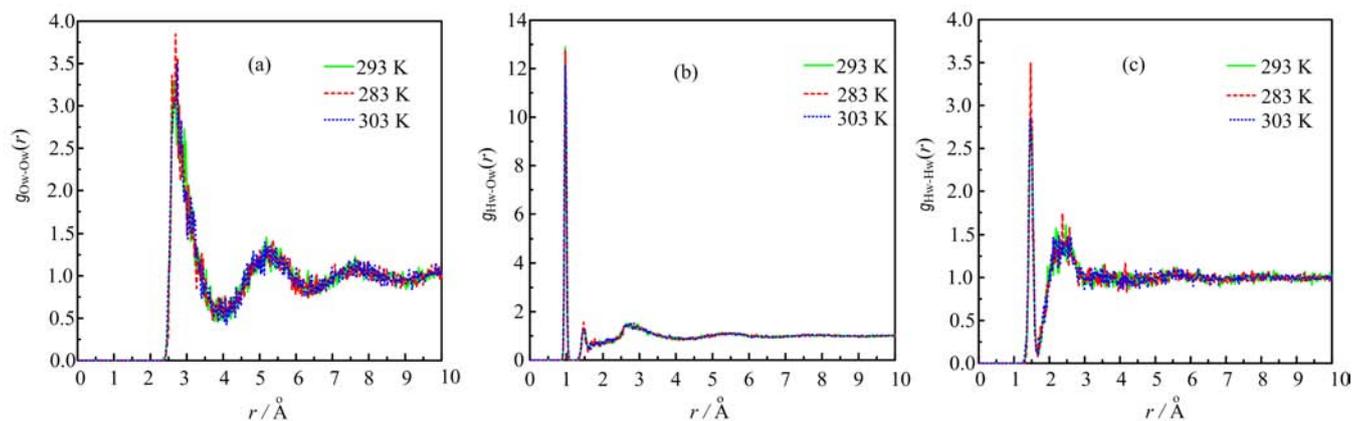


FIG. 3 Radial distribution functions for water-water of ADP solution at 283, 293 and 303 K. (a) Ow–Ow, (b) Hw–Ow, and (c) Hw–Hw.

drogen phosphate ion respectively, Hn represents hydrogen atoms of ammonium cation. The water-water radial distribution function $g_{Ow-Ow}(r)$, $g_{Hw-Ow}(r)$, and $g_{Hw-Hw}(r)$ at 283, 293, and 303 K, are shown in Fig.3.

The peaks of the distribution which represent the first, second and third coordinate zone diminish with the increasing of r . The rapid attenuation of the peaks indicates the order arrangement of water molecule disappears with the increasing of r . A pronounced maximum of $g_{Ow-Ow}(r)$, $g_{Hw-Ow}(r)$, and $g_{Hw-Hw}(r)$ appears near 2.8, 1.0, and 1.5 Å, respectively (see Fig.4). The first peak of $g_{Hw-Ow}(r)$ at three different temperatures (see Fig.4 (b)) shows obvious difference, which indicates the average H-bond number changes obviously with temperature. And comparing with $g_{Hw-Ow}(r)$ functions at three temperatures we can find that the first peak at 293 K is higher than that at 283 and 303 K which indicates that the H-bond number of saturated solution is maximal.

The water-ion radial distribution functions at 283, 293 and 303 K are shown in Fig.4 and Fig.5. Figure 4 shows that the radial distribution function approach to zero while the distance r is less than the effective colli-

sion diameter 1.3 Å between water molecule and ammonium dihydrogen phosphate molecule. And we can find that the radial distribution function approach to one while the distance r is greater than 3 Å, which indicates that the local partial number density is equal to the average partial number density at this point. The first peak of $g_{Hw-Op}(r)$ appears near 1.45 Å (see Fig.4(e)) followed a broader second maximum due to second hydration shell which is not involved in the hydrogen bond with the dihydrogen phosphate ion [12]. The maximal peaks of $g_{Hw-Hn}(r)$ and $g_{Hw-Hp}(r)$ appear near 1.5 Å (see Fig.4 (b) and (d)) which indicates that the water molecule has a strong interaction with the ammonium dihydrogen phosphate molecule.

