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Force Field Parameterization of CH_4 - ZIF8 using Diversity based Self Adaptive PSO

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Abstract

Reduction in geenhouse gases is prime concern for the healthy atmosphere. Methane is one of the important contributors in the greenhouse gases. Porous material can be applied to reduce the greenhouse gases through gas separation and storage. Better understanding of physical and chemecical process at the molecular level can enhance the quality of involved material for greenhouse gasses reduction process. In this paper, intermolecular interaction variables have been optimized between methane (CH_4) and 2 methylimidazolate ($[C_4N_2H_5]^-$). Self adaptive form of Particle swarm optimization (SADPSO) has applied to achive the global solution. In SADPSO, present diversity available in the current population has considered for defining the adaptiveness in inertia weight. AMBER force field has used to define the parameters boundary value. Proposed solution has achived better performance in interaction energies in compare to AMBER based solution.

INTRODUCTION

In several pratical processes of life and industrial cycle, there is emission of Methane (CH_4) gas, which is one of the most harmful greenhouse gase. To reduce the percentage of this gas, there is need of efficient as well as cost effiective method. Use of porous material for gas separation and storage is the prime success towards that direction. Zeolitic imidazolate frameworks (ZIFs) have several important characteristics like high porosity, better thermal and chemeical stability etc., which make them to suite for gases separation and storage purpose. ZIF-8 is one of the ZIFs, which is composed of Zn^{2+} ion linked with ditopic 2-methylimidazolate ($[C_4N_2H_5]-$) ligands with a chemical formula of $Zn[C_4N_2H_5]_2$. It is applied for the separation of CH4 from natural gas and the reduction of CH_4 in the atmosphere. Structures of CH_4 molecule, ZIF-8 framework, and $[C_4N_2H_5]-$ molecule are shown in Figure 1. Behavior of absorption and diffussion of CH_4 in ZIF-8 can be understand better through intermolecular interaction. With the help of intermolecular interaction function and their parameterization through computational approach there is possibility to explore the intermolecular interaction much better efficiently. In this work, the parameters of Lennard-Jones are optimized based on *ab initio* using the heuristic method called the Self adaptive particle swarm optimization (SADPSO) in order to obtain the specific parameters for use in the molecular dynamic simulations of CH_4 in the ZIF-8.

RELATED WORK

A hybrid molecular simulation study ha reported [1] to examine adsorption and diffusion of CO_2 and CH_4 in zeolitic imidazolate framework-8 (ZIF-8). The structure flexibility of ZIF-8 has described using a recently developed force field (Zhang, L.*J. Am. Chem. Soc.*2013, *135*, 3722). The simulated adsorption isotherms in rigid and flexible ZIF-8 ware nearly identical and agree well with experimental data; thus, the effect of structure flexibility on adsorption is indiscernible. Diffusion and adsorption of CO_2/N_2 mixtures in the zeoliticimidazolate framework ZIF-8 has been investigated [2] by molecular dynamics (MD) and Gibbs ensemble Monte Carlo (GEMC) simulations. Structural changes called "gate opening" could be found for the adsorbed single-component gases and for the mixture. Quasi-elastic neutron scattering (QENS) measurements have been performed [3] to characterize at the molecular level the diffusion of CH_4 adsorbed at various concentrations in ZIF-8. [4] has presented an ab-initio derived force field to describe the structural and mechanical properties of metal–organic frameworks (or coordination polymers). The aim was a transferable interatomic potential that can be applied to MOFs regardless of metal or ligand identity. a general model represented in [5] for the permeation of CO_2 and CH_4 through Zeolitic Imidazole Framework-8 (ZIF-8) membrane synthesized *via in situ* layer-by-layer growth under microwave irradiation is developed. The model is formed based on the pressure drop concept in order to predict the intercrystalline properties of the ZIF-8 membrane according to the experimental permeation data of CO_2 and CH_4. A full set of flexible force field parameters for ZIF-8 is presented in [6], based on the AMBER, UFF parameters and the partial charges computed by the density-derived electrostatic and chemical charge method (DDEC). [7] presented a review focuses on research oriented toward elucidation of the various aspects that determine adsorption of CO_2 in metal–organic frameworks and its separation from gas mixtures found in industrial processes.

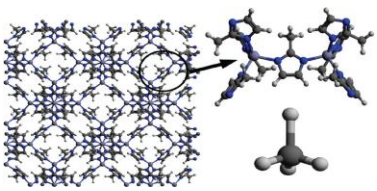

Figure 1: Structures of CH_4 molecule, ZIF-8 framework, and $[C_4N_2H_5]-$ molecule.

