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## ADVERTISEMENT

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The article by Thorne Lay and Hiroo Kanamori (2010) is an excellent review of the relationship between seismic moment and energy release. However, the authors' calculation of the energy release for a 100-megaton nuclear explosion is not correct. If the authors were to use the correct relationship between seismic moment and energy release, they would find that the energy release is approximately five times as much energy as that of a 100-megaton nuclear explosion. The 1964 Chilean earthquake had still more energy by a factor of about 3, or 15 times that of a 100-megaton nuclear explosion. The authors used the relation for seismic energy release rather than total strain energy release. I believe the authors underestimated the total strain energy release by a variable that depends on the fault plane. Accounting for total strain energy release would increase the earthquake energy number by orders of magnitude. Despite the catastrophic damage potential of nuclear bombs, the forces of nature occasionally unleash much larger energy releases. Although the nuclear bombs are under our control, earthquakes, volcanic eruptions, and extreme weather events are not. However, by judicious preparation and avoidance measures, humans can significantly diminish the damage of natural events.

**Comment on this article**

By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck team. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon, later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.

Written by Edgar Mocarvill, 14 July 2012 19:59

# Mutual diffusion coefficients of heptane isomers in nitrogen: A molecular dynamics study

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The accurate knowledge of transport properties of pure and mixture fluids is essential for the design of various chemical and mechanical systems that include fluxes of mass, momentum, and energy. In this study we determine the mutual diffusion coefficients of mixtures composed of heptane isomers and nitrogen using molecular dynamics (MD) simulations with fully atomistic intermolecular potential parameters, in conjunction with the Green–Kubo formula. The computed results were compared with the values obtained using the Chapman–Enskog (C–E) equation with Lennard-Jones (LJ) potential parameters derived from the correlations of state values: MD simulations predict a maximum difference of 6% among isomers while the C–E equation presents that of 3% in the mutual diffusion coefficients in the temperature range 500–1000 K. The comparison of two approaches implies that the corresponding state principle can be applied to the models, which are only weakly affected by the anisotropy of the interaction potentials and the large uncertainty will be included in its application for complex polyatomic molecules. The MD simulations successfully address the pure effects of molecular structure among isomers on mutual diffusion coefficients by revealing that the differences of the total mutual diffusion coefficients for the six mixtures are caused mainly by heptane isomers. The cross interaction potential parameters, collision diameter  $\sigma_{12}$ , and potential energy well depth  $\epsilon_{12}$  of heptane isomers and nitrogen mixtures were also computed from the mutual diffusion coefficients.

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## I. INTRODUCTION

Transport properties represent the response of a system to a perturbation, such as change in temperature or chemical gradients. Among transport properties, mass diffusion induced by chemical gradient of species is an area that still includes considerable uncertainties and has less available data than other transport properties.<sup>1</sup>

Several experiments and theoretical studies have been reported in the literature to determine the mass diffusion coefficients of various systems.<sup>2–4</sup> The majority of the experimental data, however, are available at low temperatures. Current state-of-the-art measurement techniques, from interferometric method to NMR measurements of spin relaxation and chromatographic flow-broadening techniques, based either on the broadening of the elution peaks, or on the perturbation imposed on the carrier gas flow rate, give accurate diffusivity data with an uncertainty of  $\pm 0.1\%$  but only near ambient condition.<sup>5</sup>

Theoretical analysis based on kinetic theory can predict mutual diffusion coefficients with an uncertainty of no more than 2% when it is combined with experimental measurements of viscosity. However, the viscosity data of binary pairs of polyatomic mixtures at the temperature of interest are generally not available. Therefore, mutual diffusion coefficients of gas mixture are estimated with the effective cross section that provided by the correlations of the law of corresponding state even though the accuracy of this approach to polyatomic molecules has not been clearly identified.<sup>6</sup> The use of the analytical equation, especially for a polyatomic mixture at high temperature region, needs to be assessed with

the other method that can consider detailed atomistic level interactions.

In this paper we compute the mutual mass diffusion coefficients of systems composed of heptane isomers and nitrogen molecules in the temperature range 500–1000 K, using molecular dynamics (MD) simulations. The objectives are twofold: to compute the transport properties by considering full atomistic interactions and to compare the results with the values obtained using analytical models to identify the ability of corresponding state theory and the analytical equation in describing the interactions between polyatomic molecules; and to determine the effect of isomerism on the mutual diffusion coefficients at relatively high temperature condition.

Some experimental results are available in the literature for isomers: Grushka *et al.* determined the diffusion coefficients of eight heptanes isomers<sup>3</sup> and seven octane isomers<sup>4</sup> in helium at 373 K using the chromatographic broadening technique. They found out that the number and position of methyl groups greatly influence the diffusion. Grushka and Maynard<sup>4</sup> studied the effect of branching on the diffusion coefficients of octane isomers and Grushka and Schnipelsky measured the diffusion coefficients of hexane isomers at 307 and 373 K.<sup>7</sup> Although the above studies presented the great introduction of the characteristics of isomer diffusivities, their analysis was confined to very low temperature region due to the limitation of measurement.

Accurate mutual diffusion coefficients for isomers are of great importance for modeling high temperature reacting flow. McEnally *et al.* showed the consumption rate of normal heptanes is slower than that of 2,2,3-trimethylbutane in

coflow laminar nonpremixed flame experiments.<sup>8</sup> This result is inconsistent with the main consumption routes for heptanes because the hydrogen abstraction and carbon bond fission processes should consume 2,2,3-trimethylbutane less rapidly than normal heptanes due to the slower abstraction rates for primary hydrogen atoms compared with secondary hydrogen atoms<sup>9</sup> and the higher strength of the  $\alpha$  carbon–carbon (C–C) bond compared with other C–C bonds.<sup>10</sup> This inconsistency between the experimental evidence and kinetics is caused by transport properties of the two isomers.

After briefly describing the current models available to compute mass diffusivities and their limitations, we report on the Green–Kubo formula that provides the theoretical basis for the use of MD simulations to determine macroscopic transport properties. The capability of MD are initially tested to compute the diffusion coefficients of small hydrocarbons and compared with experimental data present in the literature. In Sec. IV the simulation results for mixtures of heptane isomers in nitrogen are presented and discussed in the context of available empirical models. The results reported in the following section reveal the effect of molecular structure on mass diffusivity of binary mixture, excluding the effect of mass. In addition, new cross interaction parameters (between heptane isomers and nitrogen) for 12-6 Lennard-Jones (LJ) potential function are determined and can be used in future applications to model reactive flow systems.