Figure 5 shows the corresponding radial distribution functions between the oxygen atoms of water molecule and ions. The radial distribution function between the oxygen atom of water molecule and the hydrogen atom of the dihydrogen phosphate ion ($g_{Ow-Hp}(r)$) shows a very strong hydrogen bond structure with the first maximum at 1.65 Å (see Fig.5(d)) compared with the first peak of $g_{Ow-P}(r)$ and $g_{Ow-Op}(r)$ (2.7 and 2.68 Å). The first peak of $g_{Ow-Hn}(r)$ appears near 1.7 Å with a

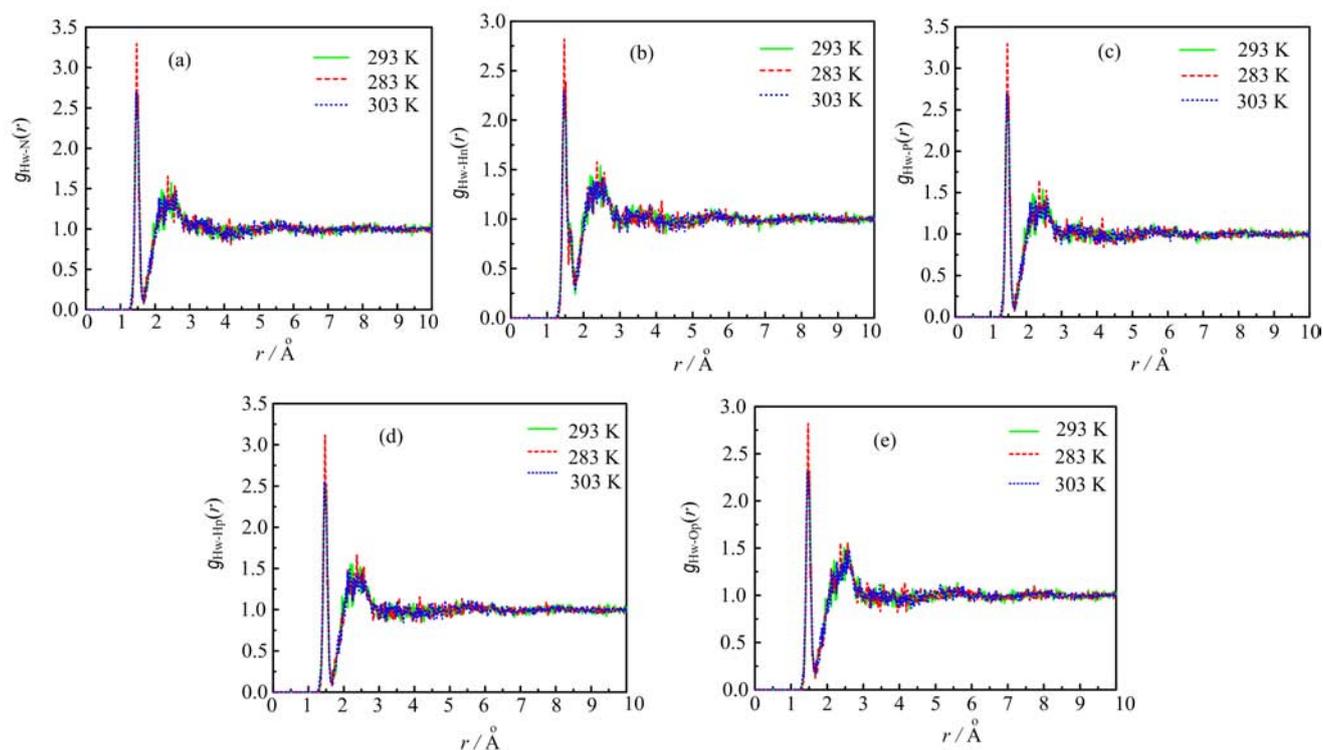


FIG. 4 Radial distribution functions between the ion sites and hydrogen of water molecule at 283, 293, and 303 K. (a) Hw–N, (b) Hw–Hn, (c) Hw–P, (d) Hw–Hp, and (e) Hw–Op.

