Molecular dynamics simulation on moisture diffusion process for drying of porous media in nanopores

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ABSTRACT

Aiming at the problem that the mechanism of the moisture transfer in the nanopores of porous media has not been researched clearly. In this work, the molecular dynamics model of moisture diffusion in nanopores of porous media was established and the moisture diffusion process was analyzed by the molecular dynamics (MD) method. The Kelvin effect of water diffusion in nanopores of porous media was simulated and the model was validated by drying of potato slices. The results of simulation and verification showed that the molecular dynamics model could simulate and calculate the moisture diffusion coefficient of potato slices well. The maximum relative error of the diffusion coefficient between the simulation and experimental results is 8.6%. During the drying process, the temperature, pore size, wall roughness and the phase area fraction have important effects on the water diffusion in the nanopores. With the increase of the temperature, pore size and phase area fraction, and with the decrease of the wall roughness, the diffusion coefficients of porous media drying increased accordingly.

1. Introduction

The process of porous media drying includes heat and mass transfer processes, and its mechanism of mass transfer is quite complex [1–4]. There have been developed some theories of moisture transfer in porous media drying e.g. Philip-De Vries theory, Liquid diffusion theory, Evaporation-condensation theory, Luikov theory, Capillary flow theory, Whitaker's volume mean theory, Pore network theory [5–8]. These theories do not take full account of the influence of microscale effects (e.g. capillary effect, Kelvin effect, etc.) and microporous structure on the drying process. The existing problems of moisture transfer on drying process are that the pore size of porous media and the structure of holding water is complex [9], the physical mechanism of moisture transfer process is varied and the transmission process cannot be observed directly [10]. So, The mechanism of moisture transfer in the nanopores during drying process of porous media has not been researched clearly [11,12]. The rate of moisture transfer is influenced for many factors, such as, temperature, moisture gradients, topology of the porous media and physicochemical features of the porous walls during the drying

process of porous media [13], but the main factor is the moisture diffusion coefficient in nanopores. The greater the moisture diffusion coefficient, the higher the moisture transfer rate, the shorter the drying time [14] It is necessary clarify the influence of the diffusion coefficient on the drying process, mainly at nanopore scale [15]. The study on the fluid flow, adsorption and diffusion in nanopores by the method of molecular dynamics simulation have been widely concerned by many researchers. They have built different microporous structures during the research. For example, Kasiteropoulou et al. [16] studied the fluid flow in periodically grooved microchannels and the channel geometry they built was two parallel walls. The lower wall was flat whereas the upper wall consisted of protrusions modeled by rectangular elements. Huang et al. [17] studied the liquid-vapor interaction and adsorption of formaldehyde, oxocarbons, and water in graphitic slit pores and the parallel walls of the graphitic pores was built. Both sides of the slit walls consisted of three layers of graphitic and the pore width range was 2.6–8.3 nm. Huang [18] studied the separation of hydrogen sulfide from acidic gas mixtures inside metal-doped graphite micropores and the parallel walls of the slit pores was also built. The difference was one side of the wall consists of three layers of graphitic, but the other side of the wall was created by the metal Au and the pore width was 2.3 nm.

Therefore, the molecular dynamics simulation (MD) method [19–21] was used to analyze the drying process of moisture diffusion in nanopores of porous media and the molecular

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Nomenclature

p_0	saturated vapor pressure on straight liquid surface
p_r	saturated vapor pressure on curved liquid surface
σ	surface tension
M	liquid molar mass
R	ideal gas constant
T	system temperature
h	height of the protrusion,
b	width of the grooves
a	width of the protrusion
r	roughness factor
U_{ij}	total potential energy
U_{coul}	long-range electrostatic potential energy
U_{LJ}	short-range electrostatic potential energy
a, b	two different points of molecular electrostatic interaction,

i, j	two different water molecules,
q_i^a	charge of the action point a in the molecule i
q_j^b	charge of the action point b in the molecule j
r_{ij}^{ab}	distance between points a, b in molecule i, j
r_{ij}^{OO}	distance between atoms O in molecule i, j
O	oxygen atom
N	number of molecules
d	dimensionality of the system
MSD	mean square displacement

Greek symbols

σ_O	length parameters between atoms O
ε_O	energy parameters between atoms O
φ	phase area fraction

dynamics model of moisture diffusion was established in this paper. The model was validated by the diffusion coefficient of potato slice drying. The effects of drying temperature, pore size, pore wall roughness and phase area fraction on the moisture diffusion process in nanopores were studied.