## II. THEORETICAL BACKGROUND

### A. Empirical diffusion models

The mass diffusion coefficient  $D_{12}$  for a binary mixture is function of temperature, pressure, and composition. At low pressure,  $D_{12}$  is inversely proportional to the pressure, increases with increasing temperature, and is almost independent of composition for a given gas pair. These variations are all described, with different degrees of precision, by empirical equations of the kinetic theory of gases.

The kinetic theory of gases postulates transport processes entirely due to molecules in motion and collisions controlled by molecular interactions. The Chapman–Enskog solution of the Boltzmann equation expresses the transport properties as a series of collision integrals,  $\Omega^{(l,s)}$ , related to the interaction energy and the scattering mechanism of molecular collisions and, therefore to the interaction potential,  $V(r)$ . The collision integrals for a given pair of molecules are normally tabulated as a function of the reduced temperature,  $T^*$ , for a given mathematical form of the potential function.

Hirschfelder *et al.* followed the Chapman–Enskog kinetic approach and, using the Lennard-Jones 6-12 intermolecular potential function, obtained the Hirschfelder–Bird–Spotz (HBS) equation for a binary mass diffusion coefficient<sup>1</sup>

$$D_{12} = \frac{3}{8} \frac{\sqrt{(k_B T)^3 / (2\pi m_{12})}}{n \sigma_{12}^2 \langle \Omega^{(1,1)*} \rangle}, \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the temperature of a system,  $m_{12}$  is the reduced mass of the pair components,  $n$  is the average number density,  $\sigma_{12}$  is the collision diameter of two species, and  $\Omega^{(1,1)*}$  is the collision integral. The

collision integral term depends on the reduced temperature,  $T^* = k_B T / \varepsilon_{12}$ , where  $\varepsilon_{12}$  is the energy well depth of the intermolecular potential  $V(r)$ .<sup>11</sup> The use of Eq. (1) relies on the values of the collision diameter,  $\sigma_{12}$ , potential energy well depth,  $\varepsilon_{12}$ , and collision integral,  $\Omega^{(1,1)*}$ , the majority of which have been obtained from viscosity measurements.

The success of the various models to determine the diffusion coefficients, whether founded on theory or empirically determined, has been with monatomic or very small polyatomic molecules. The kinetic theory for polyatomic molecules, however, differs fundamentally from that of the monatomic molecules. Polyatomic molecules have internal degrees of freedom in the form of rotational and vibrational modes of motion and molecular collisions involve anisotropic force interactions or the energy transfer between two molecules. These molecules interact through nonspherical intermolecular pair potentials.

### B. Statistical mechanics and Green–Kubo formula

The fluctuation dissipation theorem relates mass diffusion coefficients with the time integrals of correlation functions of microscopic particle velocities.<sup>12,13</sup> The mathematical formulation of the theorem is expressed as the Green–Kubo (GK) formula,<sup>12</sup> that establishes the theoretical basis for computing the mass diffusion coefficients.<sup>14</sup> The mutual diffusion coefficient,  $D_{12}$ , can be expressed as<sup>15</sup>

$$D_{12} = Q \left[ x_2 D_1 + x_1 D_2 + x_1 x_2 \left( \frac{f_{11}}{x_1^2} + \frac{f_{22}}{x_2^2} - 2 \frac{f_{12}}{x_1 x_2} \right) \right], \quad (2)$$

where  $D_\alpha$  is the time integral of velocity autocorrelation functions of species  $\alpha$ ;  $f_{\alpha\alpha}$  and  $f_{\alpha\beta}$  are the time integrals of velocity cross-correlation function between the same species and between species  $\alpha$  and  $\beta$  respectively.  $x_\alpha$  is the mole fraction of each species.  $Q$  is a thermodynamic factor related to the compositional derivative of chemical potential and corrects compositional dependence in diffusion flux.<sup>16</sup> The  $Q$  factor can be determined from the integral of the radial distribution functions.<sup>15</sup> For a thermodynamically ideal mixture, defined as the perfectly mixed state of a mixture, the integrals of the radial distribution functions of each species are identical, and  $Q$  can be approximated as unity.<sup>17</sup>

## III. COMPUTATIONAL METHOD

### A. Force field parameters

The approach used in this paper to determine the diffusion coefficients of heptane isomers/nitrogen systems consists of two steps: (1) MD simulations are used to compute the time evolution of the molecules at various temperatures and 1 atm, and (2) the Green–Kubo formula Eqs. (2)–(5) is then employed to determine the mass diffusion coefficients using the integrals of correlation functions of microscopic particle velocities obtained from MD simulations.

The accuracy of mass diffusion coefficients obtained from MD simulations relies on the parameters used to describe the intermolecular potentials between molecules. Most of the previous MD simulations have been carried out using effective intermolecular potential parameters that assume a spherical shape of the molecules and, more recently, the united atom potential parameters have been employed to describe the nonbonded molecular interactions with increased accuracy. These approaches, which are computationally appealing and produce averaged information of the effective potentials, become increasingly inaccurate in complex polyatomic molecules which have structures that is highly deviated from spherical shapes.

Previous work by Stoker and Rowley demonstrated that mutual diffusion coefficients are extremely sensitive to the repulsive part of the potential function under combustion system.<sup>17</sup> Too stiff repulsive wall of the LJ potential function results in underprediction of the mass diffusion coefficient of small species.<sup>18</sup> The study of the effect of varying energy well depth,  $\epsilon_{12}$ , on the mass diffusivity showed that a decrease in the value of  $\epsilon_{12}$  caused an increase in the mass diffusion coefficient and vice versa.<sup>19</sup> Therefore, accurate intermolecular potential parameters are the first step to calculate diffusion coefficients.

In this study, we used the OPLS (Optimized Potentials for Liquid Simulations) AA (all-atom) potential parameters to describe the bonded and nonbonded interactions for the heptane/nitrogen systems. This fully atomistic force field that uses single atomic sites, such as C–C, C–H, and H–H, to obtain total nonbonded interactions between molecules, describes also the molecular flexibility by stretching, bending, and dihedral interactions.<sup>20</sup> The OPLS AA potential model has been widely used to obtain thermodynamic and transport properties of various gas or liquid systems that consist of polyatomic molecules.<sup>21</sup>

All potential parameters and functional forms for intramolecular and intermolecular interactions are listed in the supplemental material.<sup>22</sup>

## B. Simulation procedure

The Lennard-Jones 12-6 potential was used to describe the interactions between the molecules in the ensemble

$$V_{12} = 4\epsilon_{12} \left[ \left( \frac{\sigma_{12}}{r} \right)^{12} - \left( \frac{\sigma_{12}}{r} \right)^6 \right]. \quad (3)$$

The simulations were carried out using a total of 3300 molecules with 300 alkanes. Various concentrations have been analyzed, including 1%, 5%, and 10% mole fractions of alkanes in nitrogen in the temperature range 500–1000 K, and we did not determine any significant difference in the final values of the mutual diffusion coefficients, as reported in Table I.