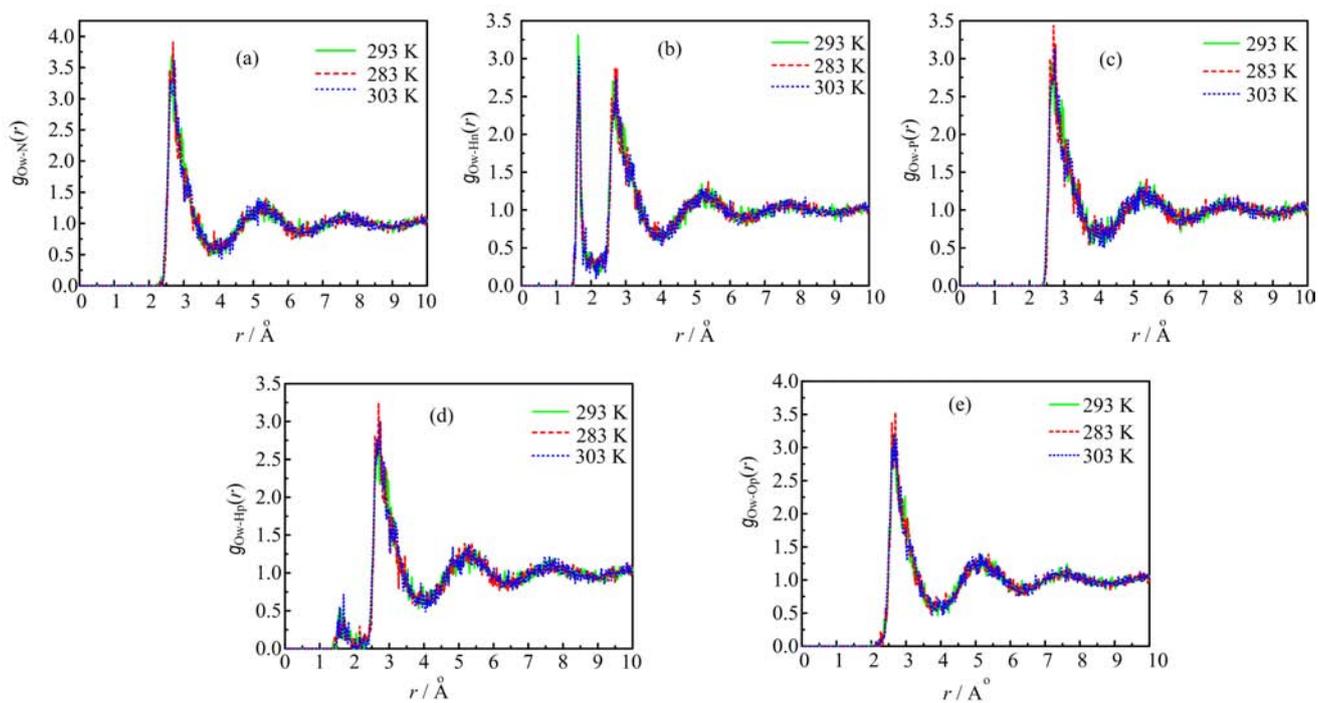


FIG. 5 Radial distribution functions between the ion sites and oxygen of water molecule at 283, 293, and 303 K. (a) Ow–N, (b) Ow–Hn, (c) Ow–P, (d) Ow–Hp, and (e) Ow–Op.

