Supporting Information for

Theoretical Studies on Lennard-Jones Parameters of Benzene and Polycyclic Aromatics Hydrocarbons

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In order to explore the effect of molecular structure on Lennard-Jones (L-J) parameters, 10 kinds of PAHs were selected and divided into 3 groups. Molecules in the same group have similar molecular mass but different molecular structures. Their L-J self-collision parameters (by σ-ε and η-ξ methods with He as bath gas) are listed in Table S1, and plotted as a function of molecular mass in Fig. S1.

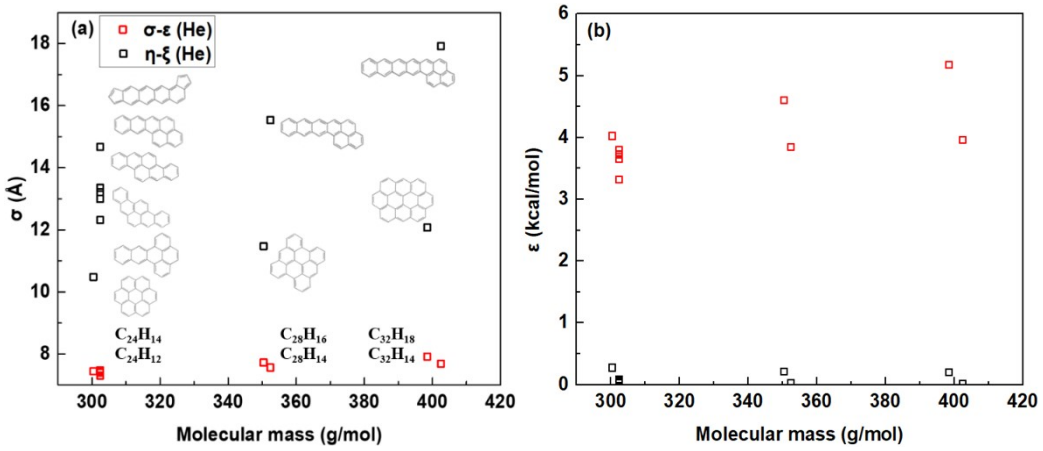

Fig. S1. Comparison of the L-J self-collision parameters obtained by σ-ε and η-ξ methods (He as bath gas) as a function of molecular mass. These PAHs are divided into three groups and their corresponding molecular structures and chemical formulas are marked next to and below the icons, respectively.

Table S1 Calculated effective collision diameters and well depths (σ_{AM}, ε_{AM}) by different averaging rules for a set of target-bath pairs.

Target	Bath gas	Averaging Rules					
		SA		σ-ε		η-ξ	
		σ(Å)	$\varepsilon(K)$	σ(Å)	$\varepsilon(K)$	σ(Å)	$\varepsilon(K)$
benzene	He	4.50	42	3.99	74	4.41	40
C_6H_6	N_2	5.09	79	4.80	92	5.03	80
1,3,5-cycloheptatriene	He	4.71	43	4.19	74	4.64	41
C_7H_8	N_2	5.27	94	4.92	116	5.19	99
toluene	He	4.96	33	4.16	78	4.81	34
C_7H_8	N_2	5.50	78	4.94	116	5.35	87
phenylacetylene	He	5.90	15	4.17	84	5.35	22
C_8H_6	N_2	6.49	25	5.18	73	6.00	41
styrene	He	5.60	21	4.22	84	5.21	27
C_8H_8	N_2	6.12	45	5.09	103	5.78	63
indene	He	5.23	33	4.30	87	5.03	36
C_9H_8	N_2	5.81	64	5.16	101	5.62	76
azulene	He	5.44	32	4.34	94	5.21	35
$C_{10}H_8$	N_2	6.03	58	5.30	93	5.82	70
naphthalene	He	5.45	32	4.33	94	5.23	34
$C_{10}H_8$	N_2	6.05	58	5.30	91	5.85	67
acenaphthylene	He	5.50	37	4.46	103	5.32	38
$C_{12}H_8$	N_2	6.12	61	5.48	85	5.98	69
biphenyl	He	6.32	20	4.52	98	5.96	25
$C_{12}H_{10}$	N_2	6.90	40	5.49	104	6.57	52