The canonical (NVT) ensemble was used for the simulations. The isothermal–isobaric (NPT) ensemble was tested to determine its suitability for this study, but it was not chosen for our calculations because of the strong dependence between the coupling parameter of barostat and mass diffusion results. As the value of the coupling strength increases,

TABLE I. Mutual diffusion coefficients of *n*-heptane/N<sub>2</sub> at 500 K, 1 atm for different concentrations of heptane (1%, 5%, and 10%).

| Mixture                                                  | $D_{12}$ [cm <sup>2</sup> /s] |        |        |
|----------------------------------------------------------|-------------------------------|--------|--------|
|                                                          | 1%                            | 5%     | 10%    |
| <i>n</i> -C <sub>7</sub> H <sub>16</sub> /N <sub>2</sub> | 0.1719                        | 0.1728 | 0.1723 |

the diffusivity increases, and the deviation between large and small coupling parameters was more than 100%. Periodic boundary conditions were utilized, and the cutoff radius was set to be 18 Å. All MD simulations were carried out with GROMACS package.<sup>23</sup>

The initial velocities of the molecules were derived from the Boltzmann distribution. The Verlet leapfrog numerical integration algorithm was employed with a time step of 1.0 fs. The total simulation time was 14 ns and the sampling time for the velocity correlation was chosen to be 7 ns for the temperature range considered. The velocities and positions of the molecules were recorded every 50 time steps.

In theory, the value of the diffusion coefficient is determined solving the time integral between zero and infinity. In real simulations, therefore, the upper limit must be selected carefully. Typically longer sampling time is required for polyatomic molecules than monatomic molecules because the translational and vibrational motions have different relaxation time. A sampling time of 7 ns was found to be adequate for the complete decay of the correlation functions for the systems of heptane/nitrogen analyzed in this study.

Figure 1 shows the structures of the six isomers of heptane: normal heptane (*n*-C<sub>7</sub>H<sub>16</sub>) with a relatively long chain, 2-methylhexane (2-C<sub>7</sub>H<sub>16</sub>), 2,2-dimethylpentane (2,2-C<sub>7</sub>H<sub>16</sub>), 2,3-dimethylpentane (2,3-C<sub>7</sub>H<sub>16</sub>), 3,3-dimethylpentane (3,3-C<sub>7</sub>H<sub>16</sub>), and 2,2,3-trimethylbutane (2,2,3-C<sub>7</sub>H<sub>16</sub>) with a semi-spherical shape.

## IV. RESULTS AND DISCUSSION

### A. Benchmark of the computational approach

In order to assess the accuracy of our approach, we initially computed the transport coefficients for hydrocarbon systems that have been studied experimentally.<sup>24,25</sup> Table II

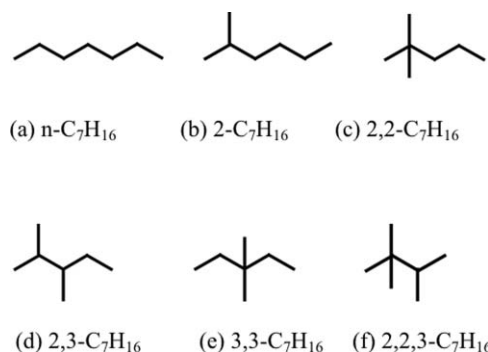


FIG. 1. Molecular structures of the six heptane isomers considered in this study.

TABLE II. Mutual diffusion coefficients for the  $C_2H_6/N_2$  and  $n-C_5H_{12}/N_2$  mixtures at different temperatures at 1 atm (Exp: experiments<sup>26,27</sup>; MD: molecular dynamics—Maynard *et al.* (1975) for ethane mixture and H. J. Amikar *et al.* (1969) for pentane mixture, MD: molecular dynamics).

| Mixture         | $T$ [K] | $D_{12}$ [ $cm^2/s$ ] |       |
|-----------------|---------|-----------------------|-------|
|                 |         | Exp                   | MD    |
| $C_2H_6/N_2$    | 345     | 0.193                 | 0.186 |
|                 | 407     | 0.256                 | 0.259 |
|                 | 449     | 0.303                 | 0.294 |
| $C_5H_{12}/N_2$ | 353     | 0.136                 | 0.121 |

shows the results for binary mixtures of ethane in nitrogen and normal pentane in nitrogen. The agreement between MD simulations and experimental data is within 3%.

Figure 2 reports the mutual diffusion coefficients of ethane/nitrogen mixtures versus experimental values at different temperatures.

Condensed systems, such as liquids or highly dense gases usually have less than 20 ps time span for the decay of the velocity time correlations because of the high collision rate. Dilute gases—as the systems analyzed in this study—need longer time to dissipate the microscopic fluctuations. As we can expect, the net effect of the cross correlation terms is negligible for all cases (less than 0.1%) because of the low density of the system.

## B. Heptane isomers

Previous studies have investigated the effect of molecular structures on mutual diffusion coefficients by defining the translational rotational coupling parameter,  $A_{12}$ , and correlating it with the diffusivity of spherical shape molecules.<sup>28</sup> The coupling between translational and rotational motions accelerates the relaxation of the velocity correlation functions. The results showed that as the geometry of the molecules becomes spherical, the value of the coupling parameter,  $A_{12}$ , decreases.<sup>28</sup>

Figure 3 reports the mutual diffusion coefficients for three heptane isomers in nitrogen as a function of tempera-

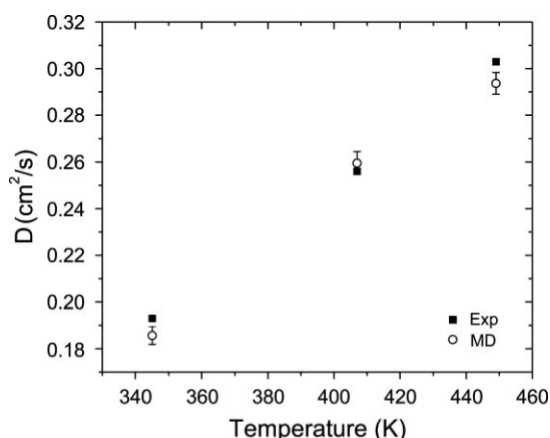


FIG. 2. Mutual diffusion coefficients of ethane in nitrogen at 1 atm (Exp: experiments, MD: molecular dynamics).