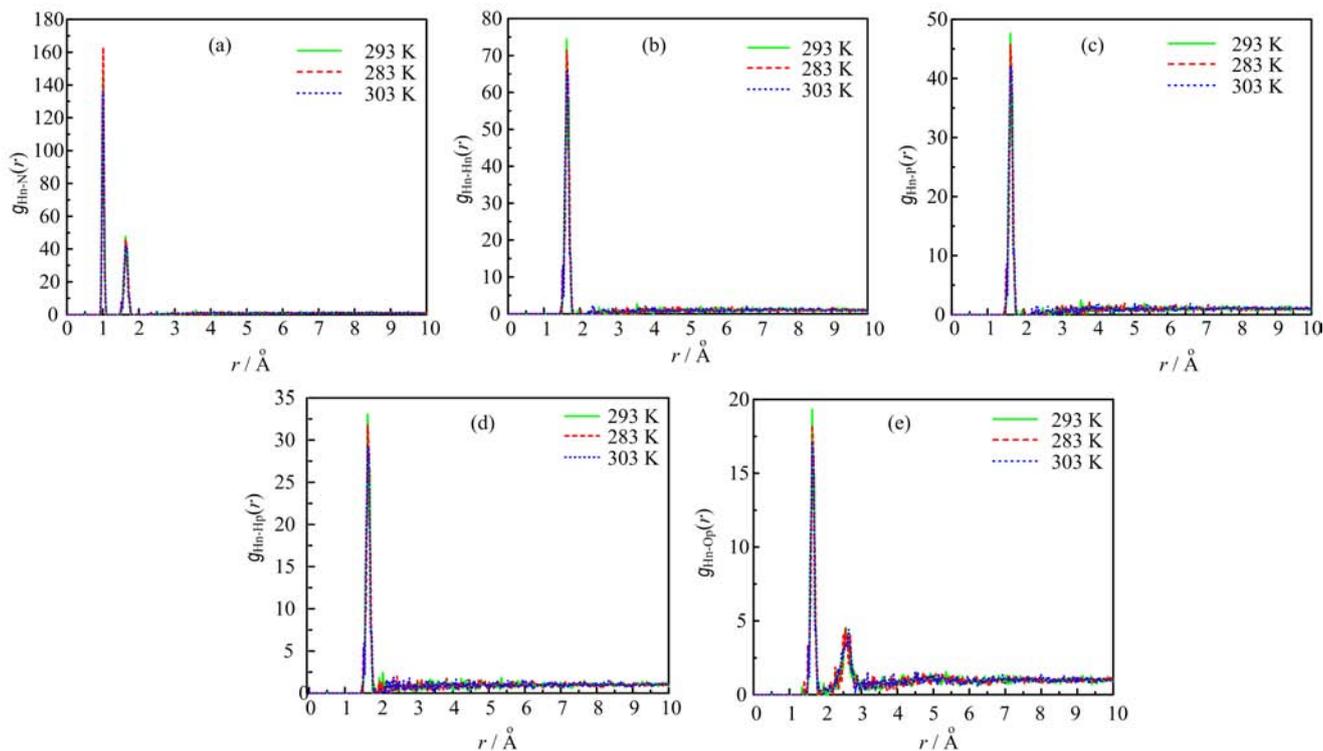


FIG. 6 Radial distribution functions for (a) Hn–N, (b) Hn–Hn, (c) Hn–P, (d) Hn–Hp, (e) Hn–Op pairs at 283, 293, and 303 K.

broader second sharp peak (see Fig.5(b)) due to second hydration which is not involved in the hydrogen bond with the dihydrogen phosphate ion. From $g_{\text{Ow-Hp}}(r)$ and $g_{\text{Ow-Hn}}(r)$ functions at different temperatures we can find that the second peak at 283 K is higher than that at 293 and 303 K, which indicates that the second hydration is inclined to occur at over-saturated solutions.

Figure 6 shows the radial distribution functions for Hn–N, Hn–Hn, Hn–P, Hn–Hp, Hn–Op pairs respectively at 283, 293 and 303 K. The first peak of $g_{\text{Hn-Hn}}(r)$, $g_{\text{Hn-P}}(r)$ and $g_{\text{Hn-Hp}}(r)$ appears near 1.7 Å compared with the first peak of $g_{\text{Hn-N}}(r)$ (1.0 Å), which indicates that the hydrogen atom of ammonium cation has a strong interaction with the nitrogen atom. The first peak of $g_{\text{Hn-Op}}(r)$ appears near 1.7 Å followed by a second maximum at 2.1 Å (see Fig.6(e)), which means that the second hydrogenation also occurs between the hydrogen atom of ammonium cation and oxygen atom of dihydrogen phosphate anion. The first peak of $g_{\text{Hn-Op}}(r)$ at three different temperatures (see Fig.6(e)) shows obvious difference, which indicate that the average H-bond number changes obviously with the temperature.

Figure 7 shows the radial distribution functions for Op–Hp, Op–Op, Op–N, Op–P, P–P pairs at 283, 293, and 303 K, respectively. The radial distribution function between the oxygen atom and the hydrogen of the dihydrogen phosphate ion ($g_{\text{Op-Hp}}(r)$) shows a very

hydrogen bond structure with the first peak at 1.0 Å followed by a broader second maximum due to the second hydration shell, which is not involved in the hydrogen bond with the dihydrogen phosphate ion. The first peak of $g_{\text{Op-P}}(r)$ (see Fig.7(d)) at 303 K is much higher than that at 283 and 293 K, which illustrates that temperature has an influence on the combination between oxygen atoms and phosphorus atoms of dihydrogen phosphate ion. There is no instinct peak in $g_{\text{P-P}}(r)$ (see Fig.7(e)), indicating there is no direct interaction between phosphorus atom.