acenaphthene	He	5.50	39	4.53	100	5.33	40
$C_{12}H_{10}$	N_2	6.08	76	5.44	110	5.92	86
fluorene	He	6.27	23	4.56	103	5.89	28
$C_{13}H_{10}$	N_2	6.85	43	5.55	101	6.50	58
4,5-benzindane	He	6.07	28	4.63	102	5.77	32
$C_{13}H_{12}$	N_2	6.62	60	5.52	125	6.32	79
anthracene	He	6.63	19	4.57	110	6.21	24
$C_{14}H_{10}$	N_2	7.21	36	5.64	95	6.83	49
phenanthrene	He	6.35	23	4.59	110	5.98	28
$C_{14}H_{10}$	N_2	6.93	42	5.65	94	6.59	58
fluoranthene	He	6.46	25	4.69	117	6.08	30
$C_{16}H_{10}$	N_2	7.05	44	5.82	87	6.72	59
pyrene	He	6.21	29	4.68	119	5.88	35
$C_{16}H_{10}$	N_2	6.82	50	5.80	87	6.54	65
1,2-benzofluorene	He	7.29	16	4.77	115	6.75	21
$C_{17}H_{12}$	N_2	7.87	30	5.85	102	7.37	45
1,2-benzanthracene	He	7.51	15	4.78	122	6.95	20
$C_{18}H_{12}$	N_2	8.11	27	5.93	96	7.58	43
chrysene	He	7.48	15	4.77	123	6.91	21
$C_{18}H_{12}$	N_2	8.06	28	5.93	96	7.53	43
triphenylene	He	6.69	26	4.80	125	6.32	30
$C_{18}H_{12}$	N_2	7.27	48	5.96	96	6.95	62
1,2-diphenylbenzene	He	6.56	28	5.07	102	6.18	36
$C_{18}H_{14}$	N_2	7.14	52	6.05	117	6.82	70
1,3-diphenylben-	He	7.84	13	4.85	113	7.20	19

zene $C_{18}H_{14}$	N_2	8.39	25	5.96	113	7.83	40
11,12-benzofluoranthene $C_{20}H_{12}$	He	7.73	14	4.86	127	7.10	21
	N_2	8.33	24	6.08	90	7.74	42
perylene $C_{20}H_{12}$	He	6.72	29	4.87	132	6.43	32
	N_2	7.31	52	6.08	91	7.07	63
acenaphthan-thracene $C_{20}H_{14}$	He	7.83	13	4.87	127	7.17	21
	N_2	8.40	26	6.03	127	7.75	48
picene $C_{22}H_{14}$	He	8.54	10	4.92	132	7.83	16
	N_2	9.12	20	6.15	98	8.47	34
Coronene $C_{24}H_{12}$	He	6.73	36	5.01	144	6.53	37
	N_2	7.37	59	6.34	81	7.22	66

Table S2 Lennard-Jones self-collision parameters for H_2, He, N_2, O_2, Ar obtained from Jasper and Miller.[1]

Bath gas	σ (Å)	ε (K)
H_2	2.92	38
He	2.58	10
N_2	3.68	98
O_2	3.46	107
Ar	3.33	137

Table S3 Self-collision diameters (σ_A) and well depths (ε_A) calculated by different averaging rules with He as bath gas.

Target		Averaging rules			
Chemical formular	Compound name	$\sigma-\varepsilon$		$\eta-\xi$	
		σ	$\varepsilon\ (K)$	σ (Å)	$\varepsilon\ (K)$
$C_{24}H_{12}$	coronene	7.44	2027	10.48	137
$C_{24}H_{14}$	dibenzo(A,H)pyrene	7.42	1874	13.21	26
	naphtho[2,3-e]pyrene	7.47	1911	12.32	44
	dibenzo(A,I)pyrene	7.43	1881	13.00	30
	naphtho[2,3-a]pyrene	7.40	1839	13.36	25
	hexacyclo[11.11.0.0^{3,11}.0^{4,8}.0^{15,23}.0^{17,21}]tetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecaene	7.30	1673	14.67	15
$C_{28}H_{14}$	phenanthro[1,10,9,8-opqra]perylene	7.73	2320	11.47	106
$C_{28}H_{16}$	naphtho(2,1,8-uva)pentacene	7.56	1937	15.53	14
$C_{32}H_{14}$	ovalene	7.92	2606	12.08	101
$C_{32}H_{18}$	naphtho(2,1,8-yza)hexacene	7.69	1995	17.92	8