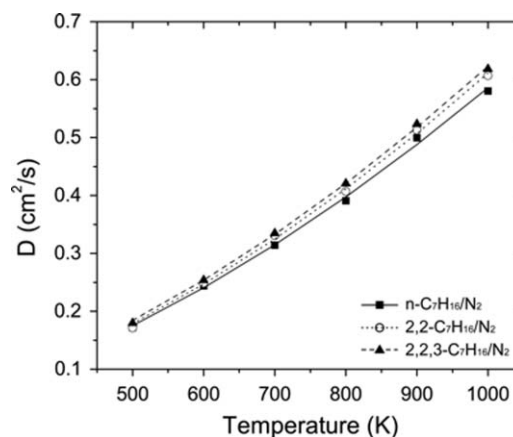


FIG. 3. Mutual diffusion coefficients of three heptane isomers in nitrogen from MD simulations as a function of temperature at 1 atm. Symbols: MD results; curves: least square curve fittings of MD results.

ture. 2,2,3- $C_7H_{16}/N_2$  has the highest mass diffusivities in the temperature range considered. The differences of diffusivities among isomers are very small at low temperature and increasing as temperature increases.

Figure 4 reports the mutual diffusion coefficients of heptane isomers in nitrogen at two different temperatures (500 and 1000 K) with error bars. At 500 K, the computed diffusivities have similar values, but as the temperature increases, the isomers show different values of the diffusivities. The diffusion values are distributed over narrower ranges at 500 K (0.17–0.18  $cm^2/s$ ) when compared with those at 1000 K (0.58–0.62  $cm^2/s$ ) because of the higher kinetic energy at 1000 K. The absolute values of standard errors of mutual diffusion coefficients of the heptane isomers are nearly the same irrespective of temperature conditions. Therefore, in this work, the structural effects can be detected more distinctively under high temperature region.

The diffusion coefficients of branched isomers have the highest values since the main parameter that affects the mass diffusivity is the length of the main chain of the molecule. As the number of branches increases, which means shorter main chain length, the mutual diffusion coefficients increase. Normal heptane ( $n-C_7H_{16}$ ) has the lowest diffusivity due to the longest chain length while 2,2,3-trimethylbutane (2,2,3- $C_7H_{16}$ ), which has the shortest chain length shows the highest diffusion values; that is, branched molecules have smaller collision cross sections than linear molecules. Mutual diffusion coefficients of the six systems analyzed in the temperature range 500–1000 K using molecular dynamics (MD) simulations and the Chapman–Enskog equation (CE) are listed in Table 1S in the Supplemental Material.<sup>22</sup>

The decrease in the collision cross section can be discussed using the shielding theory introduced by Fuller *et al.*<sup>29</sup> In complex molecules, some structural groups can be partially shielded from collision by other groups, which exempt certain collision paths. When a group is completely shielded it does not contribute to the cross section of the target molecule. Extended molecules, with exposed (minimally shielded) groups, have relatively large total cross sections. The explanation for the mass diffusivities of dimethyl group isomers is directly

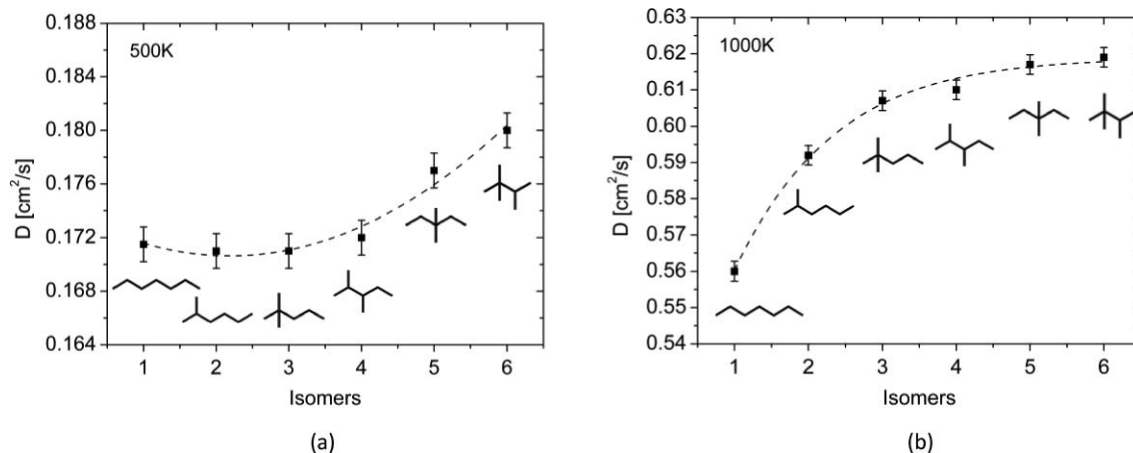


FIG. 4. Computed mutual diffusion coefficient of six heptane isomers in nitrogen at 1 atm and two temperatures (a) 500K, and (b) 1000K with error bars. The values were obtained using MD simulations. Isomers—[(1)  $n$ -C<sub>7</sub>H<sub>16</sub>, (2) 2-C<sub>7</sub>H<sub>16</sub>, (3) 2,2-C<sub>7</sub>H<sub>16</sub>, (4) 2,3-C<sub>7</sub>H<sub>16</sub>, (5) 3,3-C<sub>7</sub>H<sub>16</sub>, (6) 2,2,3-C<sub>7</sub>H<sub>16</sub>].

related to the locations of methyl groups. Our results show that the most effective positions to shield methyl group are in 3,3-dimethylpentane (3,3-C<sub>7</sub>H<sub>16</sub>), which has two methyl groups at the center of a molecule, and 2,3-dimethylpentane (2,3-C<sub>7</sub>H<sub>16</sub>) with one methyl group at the center. Grushka and Schnipel<sup>3</sup> mentioned the effect of the location of methyl group on diffusivity when the two methyl groups are close to each other and, the linear portions of the molecule shield the two methyl groups effectively, thus reducing their contribution to the diffusion coefficient. Therefore they justified the smaller diffusivity of 2,4-dimethylpentane as compared with the other dimethyl group heptanes isomers, such as 2,2-C<sub>7</sub>H<sub>16</sub>, 2,3-C<sub>7</sub>H<sub>16</sub>, and 3,3-C<sub>7</sub>H<sub>16</sub>.

From the results reported above, we can conclude that the methyl groups are shielded most effectively when located at the center of the molecule. When one of the methyl groups is located at the center of the molecule or two methyl groups are close together, they can be shielded by the linear portion of the molecule more effectively than cases in which none of the methyl groups is located at the center of the molecule. Our MD simulations successfully showed the structural effects on

the diffusivity and reproduced the experimental trends of heptanes isomers in helium reported by Grushka *et al.*<sup>3,4</sup>

For the simulations reported in this study, we assumed the factor  $Q$  equal to unity. As reported in elsewhere<sup>15</sup>  $Q$  is function of the radial distribution functions (RDF) of the system considered. In order to validate this assumption, we determined the RDF for the six heptane systems and obtained similar values of the heptane–heptane, heptane–N<sub>2</sub>, and N<sub>2</sub>–N<sub>2</sub> curves. As an example, Fig. 5 shows the radial distribution functions for the system  $n$ -C<sub>7</sub>H<sub>16</sub>/N<sub>2</sub> at 500 K and 1 atm. The values of thermodynamic factors are in the range of 0.9990–0.9993 for the temperature range considered and Table III shows the results.

