separations

MDPI

Supplementary Material

Study of the Dissolution and Diffusion of Propane, Propylene and Nitrogen in Polydimethylsiloxane Membranes with Molecular Dynamics Simulation and Monte Carlo Simulation

Weibin Cai [1], Mingqian Wang [1], Gary Q. Yang [2,*], Zhijun Zhang [1], Yujun Wang [3] and Jiding Li [3]

Through the analysis of the optimization model, the characteristic parameters of the membrane can be obtained, such as fraction of accessible volume (FAV), cohesive energy density (CED) and radial distribution function (RDF). Part of the PDMS membrane volume is occupied by molecular chains, and the other part is free volume. FAV represents the percentage of free volume available in the membrane in the total volume of the membrane. CED is used to characterize the intermolecular force of polymer and judge the stacking degree of chain segments. RDF can reflect the aggregation characteristics between atoms or molecules. The Supporting Information (SI) presents the relevant knowledges and calculation techniques of FAV, CED, RDF, Diffusion coefficient, Solubility coefficient and permeability coefficient.

1. Fraction of free volume (FFV) and Fraction of accessible volume (FAV)

FAV represents the percentage of free volume available in the membrane in the total volume of the membrane. A probe sphere was used to determine FAV. When the radius of the probe sphere equals zero, the FAV obtained is FFV. The "Atom Volume & Surface" module can be used to calculate FFV and FAV. The Connolly surface was continuously rolled by a spherical probe to measure the free Volume. The FAV of PDMS membrane can be estimated by equation (1).

$$\mathrm{FAV} = \frac{V - V_O}{V} \times 100\% \quad (1)$$

where V is the cell volume and the Vo is the occupied volume. When the Connolly radius is zero, the FAV calculated according to equation 1 is considered to be equal to FFV.

2. Cohesive energy density (CED)

Cohesion energy (ΔE) is defined as the energy required to move 1mol of liquid or solid apart beyond the interaction range among its molecules. Cohesive energy density is the energy required per unit volume of the liquid or solid, which can reflect the intermolecular forces and judge the stacking degree of chain segments. CED can be calculated with equation (2).

$$\mathrm{CED} = \frac{\Delta E}{V} \quad (2)$$

where V is the cell volume. The Cohesive energy density was calculated by the "Analysis" module of Material Studio.

3. Radial distribution function (RDF)

RDF evaluates the microstructure of materials. It reflects the aggregation characteristics among atoms or molecules and represents the probability density of finding another atom at a certain distance away from one atom.

$$g_{AB}(r) = \frac{1}{\rho_{AB} 4\pi r^2 \delta_r} \frac{\sum_t^K \sum_{j=1}^{N_{AB}} \Delta N_{AB}(r \to r + \delta_r)}{N_{AB} \times K} \quad (3)$$

where ρ_{AB} is the density of the cell, N_{AB} is the number of atoms A and B in the cell, ΔN_{AB} is the number of B atoms present in the range r to $r + \delta_r$ away from atom A, and K is the total number of simulated steps.

4. Diffusion coefficient

The diffusion process of small molecules in the membrane are of great significance for the study of membranes separation performance. The different gas cells were simulated at 1200 ps at different temperatures in NVT ensemble, set the step size as 1 fs and output a frame every 500 steps, so that the total energy of NVT ensemble can be analyzed. The relationship between the total energy and time in NVT ensemble is shown in Figure S1. It can be seen from the figure that the total energy fluctuates slightly around 3600 kcal/mol. After it is determined that the system has reached equilibrium, the molecular trajectories were recorded and the mean square displacement (MSD) curves were obtained by using the "Analysis" module.

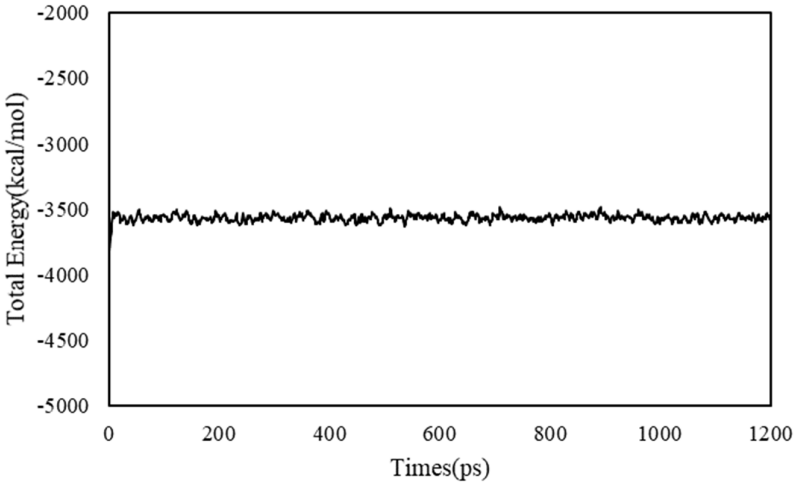

Figure S1. The relationship between the total energy and time in NVT ensemble.

