



Lennard–Jones parameters for combustion and chemical kinetics modeling from full-dimensional intermolecular potentials



Ahren W. Jasper^{a,*}, James A. Miller^b

^a Combustion Research Facility, Sandia National Laboratories, PO Box 969, Livermore, CA 94551-0969, USA

^b Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

ARTICLE INFO

Article history:

Received 21 June 2013

Received in revised form 29 July 2013

Accepted 11 August 2013

Available online 30 August 2013

Keywords:

Lennard–Jones parameters

Transport

Anisotropy

Intermolecular potential

Ab initio

Quantum chemistry

ABSTRACT

Lennard–Jones parameters for use in combustion modeling, as transport parameters and in pressure-dependent rate-coefficient calculations as collision rate parameters, are calculated from accurate full-dimensional intermolecular potentials. Several first-principles theoretical methods are considered. In the simplest approach, the intermolecular potential is spherically averaged and used to determine Lennard–Jones parameters. This method works well for small species, but it is not suitable for larger species due to unphysical averaging over the repulsive wall. Another method considered is based on full-dimensional trajectory calculations of binary collisions. This method is found to be very accurate, predicting Lennard–Jones collision rates within ~10% of those obtained via tabulated (experimentally-based) Lennard–Jones parameters. Finally, a computationally efficient method is presented based on one-dimensional minimizations averaged over the colliding partners' relative orientations. This method is shown to be both accurate and efficient. The good accuracy of the latter two approaches is shown to be a result of their explicit treatment of anisotropy. The effects of finite temperature vibrations and multiple conformers are quantified and are shown to be small. The choice of potential energy surface has a somewhat larger effect, and strategies based both on efficient semiempirical methods and on first-principles direct dynamics are considered. Overall, 75 systems are considered, including seven baths, targets as large as heptane, both molecules and radicals, and both hydrocarbons and oxygenates.

© 2013 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

Non-bonding intermolecular potentials play an important role in combustion chemistry. First and foremost (from our point of view), they govern collisional energy transfer from highly vibrationally excited molecules. In turn, energy transfer can be a kinetic bottleneck and largely controls the rates of unimolecular reactions at low pressure, both thermal and chemically-activated—most notably the low-pressure-limit rate coefficients of thermal dissociation reactions. However, these same potentials also determine transport properties—the coefficients of diffusion, viscosity, heat conduction, and thermal diffusion—that are used in flame modeling [1,2]. Although some work has appeared in these areas relatively recently [3], there is still a dearth of information that can be applied directly in chemical kinetics and combustion modeling.

In two recent papers [4,5], we have shown that a relatively inexpensive electronic-structure method, MP2/aug'-cc-pVDZ, gives results for intermolecular potentials that are very close to those calculated from the high-level QCISD(T)/CBS method for CH₄ inter-

acting with several small-molecule bath gases (He, Ne, H₂, and CH₄). Furthermore, we parameterized a very efficient semiempirical potential energy surface for hydrocarbons interacting with typical atomic and diatomic baths based on the QCISD(T)/CBS interaction energies. Using these potentials we calculated energy transfer rates using trajectories that give accurate low-pressure rate coefficients for the CH₄(+M) ⇌ CH₃ + H(+M) reaction, with M being any one of several typical bath gas molecules. Subsequent work (as yet unpublished for CH₄ + H₂O, CH₃OH + He, and C_xH_y + M) has reinforced our conclusion that the MP2 and semiempirical methodologies can be workhorses for obtaining collisional energy transfer rates in highly vibrationally-excited molecules, and hence accurate unimolecular rate coefficients at low pressure.

The purpose of the present investigation is considerably less ambitious than that described above, but it is still important. We want to use the intermolecular potential energy methods discussed above to calculate accurate Lennard–Jones collision rates (or frequencies) with minimal computational effort. In unimolecular reaction rate theory [6,7], one is always referring to ⟨ΔE⟩ or ⟨ΔE_d⟩, the average energy transferred in a collision or the average energy transferred in a deactivating collision. For these quantities to have meaning one must first define what a collision is. There

* Corresponding author.