2. Simulation details

2.1. Molecular dynamics model

The pore network theory thinks that moisture transfer has great superiority in the micropores of porous media during the drying process [22]. The water flow in micro pores is caused mainly by the capillary pressure of the different pore size and the water at the meniscus of the pore surface continues to evaporate [23], as shown in Fig. 1. It can be seen that the process of water migration and capillary effect are inseparable. However, it cannot be ignored that the main reason of the capillary effect is the solid-liquid wettability, which is to say the contact angle between the water and the inner surface of the pore channel ranges is from 0° to 90°. So, the diffusion coefficient of porous media drying is closely related to the process of water diffusion in nanopores.

The liquid surface will be bent due to the existence of "Kelvin effect" in nanopores of porous media. The Kelvin equation is given as Eq. (1).

$$\ln\frac{p_r}{p_0} = \frac{2\sigma}{r}\frac{M}{\rho RT} \tag{1}$$

where p_0 is the saturated vapor pressure on straight liquid surface (Pa), p_r is the saturated vapor pressure on curved liquid surface
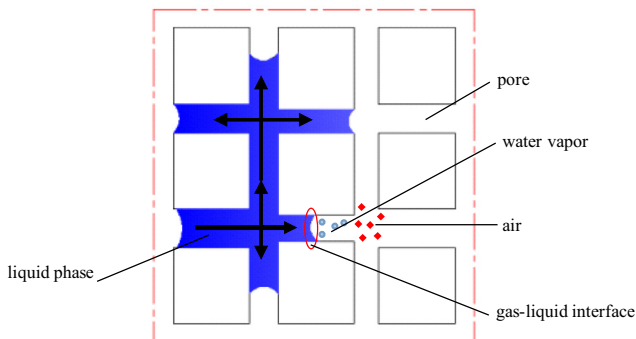
(Pa), σ is surface tension (N/m), r is meniscus radius (m), M is liquid molar mass (kg/mol), R is ideal gas constant, 8.31 J/(mol·k), T is system temperature (K).

In actual porous media, the pore walls are not completely smooth, and there are often some pits or bulge in the pore walls. This roughness can be reflected by the roughness factor r and the phase area fraction φ defined in the theories of Wenzel and Cassie [24]. The geometric parameters of the rough wall is defined as shown in Fig. 2. Where h is the height of the protrusion, b is the width of the grooves, a is the width of the protrusion, the width of the wall is l. The roughness factor r and the phase area fraction φ can be calculated by the Eqs. (2) and (3).

$$r = \frac{(a+b)l + 2hl}{(a+b)l} = 1 + \frac{2h}{a+b} \tag{2}$$

$$\varphi = \frac{al}{(a+b)l} = \frac{a}{a+b} \tag{3}$$

In this paper, the layers of FCC (face-centered cubic) atoms were used in the pore walls of the porous media, which was divided into smooth and rough pore wall. The energy parameter between wall atoms was 0.6216 kcal/mol. The SPC (Simple point charge) potential model of water molecular was used to generate liquid and vapor domains. The Materials Studio software was used to construct simulation system, while the LAMMPS code was used to solve the molecular dynamics model. The moisture diffusion models in the nanopores were shown in Fig. 3. The pores size was 180 Å × 45 Å × 45 Å ($L_x \times L_y \times L_z$). There were 3000 water molecules in the models. The wall thickness was 14.46 Å, and the layers could vary according to the roughness of the wall. The central space of the simulated box (45 × 45 × 45 Å) was the liquid phase and the water molecules were filled at the initial moment. The density of the liquid phase was 1 g/cm³. The two sides of the simulated box were the gas phase zone, and there was no water molecule at the initial time. At the beginning of the simulation, the water molecules first moved in the middle of the simulated box. When the
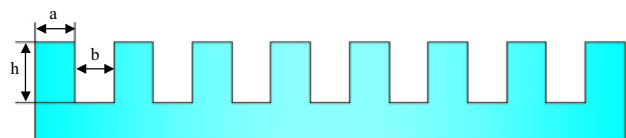

Fig. 1. Scheme of water diffusion in micro pores of porous media.

Fig. 2. Parameters of the rough wall.