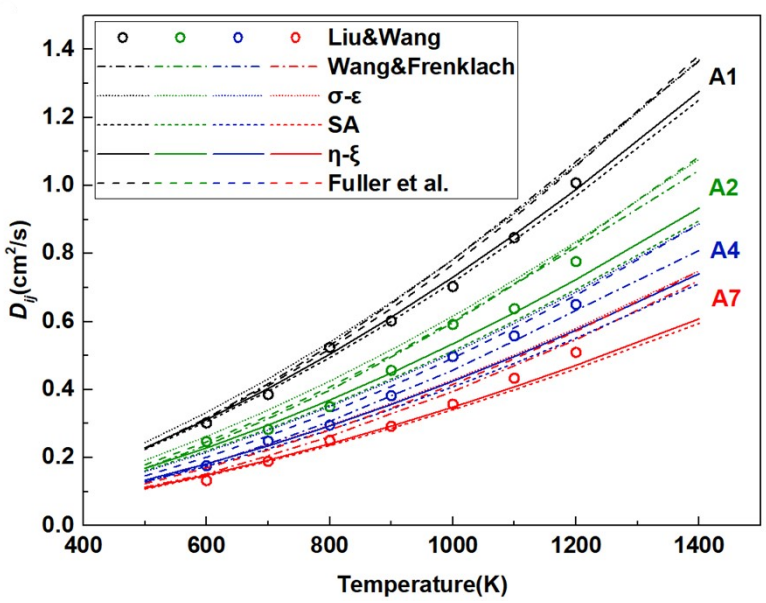

Fig. S2. Comparison of D_{ij} obtained by six different methods for four kinds of aromatic hydrocarbons in N_2 at 1 atm: benzene (A1), naphthalene (A2), pyrene (A4) and coronene (A7). The six methods are σ-ε, SA, η-ξ, empirical method by Wang and Frenklach,[2] empirical method by Fuller et al.,[3,4] and molecular dynamics simulations by Liu and Wang.[5]

As shown in Fig. S2, all six methods predict that the larger the molecular mass, the smaller the binary diffusion coefficient. In general, the binary diffusion coefficients calculated using the methods of σ-ε, Wang&Frenklach, and Fuller et al. are larger than those from SA and η-ξ by 0.02-0.12cm^2/s (8.8%-9.4% of SA method) for A1, 0.03-0.18 cm^2/s (18.7%-20.3% of SA method) for A2, 0.03-0.18 cm^2/s (23%-24.8% of SA method) for A4, 0.03-0.15 cm^2/s (24.9%-26% of SA method) for A7. This is consistent with the results of L-J self-collision diameter presented in Fig. 3. The results of SA and η-ξ are relatively close to each other, while the results of Fuller et al., Wang&Frenkalch, and σ-ε are relatively close to each other except for A4, for which Wang&Frenklach's method gives significantly smaller values than the other two methods. Among the three averaging rules, η-ξ method agrees best with the results of Liu and Wang, but there are a few special cases:

the simulated results of A2 and A4 at 1000 K are respectively 10.6% and 12.24%-17.10% larger than the corresponding results of the η-ξ method.

References

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3. E. N. Fuller, K. Ensley and J. C. Giddings, *The Journal of Physical Chemistry*, 1969, **73**, 3679-3685.
4. E. N. Fuller, P. D. Schettler and J. C. Giddings, *Industrial & Engineering Chemistry*, 1966, **58**, 18-27.
5. C. Liu and H. Wang, the 11th U. S. National Combustion Meeting, Pasadena, California, 2019.