E-mail address: ajasper@sandia.gov (A.W. Jasper).

is enormous flexibility in this definition [8,9], but by convention it is normally defined in terms of a Lennard–Jones collision rate. The origin of the use of the Lennard–Jones collision rate lies in the theory of transport processes. It is worthwhile to review this point briefly.

First, if one has a binary mixture of hard-sphere molecules, the collision rate of a molecule of species i with molecules of species j is [1]

$$Z_{ij} = \pi \sigma_{ij}^2 n_j \bar{g}_{ij}, \quad (1)$$

where n_j is the number density of j -type molecules; $\bar{g}_{ij} = \left(\frac{8k_B T}{\pi \mu_{ij}}\right)^{1/2}$ is the average relative speed for i, j collisions; k_B is Boltzmann's constant; $\mu_{ij} = \frac{m_i m_j}{m_i + m_j}$ is the reduced mass for i, j collisions; T is the temperature; and $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ is the collision diameter (with σ_i and σ_j the diameters of the two spheres). More generally, we will define σ_{ij} as the intermolecular separation where the intermolecular potential $\bar{V}(r)$ equals zero; this is the collision diameter for hard spheres. In the same hard-sphere model the binary diffusion coefficient is

$$D_{ij} = \frac{3}{16} \frac{(2\pi k_B^3 T^3 / \mu_{ij})^{1/2}}{p \pi \sigma_{ij}^2}, \quad (2)$$

where p is the pressure. Defining $z_{ij} = Z_{ij}/n_j$ to be a hard-sphere “collision rate coefficient”, the diffusion coefficient becomes

$$D_{ij} = \frac{3}{16} \frac{\bar{g}_{ij} (2\pi k_B^3 T^3 / \mu_{ij})^{1/2}}{p z_{ij}}. \quad (3)$$

Thus all of the dependence of D_{ij} on the potential is absorbed into z_{ij} .

If one considers the Lennard–Jones potential,

$$\bar{V}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^6 \right], \quad (4)$$

where σ_{ij} was defined above and ϵ_{ij} is the well depth [or any potential of the form $\bar{V}(r) = \epsilon f(r/\sigma)$], the diffusion coefficient can be written as

$$D_{ij} = \frac{3}{16} \frac{(2\pi k_B^3 T^3 / \mu_{ij})^{1/2}}{p \pi \sigma_{ij}^2 \Omega^{(1,1)*}}, \quad (5)$$

where $\Omega^{(1,1)*}$ is a reduced collision integral that depends on the intermolecular potential. Unless otherwise indicated, we have used the term “Lennard–Jones potential” to mean the 12–6 Lennard–Jones potential in particular, as in Eq. (4). This form of the Lennard–Jones potential was used almost exclusively in the present work; the “9–6 Lennard–Jones potential” was also considered briefly. Eq. (5) suggests that, by analogy with the hard-sphere case, we define the collision rate coefficient as

$$z_{ij} = \pi \sigma_{ij}^2 \Omega^{(1,1)*} \bar{g}_{ij}. \quad (6)$$

One can view this as a general result with σ_{ij} and $\Omega^{(1,1)*}$ evaluated for the particular potential under consideration ($\Omega^{(1,1)*} = 1$ for hard spheres). Results analogous to Eq. (6) can also be derived using the viscosity and conductivity [1], but in these cases $\Omega^{(2,2)*}$, another reduced collision integral, replaces $\Omega^{(1,1)*}$. We shall not be concerned with the precise definition of the collision integrals here except to note that their values are readily obtainable in tabular form. We are most interested in diffusion coefficients and hence in $\Omega^{(1,1)*}$, but the Lennard–Jones potential parameters that we determine can be used to calculate any of the reduced collision integrals. $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ are usually very similar in magnitude, commonly differing by less than 10%.

