2003

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Recommended Citation

Keffer, D., Newman, A., Adhangale, P., "Using Molecular Level Simulations To Determine Diffusivities In the Classroom", Chemical Eng. Ed. 2003 37(2), p. 156-160.

ChE *classroom*

USING MOLECULAR-LEVEL SIMULATIONS TO DETERMINE DIFFUSIVITIES

In the Classroom

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When engineers require a diffusivity for a chemical species in a fluid mixture for which experimental data is not available, there are several methods of obtaining a value. The most obvious method is to experimentally determine the value of the diffusivity, but frequently time and money constraints rule out this method. In that case, a theoretical approach to obtain the diffusivity can be used.

There are a variety of established methods for theoretical determination of diffusivities. For self-diffusivities and transport diffusivities of binary systems in gases, we can obtain values from kinetic theory and corresponding states arguments, a corresponding state chart, and the Chapman-Enskog theory,[1-3] and for self-diffusivities and transport diffusivities of binary systems in liquids, we can use the Wilke-Chang equation.[1] There are also a variety of other empiricisms summarized in the literature.[4] Needless to say, these empiricisms, while valuable, are limited in terms of the types of systems that they describe.

An alternative to obtaining the self-diffusivities for fluid mixtures, including those with an arbitrary number of components, is to conduct equilibrium molecular dynamics simulations of the system.[5-7] Engineers have been calculating self-diffusivities with this method for a number of years, but using molecular dynamics to obtain self-diffusivities has not yet become a common alternative in chemical engineering transport classes because of the historically extensive computational resources required to conduct the simulations.

In this paper we describe our efforts and our results in incorporating molecular-level simulations into a graduate transport phenomena course. Above all, our philosophy was to provide a utilitarian tool that could be used in a manner analogous to existing techniques, such as the Wilke-Chang equation, to obtain transport diffusivities. Our target audience is the general graduate students in chemical engineering who will not necessarily perform molecular-level simulations as part of their thesis project. In the implementation of this work, we remain keenly aware of constraints due to time, computational resources, money, and target-audience qualifications.

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BACKGROUND

Academic Preparation

This transport course is taken in the second semester of the first year of graduate school. The students have already had graduate courses in thermodynamics, advanced mathematics, and fluid mechanics. The advanced mathematics course includes numerical solution of systems of ordinary differential equations (ODEs) and partial differential equations (PDEs).

The course is roughly divided into two components. The first is the generation of transport properties, such as diffusivities. The second component is solution of transport equations, which are most generally systems of coupled parabolic PDEs representing transient material, energy, and momentum balances. Since the students are already equipped to tackle the equations numerically, the course, while demanding practical solutions with numerical values, focuses on conceptual understanding of transport phenomena.

Molecular-Level Simulation

In an equilibrium molecular dynamics simulation, we select an appropriate potential that describes intramolecular and intermolecular interactions.[5-7] A typical potential for the intermolecular interaction of spherical molecules is the Lennard-Jones potential, for which parameters are widely available.[1-2] With a potential, we can generate the classical equations of motion, which for N spherical molecules result in a system of 3N coupled second-order nonlinear ODEs. For the calculation of diffusivities in a bulk fluid, N is generally in the range from 200 to 1000 molecules. We solve the ODEs numerically, obtaining positions and velocities as a function of time.

By collecting, analyzing (using the Einstein relation for diffusivity), and regressing the trajectories as a function of time, we can obtain mutual self-diffusion coefficients.[5] There is one mutual self-diffusion coefficient for each species in the mixture. These coefficients are a function of the thermodynamic state (temperature, density, and composition). They are self-diffusion coefficients because they were calculated from an equilibrium simulation in the absence of macroscopic concentration gradients.

The mutual self-diffusion coefficients provide a quantitative description of each component's mobility in the system, but they are not transport diffusivities (also called Fickian diffusivities). We require transport diffusivities if we intend to use them in Fick's Law in a transport equation (material balance) in order to obtain the solution to an applied engineering problem.