Figure 8 shows the structural pair correlations for Hp–Hp, Hp–N, Hp–P, N–P, N–N pairs at 283, 293, and 303 K, respectively. It can be seen that the first peak of $g_{\text{Hp-P}}(r)$ is located at 2.0 Å. The first peak at 293 K is much higher than that at 283 and 303 K (see Fig.8(c)), which means temperature has an influence on the combination between hydrogen atoms and phosphorus atoms of dihydrogen phosphate ion and there are much more growth units at saturated solutions. In the ADP solution there is hardly any structure to be observed between N–P, N–N, Hp–N and Hp–Hp which illustrates that there is no direct interaction between them.

IV. CONCLUSION

Molecular dynamics simulations were carried out to study the configuration energy and radial distribution

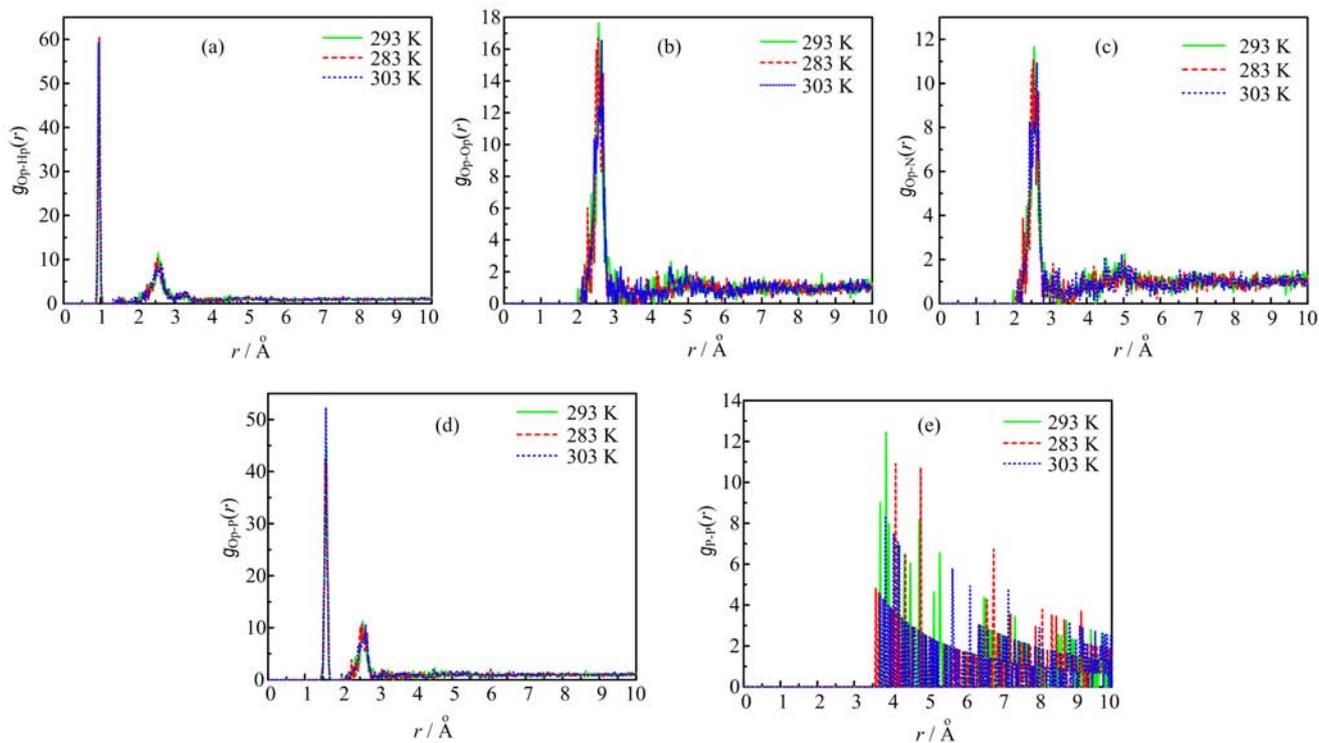


FIG. 7 Radial distribution functions for (a) Op-Hp, (b) Op-Op, (c) Op-N, (d) Op-P, and (e) P-P pairs at 283, 293, and 303 K.