One is tempted to think that this is all well and good, but real molecules are not point particles (or hard spheres). They have structure—their potential depends on more than just the distance

between the centers of mass of the two colliding molecules. Interestingly, high level quantum scattering calculations on *ab initio* potential energy surfaces show that transport properties can be computed quite accurately by using only the “spherically-averaged,” isotropic part of the potential, i.e. by assuming point particles, at least for small molecules [10–12]. Also, the decades-old practice of fitting experimental data to Lennard–Jones potentials suggests that this simplification may be accurate.

In the present article we discuss different methods of obtaining Lennard–Jones parameters from detailed, full-dimensional intermolecular potentials. We compare the results with the experimental results available, normally by comparing collision rate coefficients for the different sets of Lennard–Jones parameters. We primarily consider cases where helium is one of the collision partners. This simplifies the electronic-structure calculations and eliminates any effects of dipole–dipole interactions. The pure-gas parameters can be determined from whatever combining rules one may wish to use, as discussed recently by Brown et al. [3]

We would be remiss if we did not mention evidence that the Lennard–Jones potential may be too repulsive at short distances, leading to the underprediction of some diffusion coefficients at high temperatures by ~20% [13]. Paul and Warnatz [14] suggest that an exponential repulsive part may be more appropriate at high temperatures. The present methodology could be generalized to obtain potential parameters for such a potential as well. However, for now the Lennard–Jones potential is still in common use, largely because it is the potential used in CHEMKIN [15]. Brown et al. [3] recommend the use of Lennard–Jones parameters in combustion modeling over other forms, as well. We will focus on determining those parameters in the present article; the effect of using a softer repulsive wall as in the 9–6 Lennard–Jones potential will only briefly be considered. We also want to note that transport properties, particularly thermal conductivity and viscosity, depend on some other molecular properties, most notably dipole moments and polarizabilities. These properties can be computed accurately using relatively low-level electronic structure methods. We hope to address this issue in the near future.

2. Theory

Here we describe several methods for calculating spherically-averaged intermolecular potentials and/or Lennard–Jones collision parameters for a molecule or radical (A) interacting with a bath gas atom or molecule (B). All of the methods involve averaging the full-dimensional anisotropic intermolecular potential, $V(\mathbf{R})$, in some way over the colliding species' relative orientation and internal structures. This is simpler than evaluating the collision integrals directly using the full anisotropic potential. Instead, Lennard–Jones collision rate coefficients, z , are obtained from the calculated Lennard–Jones parameters σ and ϵ using Eq. (6) and tabulated [16] values of $\Omega^{(1,1)*}$.

The total geometry of the interacting binary A + B system can be written as $\mathbf{R} \equiv (\mathbf{R}^A, \mathbf{R}^B, \mathbf{R}^\Omega, r)$, where \mathbf{R}^A labels the internal coordinates of the target species, \mathbf{R}^B labels the internal coordinates of the bath gas (if any), and the remaining coordinates define the relative orientation of the target and bath, \mathbf{R}^Ω , and their center-of-mass separation, r . The full-dimensional intermolecular potential is defined relative to the separated *unrelaxed* species, i.e.,

$$V(\mathbf{R}) = E(\mathbf{R}) - E^A(\mathbf{R}^A) - E^B(\mathbf{R}^B), \quad (7)$$

where $E(\mathbf{R})$ is the total energy of the interacting target and bath gas evaluated at \mathbf{R} , $E^A(\mathbf{R}^A)$ is the energy of the isolated target molecule or radical evaluated at \mathbf{R}^A , and $E^B(\mathbf{R}^B)$ is the energy of the isolated bath gas atom or molecule evaluated at \mathbf{R}^B (which for atomic baths is zero).

Download English Version:

<https://daneshyari.com/en/article/168794>

Download Persian Version:

<https://daneshyari.com/article/168794>

[Daneshyari.com](https://daneshyari.com)