Irreversible Thermodynamics

The connection between mutual self-diffusivities and transport diffusivities is provided in the framework of irreversible or nonequilibrium thermodynamics. One commonly used equation relates the transport diffusivity to the self-diffusivity via the thermodynamic partial derivative[8]

$$D_{ij} = D_{\text{self},i}\,\frac{c_i \partial \ell n(p_i)}{c_j \partial \ell n(c_j)} \tag{1}$$

Equation (1) contains numerous, potentially serious, assumptions. (Critical discussions of the applicability of the equation are available elsewhere.[9-17]) Regardless, Eq. (1) is widely used for lack of an alternative. (One alternative is to perform full-blown nonequilibrium molecular dynamics simulations, which has also been done.[18]) For a binary mixture, Eq. (1) yields four diffusivities, which are intended to be used in Fick's law[13]

$$\underline{N}_A = c_A \underline{v}_A = -D_{AA}\nabla C_A - D_{AB}\nabla C_B \tag{2a}$$

$$\underline{N}_B = c_B \underline{v}_B = -D_{BA}\nabla C_A - D_{BB}\nabla C_B \tag{2b}$$

Traditional ChE Description of Diffusion

Chemical engineers know that the diffusive behavior of a binary system can be completely described by a single diffusivity. Traditionally, we write Fick's law relative to a molar average velocity, $\underline{v}^*$, and Fick's law is written (for a binary mixture)

$$\underline{J}_A^* \equiv c_A\left(\underline{v}_A - \underline{v}^*\right) = -cD_{BSL}\nabla x_A \tag{3a}$$

$$\underline{J}_B^* \equiv c_B\left(\underline{v}_B - \underline{v}^*\right) = -cD_{BSL}\nabla x_B \tag{3b}$$

where D_{BSL} is the only independent diffusivity.[1]

In the course we begin by calculating diffusivities for binary mixtures using the traditional correlations and theories, following the formalism and notation used in Reference 1. In order to compare the diffusivities of molecular dynamics simulations to traditional methods, we must present the diffusivities in Eq. (2) as a single number that can be directly compared to D_{BSL} in Eq. (3).

We have derived this relationship for a binary mixture and it is given as

$$\begin{aligned} D_{BSL} &= x_B\left(D_{AA} - D_{AB}\right) + x_A\left(D_{BB} - D_{BA}\right) + \\ &\quad \frac{1}{c}\left(x_A x_B D_{AA} - x_A^2 D_{BA} + x_B^2 D_{AB} - x_A x_B D_{BB}\right)\left(\frac{\partial c}{\partial x_A}\right) \end{aligned} \tag{4}$$

If the fluid is an ideal gas or we make some other assumption in which the density is not a function of composition, then $(\partial c/\partial x_A)$ is zero. We can use Eq. (4) to obtain a single transport diffusivity for the binary mixture. Since this diffusivity is the same property with respect to the same frame of reference that is generated by traditional methods of estimating

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the diffusivity of a binary system (such as the Wilke-Chang equation), we can make a direct comparison.

A FEASIBILITY STUDY

Time, Money, and Computational Constraints

Part of the reason that using molecular-level simulations to determine diffusivities isn't as prevalent in chemical engineering classrooms as it could be lies with the perception that the simulations simply require too much computer power. While this was true as recently as the 1990s, it is no longer true. Rigorous molecular-level simulations generating diffusivities (with error bars small enough to permit publication) now take only a few minutes on a several-year-old processor (for example, an AMD Athlon 850 MHz processor). In the example below, we provide specific program clocking. Certainly the impediment is no longer computational resources.

Efficient molecular-level simulations do require a FORTRAN or C compiler. Using a software platform that interprets code rather than compiling it is not an alternative due to the computational efficiency. In our example, we ran the simulations on

- *Compaq FORTRAN in the Microsoft Windows environment*
- *Intel FORTRAN in the Linux environment*
- *Matlab in the Microsoft Windows environment*

We shall show that a software platform that interprets code, rather than compiling it, is about four orders of magnitude slower than a structured code, and is thus not an option. Of the first two choices above, both have advantages. The advantage of the Windows environment is its ubiquity—the disadvantage is that the FORTRAN compilers for the Windows environment are relatively expensive. The advantage of the Linux environment is that both it and the FORTRAN compiler software for it are free.

Constraints Based on Target-Audience Qualifications

Our target audience are first-year chemical engineering graduate students, including those who do not intend to perform simulations as part of their thesis work. With this in mind, we structured the course to address that audience. Each part of the process that generates the diffusivity (including the molecular-level simulation, the irreversible thermodynamics, and the traditional description of diffusion) is presented with a pragmatic attitude: we are engineers who need a transport diffusivity; we first want to understand the techniques used to obtain the diffusivity; after we understand it, we want a simple, methodical, (preferably foolproof) algorithm to follow that generates a reliable transport diffusivity that we can use in material balances describing applied engineering systems.