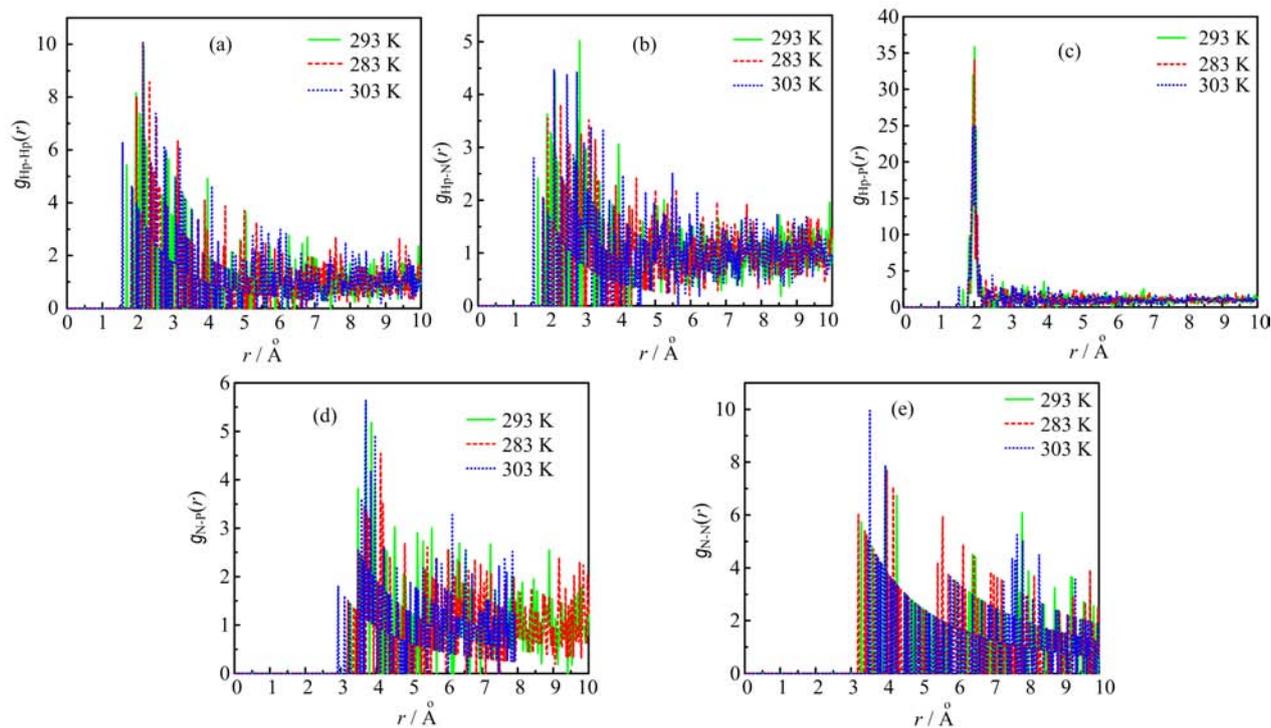


FIG. 8 Radial distribution functions for (a) Hp-Hp, (b) Hp-N, (c) Hp-P, (d) N-P, and (e) N-N pairs at 283, 293, and 303 K.

functions of ammonium dihydrogen phosphate (ADP) solutions at different temperatures. By simulating relatively large systems for long sampling periods, quantitatively useful results have been obtained. Firstly, an unusually local particle number density fluctuation was observed in the system at saturation temperature, and the potential energy increases slowly with the temperature from 373 K to 404 K, which indicates that the ammonium dihydrogen phosphate has partly decomposed. Secondly, the radial distribution function between the hydrogen atom of ammonium cation and the oxygen atom of dihydrogen phosphate ion at three different temperatures shows obvious difference, which indicate that the average H-bond number changes obviously with the temperature. Finally, the temperature has an influence on the combination between hydrogen atoms and phosphorus atoms of dihydrogen phosphate ion and there are much more growth units at saturated solutions.

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