Table 1. The AMBER force field for atoms of ZIF-8 framework andCH4 molecules.

Molecules	Atoms	σ (˚ A)	ε (kcal/mol)
ZIF-8	Zn	1.960	0.013
	CR	3.400	0.086
	N	3.250	0.170
	CC	3.400	0.086
	H4	2.421	0.015
	CT	3.400	0.110
	HT	2.650	0.016
CH4	H	2.650	0.016
	C	3.400	0.110

MODELS AND CALCULATIONS

The geometrical structure of $[C_4N_2H_5]-$ is cut directly from the framework of single-crystal XRD data and the geometric model of CH_4 molecule is taken from the interaction site model with the bond length of 1.089 and bond angle of 109.5 . The interaction energy with the corrected basis sets superposition error ΔE_{CC} is represented by the following equation:

$$\Delta E_{cc} = E_{AB}(AB) - E_{AB}(A) - E_{AB}(B) \quad (1)$$

whereE_{AB} (AB), $E_A(A)$, and $E_{AB}(B)$ are the total energy of CH_4-$[C_4N_2H_5]-$ complex, the energy of CH_4 molecule, and the energy of $[C_4N_2H_5]^-$ molecule with the basis sets of both molecules, respectively . The Lennard-Jones function is used to estimate the intermolecular interaction between CH_4 with zero charges and $[C_4N_2H_5]-$ molecules:

$$U(r) = \sum_{i=1}^{m}\sum_{j=1}^{n}\left[\left(\frac{A_{ij}}{r_{ij}^{12}}\right) - \left(\frac{B_{ij}}{r_{ij}^{6}}\right)\right] \quad (2)$$

whereA_{ij}= $4\varepsilon_{ij}\sigma^{12}{}_i$, B_{ij}= $4\varepsilon_{ij}\sigma^{6}{}_{ij}$, σ_{ij}= $(\sigma_i+ \sigma_j)/2$, and ε_{ij}=$\sqrt{\varepsilon_i\varepsilon_j}$. σ and ε used for computing the interactions are shown in Table 1.

Although the general AMBER force field is famous for use in molecular dynamics, it is not suitable for some specific models.Thus, we use SADPSO algorithm with the interaction energies from quantum mechanics method with zero charges to optimize the specific intermolecular interaction parameters A and B.The objective function is the following chi-square equation:

$$\chi^2 = \sum_{k=1}^{N} w(k)\frac{\left(E_{CC}(k) - U(k)\right)^2}{df} \quad (3)$$

Counterpoise corrected interaction energy, (k) is the Lennard-Jones energy, (k) = $1/|E\mathrm{CC}(k) - wE|$ is the weighted value with respect to wE which is set very close to the minimum energy of ECC, $df = N - D$ is the degree of freedom, N is the total number of energies, and D is the total number of parameters. The optimized molecular interaction parameters and the original AMBER parameters are used in computer simulations for studying the adsorption and diffusion of CH_4 inporous material ZIF-8 by using DL POLY program. The flexible ZIF-8 framework is composed of eight (2 × 2 × 2) unit cells and loadings of CH4 molecules perunit cell are 1, 2, 4, 6, and 8, respectively. The NVT ensemble is set at 300K and time step of 1.0 fs. The simulations are equilibrated for 1.0 ns (1,000,000 steps), and further 1.0ns trajectories data are collected at every 200 time steps for studying the structural and dynamical properties. The site-site radial distribution functions (RDFs), (r), are a statistical analysis which is the probability of finding an atom β around a reference atom α:

$$g_{\alpha\beta}(r) = \frac{n(r)V}{4\pi r^2 N_\beta dr} \quad (4)$$

Where (r) is the number of β atoms in thickness of radius of circle dr at distance r, V is the volume of box, and $N\beta$ is the number of all β atoms. A smaller particle will diffuse without direction. The self diffusion coefficient, Ds (m^2/s), is computed by mean squared displacement (MSD) method using the Einstein relation for a three-dimensional system :

$$D_s = \lim_{t\to\infty}\frac{1}{6t}\langle\frac{1}{N}\sum_{i=1}^{N}|r_i(t) - r_i(t_0)|^2\rangle \quad (5)$$

Where N is the total number of guest particles and $r_i(t)$ and $r_i(t_0)$ are the position vectors of the diffusing molecule in framework at time t and time origin t_0.