The movement of gas molecules in the polymer is mainly a long-time oscillatory movement in holes and a short-time transition between holes, which leads to the diffusion process of gas molecules in the membrane from abnormal diffusion to Fick diffusion and then to abnormal diffusion. The diffusion coefficient of gas molecules in Fick diffusion state can be calculated according to the slope of mean square displacement curve by using Einstein's relation. The Einstein's relation is shown in equation (4).

$$D = \frac{1}{6N} \frac{d}{dt} \lim_{t \to \infty} \sum_{i=1}^{N} \langle \left(r_i(t) - r_i(t_0) \right)^2 \rangle \quad (4)$$

where N is the total number of diffused molecules a in the system, t is the simulation time, and $r_i(t_0)$ and $r_i(t)$ are the positions of a molecule i at the initial time t_0 and at time t, respectively, and D is the diffusion coefficient.

The relationship between MSD and time can be expressed as equation 5, according to equations 4 and 5, Einstein's relationship can be simplified to equation (6)

$$\text{MSD}(t) = < |r_i(t) - r_i(t_0)|^2 > \quad (5)$$

$$D = \frac{1}{6}\frac{d}{dt}\lim_{t\to\infty} \mathrm{MSD}(t) \tag{6}$$

In other words, if the molecules are in Fick diffusion, their diffusion coefficient can be expressed as 1/6 of the slope of the MSD-t curve.

5. Solubility coefficient

"Sorption" module was used to calculate the grand canonical Monte Carlo (GCMC) for the optimized simulation system. The pressure variation range was set to 10 to 1000 kPa, the task type was "Adsorption isotherm", and the simulation process was controlled by the "Metropolis" algorithm. Different small molecules (C_3H_8, C_3H_6, N_2) were selected as adsorbents, and the solubility coefficients of different gases molecules in PDMS membranes were calculated at different temperatures.

In this paper, the adsorption isotherm is fitted by Langmuir adsorption isotherm, and the linear expression of Langmuir adsorption formula is shown in equation (7):

$$\frac{p}{a} = \frac{1}{a_m b} + \frac{p}{a_m} \tag{7}$$

where p is pressure, a is the number of adsorbed molecules, a_m and b are constant.

As shown in equation (8), when the pressure is 0, the slope of the adsorption isotherm curve is the solubility coefficient:

$$S = \lim_{p\to 0}\frac{C}{p} \tag{8}$$

where C is adsorption concentration, S is the solubility coefficient.

6. Permeability coefficient

The permeability coefficient indicates the difficulty of gas molecules passing through the polymer membrane. The permeability coefficient depends on the solubility and diffusivity. The relationship between them is shown in equation (9).

$$P = D \times S \tag{9}$$

where P is the permeability coefficient, D is the diffusion coefficient and S is the solubility coefficient. The diffusion coefficient reflects the kinetic parameters of the gases and the polymer membranes, and the solubility coefficient reflects the thermodynamic characteristics of the polymer membranes.

7. Ewald sum and van der Waals interaction computation

The Ewald sum is the best technique for calculating electrostatic interactions in a periodic (or pseudo-periodic) system. The basic model for a neutral periodic system is a system of charged point ions mutually interacting via the Coulomb potential. The Ewald method makes two amendments to this simple model. Firstly, each ion is effectively neutralised (at long-ranged) by the superposition of a spherical Gaussian cloud of opposite charge centered on the ion. The combined assembly of point ions and Gaussian charges becomes the Real Space part of the Ewald sum, which is now short ranged and treatable. The second modification is to superimpose a second set of Gaussian charges, this time with the same charges as the original point ions and again centered on the point ions (so nullifying the effect of the first set of Gaussians). The potential due to these Gaussians is obtained from Poisson's equation and is solved as a Fourier series in Reciprocal Space. The complete Ewald sum requires an additional correction, known as the self energy correction, which arises from a Gaussian acting on its own site, and is constant. Ewald's method, therefore, replaces a potentially infinite sum in real space by two finite sums: one in real space and one in reciprocal space; and the self energy correction.

The VDW interaction was computed using the Lennard-Jones equation:

$$U(r_{ab}) = 4\varepsilon[(\frac{\sigma}{r_{ab}})^{12} - (\frac{\sigma}{r_{ab}})^{6}] \quad (10)$$

where ε is the minimum value of the potential function and σ is the distance when the potential is zero.

Nomenclature

Abbreviation	Full name
CED(cal·m^{-3})	Cohesive energy density
D(cm^2·s^{-1})	Diffusion coefficient
FFV	Free volume fraction
FAV	Fraction of accessible volume
MD	Molecular dynamics
MSD	Mean square displacement
PDMS	Polydimethylsiloxane
P(Barrer)	Permeability coefficient
RDF	Radial distribution function
S(cm^3 (cm^3·cmHg)$^{-1}$)	Solubility coefficient