The course is in no way intended to be an exhaustive survey of molecular-level simulation techniques, or of irreversible thermodynamics, or of the numerical solutions of ODEs and PDEs. On the contrary, the course describes a procedure that incorporates each of these elements. As we stated before, the students have obtained enough background during their first semester as graduate students to make this course content feasible.

When discussing molecular dynamics, we present a complete, self-enclosed description of the procedure.[19] We discuss only equilibrium molecular dynamics in the microcanonical ensemble, since that is the simplest system to simulate. A "base-case" FORTRAN code for this system is provided and discussed subroutine-by-subroutine in a lecture.[19]

AN EXAMPLE

As a practical example, we work problem 17.A.5 of Bird, Stewart, and Lightfoot.[1] The problem asks the students to calculate the quantity, cD_{BSL}, of an equimolar mixture of ni-

TABLE 1
Simulation Parameters

Number of N_2 molecules	108
Number of C_2H_6 molecules	108
Volume (Å^3)	1.88153×10^5
Intermolecular potential	Lennard-Jones
σ_{N_2} (Å)	3.667
$\sigma_{C_2H_6}$ (Å)	4.388
ε_{N_2} (K)	99.8
$\varepsilon_{C_2H_6}$ (K)	232
Integration algorithm	Gear fifth-order predictor corrector[22-23]
Time step (fs)	4
Long-range cut-off distance (Å)	12
Number of equilibration steps	50000
Number of data production steps	500000

trogen and ethane at 288.2 K and 40 atm. In the problem, the student is instructed to solve the problem using (a) an experimental data point and kinetic theory and (b) correlations and kinetic theory. If we obtain the concentration, c, of the mixture via the Lennard-Jones equation of state[20] with standard mixing rules,[21] the values of D_{BSL} are (a) 3.04×10^{-3} cm^2/s and (b) 2.78×10^{-3} cm^2/s.

The students then perform a molecular-level simulation using the parameters given in Table 1. From the simulations, they obtain self-diffusivities. They use Eq. (1) to generate transport diffusivities from the self-diffusivities, and they use the Lennard-Jones equation of state to provide the thermodynamic derivatives in Eq. (1). They use Eq. (4) to obtain a single transport diffusivity for the binary system.

TABLE 2
Simulation and Equation-of-State Results

Molecular Dynamics Results		*Equation-of-State Results*	
T(K)	293	T(K)	288.2
p(atm)	39.7	p(atm)	40
x_{N_2}	0.5	x_{N_2}	0.5
c(molecules/Å^3)	1.148×10^{-3}	c(molecules/Å^3)	1.148×10^{-3}
D_{self,N_2} (cm^2 / s)	3.445×10^{-3}	$\frac{c_{N_2}}{p_{N_2}} \frac{\partial p_{N_2}}{\partial c_{N_2}}$	1.1025
D_{self,C_2H_6} (cm^2 / s)	2.333×10^{-3}	$\frac{c_{N_2}}{p_{N_2}} \frac{\partial p_{N_2}}{\partial c_{C_2H_6}}$	-0.2150
D_{N_2,N_2} (cm^2 / s)	3.798×10^{-3}	$\frac{c_{C_2H_6}}{p_{C_2H_6}} \frac{\partial p_{C_2H_6}}{\partial c_{N_2}}$	2.3916
D_{N_2,C_2H_6} (cm^2 / s)	-7.405×10^{-4}	$\frac{c_{C_2H_6}}{p_{C_2H_6}} \frac{\partial p_{C_2H_6}}{\partial c_{C_2H_6}}$	0.7850
$D_{C_2H_6,N_2}$ (cm^2 / s)	2.392×10^{-4}	$\frac{\partial c}{\partial x_{N_2}}$ (molecules/Å^3)	-4.1060×10^{-4}
$D_{C_2H_6,C_2H_6}$ (cm^2 / s)	1.832×10^{-3}		
D_{BSL} (cm^2/s)	2.98×10^{-3}		

TABLE 3
CPU Usage

(The Matlab time is projected for a simulation of 550,000 steps, using the fact that a simulation of 20,000 steps used 179,360 seconds of CPU time. All codes were run on an AMD Athlon 850 MHz processor.)