An important consequence of these calculations is the assumption that the gas mixtures of isomers considered in this study have very similar mixture distributions, irrespective of their molecular structures. These results clearly show the conventional characteristics of low-density gas systems. The mean free path of the system is very large and the only crucial factor is the interaction energy at the moment of collision.

Translational order parameters were also computed for  $n$ -C<sub>7</sub>H<sub>16</sub>/N<sub>2</sub> system to show the structural property of our target systems and listed in Table IV. The order structuring parameters, such as translational or orientational order parameters, will vanish for an ideal gas and be large for high density gas, liquid, or solid system. Our result clearly shows that the translational order parameters are too small to have any

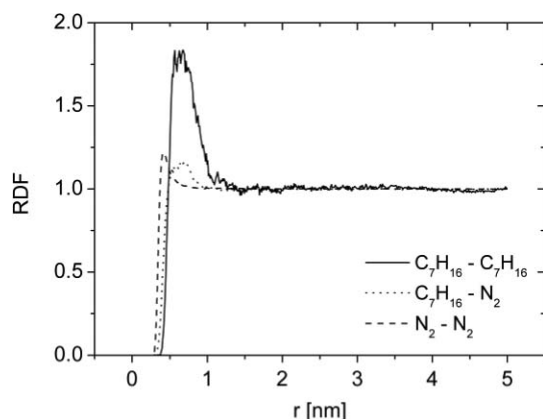


FIG. 5. Radial distribution functions (RDF) of  $n$ -C<sub>7</sub>H<sub>16</sub>/N<sub>2</sub> at 500 K and 1 atm.

TABLE III. Thermodynamic factors of the mixtures of six heptane isomers at 500 K.

| Mixture                                              | $Q$    |
|------------------------------------------------------|--------|
| $n$ -C <sub>7</sub> H <sub>16</sub> /N <sub>2</sub>  | 0.9990 |
| 2-C <sub>7</sub> H <sub>16</sub> /N <sub>2</sub>     | 0.9991 |
| 2,2-C <sub>7</sub> H <sub>16</sub> /N <sub>2</sub>   | 0.9993 |
| 2,3-C <sub>7</sub> H <sub>16</sub> /N <sub>2</sub>   | 0.9991 |
| 3,3-C <sub>7</sub> H <sub>16</sub> /N <sub>2</sub>   | 0.9990 |
| 2,2,3-C <sub>7</sub> H <sub>16</sub> /N <sub>2</sub> | 0.9990 |

TABLE IV. Translational order parameter (TOP) of  $n\text{-C}_7\text{H}_{16}/\text{N}_2$  mixture at 500 K.

| Species                                                      | TOP    |
|--------------------------------------------------------------|--------|
| $n\text{-C}_7\text{H}_{16}\text{-}n\text{-C}_7\text{H}_{16}$ | 0.0077 |
| $n\text{-C}_7\text{H}_{16}\text{-N}_2$                       | 0.0031 |
| $\text{N}_2\text{-N}_2$                                      | 0.0065 |

physical meaning and this is a conventional characteristic of low-density gas system which has a very large mean free path.

Another advantage of using MD simulations together with the Green–Kubo formula to study transport properties is the ability to determine the detailed mobility of each component in an isotropic mixture, i.e., the tracer diffusivity. Figure 6 reports the self-diffusion coefficients of heptane isomers and nitrogen as function of temperature in mixtures of heptane/nitrogen. The results reveal that differently from nitrogen [Fig. 6(b)], the diffusivities of heptane isomers [Fig. 6(a)] show significant variations with temperature. In addition, the trends reported in Fig. 6(a) are very similar to those of mutual diffusion coefficients (Fig. 3). Therefore, we can conclude that the differences of the total mutual diffusion coefficients for the six mixtures are caused mainly by heptane isomers. The MD simulations successfully address the pure effects of molecular structure among isomers on mutual diffusion coefficients. The values of self-diffusion of heptane isomers and nitrogen as function of temperature are listed in Table 2S in the Supplemental Material.<sup>22</sup>

The capability of MD simulations to determine the diffusivity of each species in a system is very important when dealing with multicomponent mixture systems. The standard formulation for  $N$  multicomponent diffusion treats the system using  $N-1$  diffusion equations and one material balance equation.<sup>30</sup> Under moderate density conditions, the multicomponent diffusivity depends largely on mutual diffusion coefficients rather than other effects. Moreover, a new to address the problem, which produces negative concentration in solving the balance equation, treats  $N$  diffusion equa-

tions that are constructed to automatically satisfy the balance equation and requires a tracer diffusivity as input data.<sup>31</sup> Therefore, accurate mutual and tracer diffusion coefficients are essential to describe the diffusivity of multicomponent mixture.

### C. Comparison with empirical models

One of the goals of this study is to compare the values of mutual diffusion coefficients obtained with MD simulations with those derived using empirical models and extend the analysis to high temperatures where experimental data are not available and the latter models do not apply.

A previous work by Fuller *et al.* compared the accuracy of empirical methods with experimental results.<sup>32</sup> The Fuller–Schettler–Giddings (FSG) method predicted the binary mass diffusivities of hydrocarbons in nitrogen within a 3% error, except for isobutene, 2,3,3-trimethylheptane, and normal dodecane that showed 10.03%, 25.39%, and 12.69% deviations from experimental results, respectively. The Hirschfelder–Bird–Spotz (HBS) method predicted the mutual diffusion coefficients of hydrocarbon–nitrogen mixtures within 15% error. Therefore to obtain accurate mutual diffusion coefficients for various hydrocarbon classes the detailed information about the molecular interactions from anisotropic force field should be considered.