PROPOSED SOLUTION & EXPERIMENTAL RESULTS

Self Adaptive PSO

PSO is similar to EC techniques in that, a population of potential solutions to the problem under consideration is used to probe the search space. However, in PSO, each individual of the population has an adaptable velocity (position change), according to which it moves in the search space. Moreover, each individual has a memory, remembering the best position of the search space it has ever visited. Thus, its movement is an aggregated acceleration towards its best previously visited position and towards the best individual of a topological neighborhood. Suppose that the search space is D dimensional, then the i-th particle of the swarm can be represented by a D-dimensional vector, Xi =[xi1, xi2,..xiD]. The velocity (position change) of this particle can be represented by another D-dimensional vector Vi = [vi1, vi2, . . . viD].The best previously visited position of the i-th particle is denoted as Pi =[pi1, pi2, . . . piD]. Defining ‘g’ as the index of the best particle in the swarm (i.e., the g-th particle is the best),’n’ is the best seen by that particular particle and let the superscripts denote the iteration number, and then the swarm is manipulated according to the (6) and (7).

$$V_{(n+1)\,id} = [w * V_{nid} + C_1 r_1 (P_{nid} - X_{nid}) + C_2 r_2 (P_{ngd} - X_{nid})] \quad (6)$$

$$X_{(n+1)\,id} = X_{nid} + V_{(n+1)\,id} \quad (7)$$

Where, ‘w’ is called inertia weight; ‘C_1’, ‘C_2’ are two positive constants, ‘C_1’ is called cognitive parameter and ‘C_2’is called social parameter. The role of the inertia weight ‘w’, in Equation (6), is considered critical for the PSO’s

convergence behavior. The inertia weight is employed to control the impact of the previous history of velocities on the current one. Accordingly, the parameter 'w' regulates the trade-off between the global (wide-ranging) and local (nearby) exploration abilities of the swarm. A large inertia weight facilitates global exploration (searching new areas), while a small one tends to facilitate local exploration. A suitable value for the inertia weight 'w' usually provides balance between global and local exploration abilities and consequently results in a reduction of the number of iterations required to locate the optimum solution. The parameters 'C_1' and 'C_2', are not very critical for PSO's convergence. However, proper fine tuning may result in faster convergence and alleviation of local minima. The parameters 'r1' and 'r2' are used to maintain the diversity of the population, and they are uniformly distributed in the range [0, 1]. PSO performances are highly depends upon the value of parameters selected. But there is no way possible to estimate the optimal values for these parameters hence best option is to develop the adaptive environment so that according to requirement it can opt the suitable value. In this paper two different environment have considered.

(a) Linear decreasing value for w (1 to 0.1) as given in Eq. 8. Initially set the inertia to a large value, in order to promote global exploration of the search space, and gradually decrease it to get more refined solutions.

$$w = M_{xw} - n*(M_{xw} - M_{nw})/(\lfloor 0.75 * M_{xn} \rfloor) \quad (8)$$

Where M_{xw} and M_{nw} are maximum amd minimum weight value, 'n' is iteration number and M_{xn} is maximum number of iteration.

(b) According to diversity status of solution population, self adaptive provision has proposed for inertia weight by Eq.9.

$$w_f = 1/\left(1 + 1.5 * e^{-2.5*f}\right) \quad (9)$$

Where 'f' is the current diversity status of population which can estimated by mean eucline distance of each solution with others and given by Eq.10.

$$f = \left(d_g - d_{\min}\right)/\left(d_{\max} - d_{\min}\right) \quad (10)$$

Where mean dg is distance value for best solution.

Mean eucline distance is estimated by (11)

$$d_i = \frac{1}{N-1}\sum_{j=1, j\neq i}^{N}\sqrt{\sum_{k=1}^{D}\left(x_i^k - x_j^k\right)^2} \quad (11)$$

Cognitive and social constant also have to change as population move one state to other and it is given by (12).

$$C_i(n+1) = C_i(n) \pm \delta, \; i = 1,2 \quad (12)$$

$$\delta \in [0.05 \; 1]$$

Depends upon value of 'f' four different state of population has considered.

(a) Embryo stage [0.8< f < 1],
(b) Exploration state [0.5< f ≤0.8],
(c) Expliotation state [0.2< f ≤0.5]
(d) Convergence state [0 < f ≤0.2].