Software	*Operating System*	*CPU Usage (Seconds)*
COMPAQ Visual FORTRAN 6.5	Windows XP Professional	443
Intel FORTRAN Compiler 5.0	Red Hat Linux 7.1 with Kernel 2.4.2-2	324
Matlab 5.1	Windows XP Professional	4.932×10^6

Following this procedure, the students obtain a value of D_{BSL} of 2.98×10^{-3} cm^2/s, which is nicely bracketed by the two estimates obtained via traditional means. A summary of the results of the molecular-level simulation that generated the self-diffusion coefficients, as well as the thermodynamic partial derivatives obtained from the Lennard-Jones equation of state and used in Eq. (1), are provided in Table 2.

Two notes of explanation are in order for Table 2. The temperature and pressure in the molecular dynamics simulation do not exactly match those stipulated in the problem. Because this is not a course in molecular simulation, we limit ourselves to simulating in the microcanonical ensemble, which is the simplest ensemble. In using the microcanonical ensemble, we fix the number of molecules of each species, the total system volume, and the total energy. Since the problem asks for the diffusivity at a given temperature and pressure, we estimate the density that corresponds to the requested T and p, using the Lennard-Jones equation of state. We then equilibrate at that density, maintaining a constant temperature with velocity scaling. For data production, we run in the microcanonical ensemble, which fluctuates about the set temperature, because there is no driving force pushing the temperature to another value.

Second, we see that D_{N_2,C_2H_6} is negative. It is acceptable to have a negative diffusivity in a Fick's law of the form of Eq. (2). This simply indicates that, all other things being equal, nitrogen would diffuse up the ethane gradients. This negative term, however, is roughly five times smaller in magnitude than the positive D_{N_2,N_2}, which yields a net positive transport diffusivity.

If we were to assume that the molar volume was not a function of composition, an assumption which is true for, among other systems, ideal gases, then the latter term from Eq. (4) would drop out and we would have a numerical value of D_{BSL} equal to 3.07×10^{-3} cm^2/s, as compared to the value from the complete version of Eq. (4), which was 2.98×10^{-3} cm^2/s. The effect of that term is to lower the diffusivity from a more ideal case.

In Table 3 we provide the CPU usage for our three cases on an AMD Athlon 850 MHz processor. Clearly, either of the FORTRAN cases makes this calculation a very reasonable homework problem, requiring less than 8 minutes of CPU time. We have solved a system of 648 (3 dimensions x 216 molecules) second-order

ODEs over 550,000 time increments (2 nanoseconds of data production—more than enough time to establish a self-diffusivity for this system) in 8 minutes.

In this demonstration, we computed the transport diffusivity of a high-density gas that could be adequately described with traditional methods, but there is nothing in the simulation code that limits it to a binary mixture, which therefore greatly expands the capabilities of molecular-level simulation.

CONCLUSION

We have presented work describing the practical use of molecular-level simulations to determine diffusivities in a course targeted at the general audience of first-year chemical engineering graduate students. We have shown how the simulation techniques can be used to directly complement traditional methods for obtaining diffusivities. We have provided an algorithm by which students can generate transport diffusivities that can be used in material balances that describe practical engineering applications. In the implementation of this work, we have shown that it is computationally feasible to include numerical simulations in the classroom. We have also shown that it is a financially modest approach for chemical engineering departments.

ACKNOWLEDGMENTS

DJK would like to thank the Departmental Chair, Dr. John Collier, for encouraging him to incorporate molecular-level simulations into the required graduate student curriculum. He would also like to thank Dr. Hank Cochran for his helpful discussions and encouragement. Finally, he acknowledges the students of ChE 548 who conducted these simulations and demonstrated that this was a worthwhile task: Keith Bailey, Yang Gao, Bangwu Jiang, Tudor Ionescu, Prajakta Kamerkar, Vishal Koparde, Austin Newan, Yizhong Wang, and Jiandong Zhou.

NOMENCLATURE

c	total molar concentration
c_i	molar concentration of component i
$D_{self,i}$	self-diffusivity of component i
D_{ij}	Darken transport diffusivity
D_{BSL}	single independent diffusivity for a binary system
$\underline{J}_A^*$	flux of component i, relative to molar average velocity
$\underline{N}_i$	flux of component i, relative to laboratory frame of reference
p	total pressure
p_i	partial pressure of component i
T	temperature
$\underline{v}_i$	velocity of component i
$\underline{v}^*$	molar average velocity
x_i	mole fraction of component i
ε_i	intermolecular potential well-depth of component i
σ_i	collision diameter of component i

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