The correlations of corresponding state values developed by Tee *et al.*<sup>33</sup> can be used to evaluate the effective Lennard–Jones self-collision diameter  $\sigma$  and energy well depth  $\varepsilon$  for pure species with the critical pressure and temperature. The authors found out that the volumetric behavior of any particular fluid is characterized by the values of  $P_c$ ,  $T_c$ , and acentric factor  $\omega$  for that fluid; the intermolecular forces should then depend on the same three quantities that can be used to predict the parameters  $\sigma$  and  $\varepsilon$  in the LJ model.

$$\sigma \left( \frac{P_c}{T_c} \right)^{\frac{1}{3}} = a_1 - b_1 \omega, \quad (4)$$

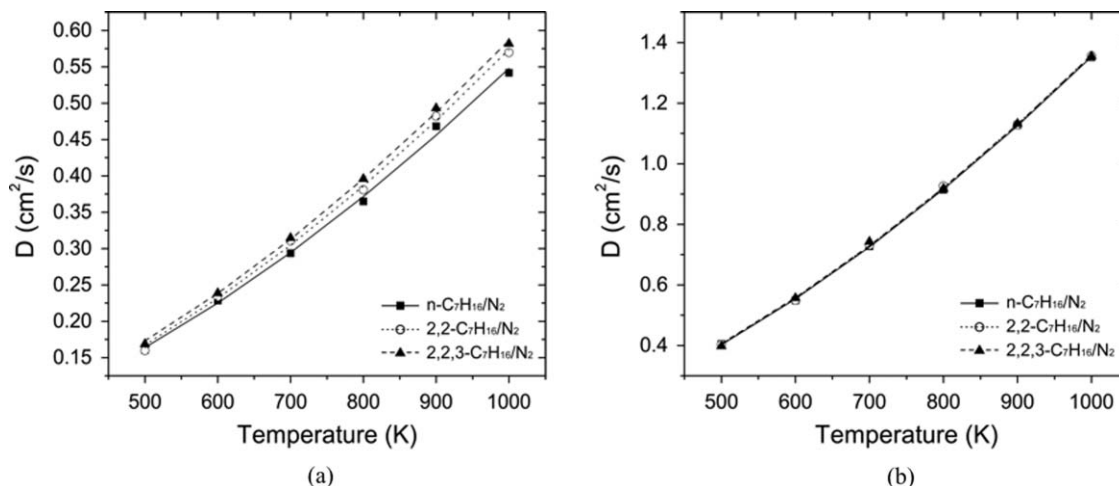


FIG. 6. Self-diffusion coefficients obtained from MD of three different heptanes/nitrogen at 1 atm: (a) heptane isomers and (b) nitrogen. The curves correspond to the least square curve fittings of MD results of each mixture.

$$\frac{\varepsilon}{k_B T_c} = a_2 + b_2 \omega, \quad (5)$$

where  $a$  and  $b$  are empirically derived coefficients. The acentric factor  $\omega$  is a macroscopic measurement of the extent to

which the force field around a molecule deviates from spherical geometry. Lee and Kesler developed an analytical correlation, based on the three-parameter corresponding states principle for  $\omega$ <sup>34</sup>:

$$\omega = \frac{\ln(P_c) - 5.92714 + 6.09648/T_{br} + 1.28862 \ln T_{br} - 0.169347 T_{br}^6}{15.2518 - 15.6875/T_{br} - 13.4721 \ln T_{br} + 0.43577 T_{br}^6}, \quad (6)$$

where  $T_{br} = T_b/T_c$ ,  $T_b$ , and  $T_c$  denote boiling and critical temperature, respectively. Tee *et al.* evaluated the force constants,  $\sigma$  and  $\varepsilon$  for 14 substances ranging from noble gases to heptane using the least-squares analysis of experimental viscosities and second virial coefficients and identified the following corresponding state correlations:

$$a_1 = 2.3511, \quad b_1 = 0.0874, \quad a_2 = 0.7915, \quad b_2 = 0.1693$$

In a recent publication Holley *et al.*<sup>35</sup> tested alternative values of the coefficients for  $n$ -alkanes systems and identified the following values:

$$a_1 = 2.3511, \quad b_1 = 0.3955, \quad a_2 = 0.8063, \quad b_2 = 0.6802$$

Table V lists the critical properties, boiling temperature, and effective Lennard-Jones potential parameters for the hydrocarbons considered in this study. The values for the critical properties are obtained from the National Institute of Standards and Technology database. Using the thermodynamic bulk properties,  $P_c$ ,  $T_c$ , and  $\omega$  and Eq. (1), we determined the mutual mass diffusion coefficients for the mixtures of heptane isomers in nitrogen and the results are reported in Table 1S in the columns of C–E.

The results show that the C–E equation predicts a maximum difference of 3% in the mutual diffusion coefficients among isomers while the MD simulations computed a maximum difference of 6% in the temperature range 500–1000 K. The empirical equations assume a spherical shape of the molecules when dealing with their collision, and therefore the only difference between the isomers is due to the thermodynamic properties mentioned above. As a result, MD simulations results can address the deviation of mutual diffusion

coefficients from the variation on molecular structure more distinctively. Figure 7 shows the diffusion coefficients for  $n$ -C<sub>7</sub>H<sub>16</sub> and 2,2,3-C<sub>7</sub>H<sub>16</sub> as a function of temperature obtained using the C–E equation and MD simulations. Normal heptane shows the largest difference between the two approaches since it has the longest chain and it deviates more from a spherical shape as compared to the other isomers. As mentioned before, the plot also expresses the fact that the difference of diffusivities is increasing as the temperature increases.

The corresponding state principle can be successfully applied to the models which are only weakly affected by the anisotropy of the interaction potentials because it still uses spherically symmetric potential models which is averaged over all possible interactions.<sup>6</sup> The role of critical properties and acentric factors is to produce different symmetric potentials, which have different well depth and diameter for each species but they cannot depict the anisotropic interactions between polyatomic molecules. Polyatomic molecules interact through nonspherically symmetric intermolecular pair potentials. Moreover, for the binary mixtures between highly dissimilar molecules, such as heptane and nitrogen, the anisotropic interaction cannot be neglected.

The results presented above reveal that the assumption of spherical molecules in the kinetic theory, even though it can consider the structural effects of molecules by using acentric factor and critical properties to a certain degree, is not enough to remove all the uncertainties that exist when dealing with polyatomic molecules especially in high temperature region.

#### D. Cross interaction potential parameters for heptane/nitrogen mixtures

Even though the C–E equation does not take into account the structural effects on mutual diffusion coefficients, it still has an advantage over other approaches due to the simplicity in its application. Once the effective cross interaction potential parameters ( $\sigma_{12}$  and  $\varepsilon_{12}$ ) of Lennard-Jones 12-6 potential functions, which already include the effects of molecular structures, are available the C–E equation can produce improved mutual diffusion coefficients with ease.