EXPERIMENTAL RESULTS

Case1: Numeric optimization

Adaptive weight based PSO (AWPSO) ,in which the inertia weight change as given by Eq.8 has also taken to understand the benefits of diversity based self adaptiveness in pso. A benchmark numeric optimization where the test bench has taken as ACKLEY'S FUNCTION ,Eq.13,which is a multimodel function and there is need to find the minima of this function. Because of multimodel characteristics ,it is very difficult to obtain the solution. For 10 dimension size ,this problem has taken .population size for both algorithms have taken as 50,and total 1000 iterations are allowed to achive the solution .the comparative performance analysis have shown in Table2 for 10 different independent trails.it is clear that DAWPSO has given the better exploration to find the minimum value. The convergence characteristic for a trail has also be shown in Fig.2. Fig.3 shows the diversity available in the population with iteration along with corresponding inertia weight value.

$$F(x) = \exp\left[-0.2\sqrt{\frac{1}{N}\sum_{i=1}^{N}x_i^2}\right] - \exp\left(\frac{1}{N}\sum_{i=1}^{N}\cos(2\pi x_i)\right) + 20 + e \quad (13)$$

Table2: Function value for 10 independent trials in Ackley's function

Trail No.	AWPSO	DADPSO
1	14.9244	8.9546
2	23.8790	15.9193
3	42.7831	10.9445
4	15.9193	34.8234
5	25.8693	19.8992
6	20.8941	3.9798
7	16.9143	5.9698
8	17.9092	6.9647
9	25.8689	19.8991
10	15.9193	14.9244
Mean	22.0881	14.2279

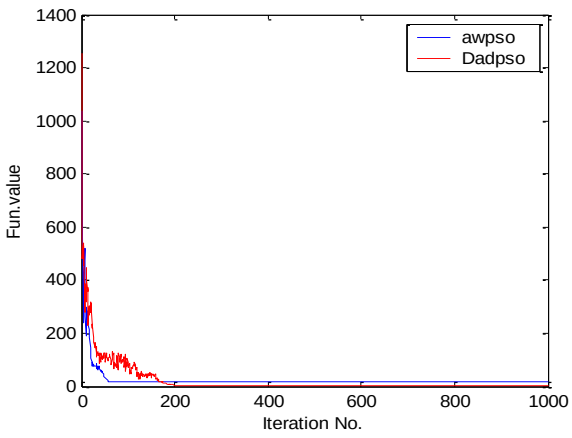

Figure 2. Convergence characteristic in Ackley's function

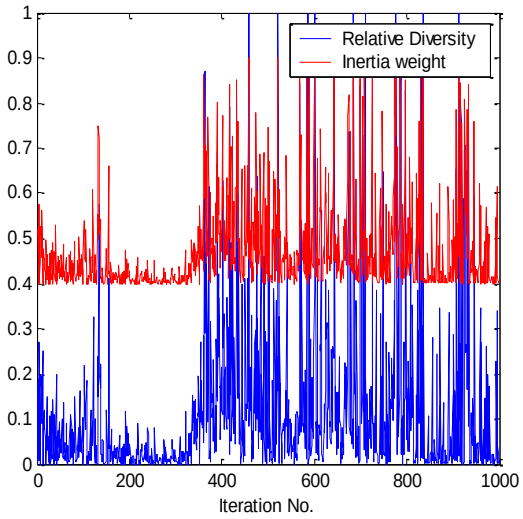

Figure 3. Diversity and Inertia weight with iteration in optimizing Ackley's function

Table 2: Parameters *Aij* and *Bij* (kcal/mol) obtained with AMBER force field and SADPSO method.

Atom		AMBER		SADPSO	
i	*j*	*Aij*	*Bij*	*Aij*	*Bij*
H	CR	86889	113	19015	103
	N	90349	137	17397	258
	CC	86889	113	19017	106
	H4	4245	15	433	26
	CT	98631	128	13592	28
	HT	7675	22	766	41
C	CR	925931	599	1677905	764
	N	1000645	740	1457348	1259
	CC	925931	599	1677910	764
	H4	60722	99	32283	34
	CT	1050025	679	1439950	347
	HT	98631	128	29849	41

Case2: Intermolecular interaction parameters

The intermolecular interaction parameters A_{ij} and B_{ij} between atom of CH_4 and atom of $[C_4N_2H_5]-$ obtained from AMBER force field and SADPSO method are presented in Table 2.It is clear that the optimized parameters provide the value of chi-square of 0.15859 which is much smaller than 35.052 obtained with AMBER parameters. Thus, the energies with SADPSO parameters are close to the QMenergies more than those obtained with the AMBER parameters.

CONCLUSIONS

Intermolucular interaction function parametrization for CH_4 molecules in the ZIF-8 framework has been investigated. To obtain the better parameters, exploration based approach self adaptive PSO has applied. The performance comparsion have given between the self adaptive PSO based solution against AMBER based solution. It is observe that there is better parameters have been achieved which has delivered the lesser chi-square value. With the proposed solution, it is hope that it will help to design the better environment to reduce the CH_4 in more efficient manner.

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