The parameters for binary mixture  $\sigma_{12}$  and  $\varepsilon_{12}$  are utilized to compute mutual diffusion coefficients from the C–E equation, can be obtained directly from accurate

TABLE V. Lennard-Jones 12-6 intermolecular potential parameters for alkanes.

| Compound                             | $T_b$ [K] | $T_c$ [K] | $P_c$ [atm] | $\omega$ | $\varepsilon/k_B$ [K] | $\sigma$ [Å] |
|--------------------------------------|-----------|-----------|-------------|----------|-----------------------|--------------|
| C <sub>2</sub> H <sub>6</sub>        | 184.6     | 305.3     | 48.36       | 0.097    | 266.3                 | 4.275        |
| C <sub>3</sub> H <sub>12</sub>       | 309.2     | 469.8     | 33.16       | 0.245    | 457.2                 | 5.454        |
| $n$ -C <sub>7</sub> H <sub>16</sub>  | 371.5     | 540.0     | 27.04       | 0.348    | 563.4                 | 6.006        |
| 2-C <sub>7</sub> H <sub>16</sub>     | 363.2     | 530.5     | 27.04       | 0.327    | 545.8                 | 5.992        |
| 2,2-C <sub>7</sub> H <sub>16</sub>   | 352.3     | 520.5     | 27.34       | 0.283    | 520.0                 | 5.979        |
| 2,3-C <sub>7</sub> H <sub>16</sub>   | 362.9     | 537.3     | 28.72       | 0.293    | 540.5                 | 5.933        |
| 3,3-C <sub>7</sub> H <sub>16</sub>   | 359.2     | 536.4     | 29.11       | 0.265    | 529.0                 | 5.933        |
| 2,2,3-C <sub>7</sub> H <sub>16</sub> | 354.1     | 531.1     | 29.11       | 0.248    | 517.8                 | 5.931        |



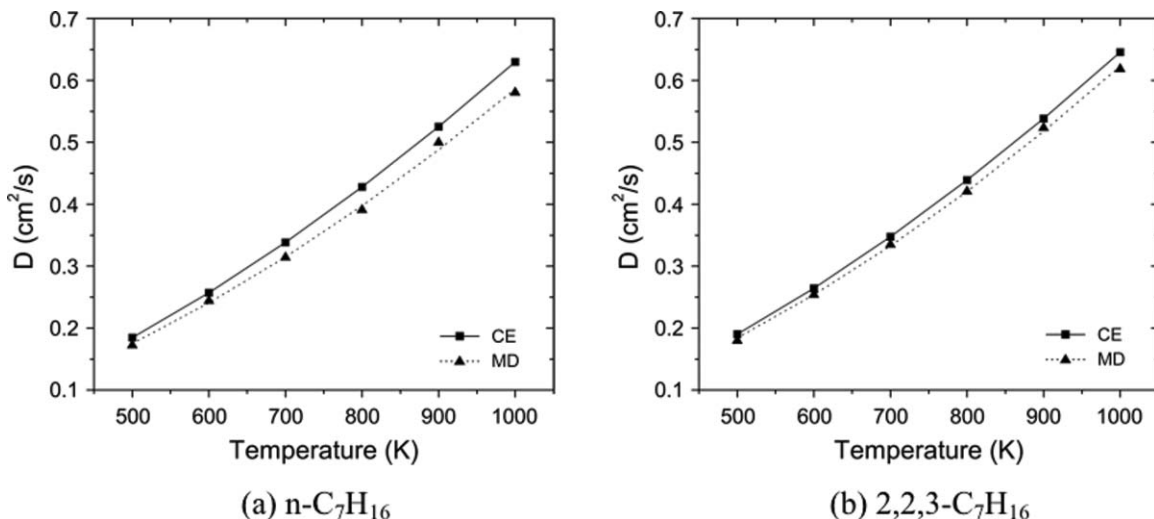


FIG. 7. Mutual diffusion coefficients of  $n\text{-C}_7\text{H}_{16}$  and  $2,2,3\text{-C}_7\text{H}_{16}$  in nitrogen as a function of temperature (CE: Chapman-Enskog, MD: molecular dynamics).

measurements of mutual diffusion coefficients or viscosities over a wide range of temperature. However, the measurements are not always available especially at high temperature conditions and therefore MD simulations have been regarded as a prominent alternative to compute diffusivities that include the effects of molecular structures.

Generally, the Lorentz-Berthelot (LB) combining rules, a geometric mean for a potential well depth ( $\varepsilon_{12} = \sqrt{\varepsilon_1 \times \varepsilon_2}$ ) and an arithmetic mean for a collision diameter ( $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ ) are used to obtain the effective potential parameters to express cross interactions. However, these combining rules include large uncertainties when the two molecules have very different potential parameters each other, such as a mixture of heptane and nitrogen. To test the ability of combining rules to capture the structural effects on diffusivities we compared LB combining rules and Kong's combining rules<sup>36</sup> (Eqs. (7) and (8)) which are proposed to work better for the mixture of highly dissimilar pairs of molecules.

$$\varepsilon_{12}\sigma_{12}^6 = \sqrt{(\varepsilon_1\sigma_1^6 \times \varepsilon_2\sigma_2^6)} \quad (7)$$

$$\varepsilon_{12}\sigma_{12}^{12} = \frac{\varepsilon_1\sigma_1^{12}}{2^{13}} \left[ 1 + \left( \frac{\varepsilon_2\sigma_2^{12}}{\varepsilon_1\sigma_1^{12}} \right)^{1/13} \right]^{13} \quad (8)$$

Table VI reports the comparison of mutual diffusion coefficients at 500 K and 1 atm. LB and Kong columns denote the combining rules used to obtain cross interaction parameters. Both the combining rules produce somewhat different results

TABLE VI. Mutual diffusion coefficients obtained from LB and Kong's combining rules.

| Mixture                                    | $D_{12}[\text{cm}^2/\text{s}]$ |                     |
|--------------------------------------------|--------------------------------|---------------------|
|                                            | LB                             | Kong                |
| $n\text{-C}_7\text{H}_{16}/\text{N}_2$     | $0.1721 \pm 0.0013$            | $0.1775 \pm 0.0015$ |
| $2,2,3\text{-C}_7\text{H}_{16}/\text{N}_2$ | $0.1797 \pm 0.0013$            | $0.1848 \pm 0.0014$ |

for same mixtures but the relative difference between two heptane isomers are very similar each other (relative differences between isomers:  $0.0054 \text{ cm}^2/\text{s}$  for LB rules and  $0.0051 \text{ cm}^2/\text{s}$  for Kong's rules). This means that the combining rules between two highly dissimilar molecules are inappropriate to address the effects of molecular structures on mutual diffusion coefficients irrespective of the relative accuracy of combining rules. Therefore, we employed LB combining rule to simplify our calculations. The only possible way to take into account the structural effect properly in using C-E equation is to obtain new cross interaction parameters directly from measurements or MD simulations.

In order to determine  $\sigma_{12}$  and  $\varepsilon_{12}$ , at least two mutual diffusion coefficients at different temperatures need to be computed with MD simulations. The detailed processes to obtain the parameters are well explained in a previous work by Gavril *et al.*<sup>25</sup> The ratio of two mutual diffusion coefficients is defined by the ratio of Eq. (1) at different temperatures:

$$\lambda = \frac{D_{12}(T_1)}{D_{12}(T_2)} = \left( \frac{T_1}{T_2} \right)^{1.5} \frac{\Omega^{(1,1)*}(T_2^*)}{\Omega^{(1,1)*}(T_1^*)} \quad (9)$$

The collision integral term,  $\Omega^{(1,1)*}$ , is tabulated as a function of reduced temperatures,  $T^* = k_B T / \varepsilon_{12}$ , for the 12-6 Lennard-Jones potential function and various analytical approximations for  $\Omega^{(1,1)*}$  are available.<sup>37</sup> Neufield *et al.*<sup>38</sup> defined the collision integral as

$$\Omega^{(1,1)*} = \frac{A}{(T^*)^B} + \frac{C}{e^{DT^*}} + \frac{E}{e^{FT^*}} + \frac{G}{e^{HT^*}}$$

$$A = 1.06036, \quad B = 0.15610, \quad C = 0.19300,$$

$$D = 0.47635, \quad E = 1.03587, \quad F = 1.52996,$$

$$G = 1.76474, \quad H = 3.89411. \quad (10)$$

Using the analytical form of Eq. (10), the potential energy well depth,  $\varepsilon_{12}$ , can be determined by solving Eq. (9). Once the  $\varepsilon_{12}$  is computed, the collision diameter,  $\sigma_{12}$ , also can be obtained by Eq. (1).

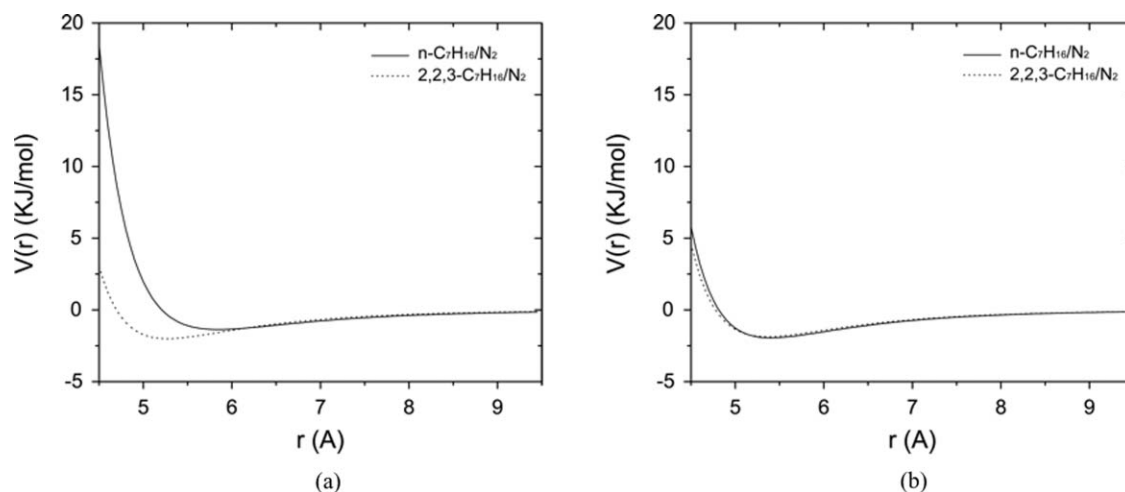


FIG. 8. Lennard-Jones 12-6 potential functions for cross interactions between heptane isomers and nitrogen molecules computed from (a) MD simulations (b) LB combining rules.

Table VII lists the cross interaction potential parameters determined from the mutual diffusion coefficients of MD simulations in the temperature 500–1000 K and the same parameters obtained using the LB combining rules. In order to compute the parameters by LB combining rule, the values in Table III are used for pure components. Figure 8 shows the Lennard-Jones potential curves plotted from the values in Table 2S. These results explain the drawback of combining rules distinctively. Figure 8(b), computed from LB combining rules, shows nearly same potential curves between  $n\text{-C}_7\text{H}_{16}/\text{N}_2$  and  $2,2,3\text{-C}_7\text{H}_{16}/\text{N}_2$ . On the other hand, the curves obtained from MD simulations [Fig. 8(a)] express large difference between the two isomers. The LB combining rules rely on simple arithmetic and geometric mean values of two molecules therefore they include large uncertainty when applying to the mixture of highly unlike molecules and moreover it is difficult to catch small deviations among molecules that have similar structures. These new cross interaction parameters obtained using MD simulations can be used directly in Eq. (1) to compute improved mutual diffusion coefficients, which can consider the effects of molecular structures.

## V. CONCLUSIONS

In this study, we carried out molecular dynamic simulations of heptane isomers in nitrogen mixtures to deter-

mine the binary diffusion coefficients and investigate the effect of molecular structures on mutual diffusion coefficients in the temperature range 500–1000 K. Molecules with a semi-spherical shape possess higher mobility when compared with long chain compounds of the same mass.

Fully atomistic intermolecular potential parameters are appropriate to assess the structural effects of hydrocarbon molecules on the mutual diffusion coefficients. The mutual diffusion coefficient obtained from MD simulations can be used to determine the cross interaction potential parameters which in turn determine the mass diffusivity with higher accuracy.<sup>25</sup> Generally, experimental data for mutual diffusion coefficients are not available at high temperature conditions. Therefore, accurate MD simulations can represent a suitable alternative to determine the cross interaction potential parameters of a binary mixture.

Future work will include a more detailed analysis of hydrocarbon molecules in different conditions for binary and multicomponent systems.

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TABLE VII. Lennard-Jones 12-6 cross interaction potential parameters obtained from MD simulations (MD) and Lorentz-Berthelot (LB) combining rule.

| Mixture                                    | $\sigma_{12}$ [Å] |       | $\epsilon_{12}/k_B$ [K] |        |
|--------------------------------------------|-------------------|-------|-------------------------|--------|
|                                            | MD                | LB    | MD                      | LB     |
| $n\text{-C}_7\text{H}_{16}/\text{N}_2$     | 5.209             | 4.813 | 164.43                  | 234.40 |
| $2\text{-C}_7\text{H}_{16}/\text{N}_2$     | 5.135             | 4.807 | 167.83                  | 230.72 |
| $2,2\text{-C}_7\text{H}_{16}/\text{N}_2$   | 4.873             | 4.800 | 240.22                  | 225.05 |
| $2,3\text{-C}_7\text{H}_{16}/\text{N}_2$   | 4.887             | 4.777 | 238.68                  | 229.59 |
| $3,3\text{-C}_7\text{H}_{16}/\text{N}_2$   | 4.842             | 4.777 | 238.18                  | 227.15 |
| $2,2,3\text{-C}_7\text{H}_{16}/\text{N}_2$ | 4.696             | 4.776 | 241.30                  | 224.72 |

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