AN INTRODUCTION TO
MOLECULAR TRANSPORT PHENOMENA

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The course "An Introduction to Molecular Transport Phenomena" is intended for upper-level undergraduates or first-year graduate students in engineering and science. The overall goal of the course is to provide a comprehensive description of the molecular basis of transport phenomena for students who have no previous background in statistical mechanics or statistical physics.

It is clear that recent dramatic advances in computational abilities (e.g., supercomputers and connection machines\textsuperscript{(1)}) and in atomic-level experimentation (e.g., atomic force microscopy and scanning tunneling microscopy\textsuperscript{(2)}) require that undergraduate engineers obtain a better molecular understanding or interpretation of engineering processes. One example is a surge in supercomputer purchases in the chemical industry; an example of the benefits of supercomputer computations is a reported $1-2 million savings in development costs for a new catalytic process.\textsuperscript{(3)} By studying the thermodynamic properties of the system through use of molecular simulations on a supercomputer, some critically unusual properties were discovered that would have been difficult to detect through physical experiments.

These new computational and experimental capabilities make it possible to examine, design, and/or enhance systems and processes beginning at a molecular level description—an approach that may be called "molecular engineering." In general, molecular engineering represents a new and powerful method of analysis where a rational and scientific framework can be utilized for the systematic study of highly complex engineering systems.

\textbf{TABLE 1}

\textbf{Course Outline}

"Introduction to Molecular Transport Phenomena"

\textbf{Prerequisites:} Undergraduate Engineering Mathematics (solution methods for ordinary and partial differential equations); Transport Phenomena (momentum, heat, and mass transfer); Chemical Engineering Thermodynamics or Engineering Thermodynamics.

\textbf{Topics for a One-Semester Course:}

- Mathematical Preliminaries (3-4)
- B. Transport Phenomena from Elementary Kinetic Theory (4)
- C. Phase Space and Liouville’s Equation (4)
- D. Reduced Distributions and the Equilibrium Behavior of Matter (7)
- E. The General Equations of Change (7)
- F. Transport Properties and Solutions to the Reduced Liouville Equation (7)
- G. An Introduction to Molecular Dynamic Computations (7)

\textsuperscript{*} Suggested number of classes are given in parentheses based on a fifteen-week semester, three classes per week; the two classes not shown are reserved for exams.

Molecular engineering also plays a critical role in the development of newly emerging areas of chemical engineering (such as advanced polymeric and ceramic materials, and biochemical and biomedical engineering) where a molecular and macromolecular description is a necessity rather than just an alternate method of analysis.\textsuperscript{(4)} There is a current need in the undergraduate curriculum for both qualitative and quantitative descriptions of processes and phenomena involving gases, liquids, and solids from a molecular viewpoint.

In this course, the macroscopic treatment of transport phenomena learned in previous courses is developed from molecular-level descriptions of matter. It is shown that the ad-hoc assumptions made in previous transport phenomena courses can be replaced by rational and scientific methods that will provide a general framework for the systematic analysis of complex systems or processes.

\textbf{COURSE OUTLINE AND DISCUSSION OF TOPICS}

The outline of this one-semester course is given in Table 1, and a more detailed discussion of each
section of material is given below. Suggested references in formulating the lecture for each section are also given.

**Mathematical Preliminaries**

Some mathematical preliminaries may be necessary, depending on the background of the students. Generally, students should have been exposed to some vector and tensor operations, such as summarized in Appendix A of Bird, Stewart, and Lightfoot.\(^6\) Additionally, some elementary concepts in probability are desirable. Our undergraduate students are exposed to such concepts\(^7\) in the second-semester engineering mathematics course. Regardless of the student backgrounds, however, I have found it important to review both of the above before proceeding with the core material.

**A. Introduction: Molecular View of Gases, Liquids, and Solids**

The purpose of this section of the course is to present a qualitative molecular picture of gases, liquids, and solids. Additionally, quantitative examples are given to illustrate the usefulness of a molecular interpretation of the three phases of matter.

An important dynamic feature of molecules is their seemingly random motion. The mechanical model shown in Figure 1 is a useful mechanical analog of the random motion of molecules. In this model, gravity causes the metallic balls to move down a cascade of inclined planes. When projected onto a screen, the balls appear to be under random molecular motion, as shown in Figure 2a. Of course, actual random motion is due to the collisions between molecules, where each molecule obeys Newton's Second Law of Motion.

The same mechanical model can also be used to provide a qualitative molecular picture of the three phases of matter. In a gas, the average intermolecular spacing is much greater than the diameter of a molecule or the average range over which intermolecular forces act; this is depicted in Figure 2a. In Figure 2b, a liquid is depicted by allowing all of the metallic balls to settle to the bottom of the container and then slightly tilting the container to one side. Although the intermolecular spacing is relatively small, there is a great degree of disorder in the molecular arrangements. This can be contrasted to a solid, shown in Figure 2c, where the container is tilted to an even greater angle. In solids, a regular arrangement of the molecules is observed and various types of packing geometries are possible.

In addition to the different geometric arrangement of molecules in gases, liquids, and solids, the trajectories or dynamics of the molecules are characteristically different. In Figure 3, adapted from Barker and Henderson,\(^7\) computer-generated trajectories of molecules (see section G below) in the three states of matter are shown. The tight spacing and strong molecular interactions in solids cause molecules to be constrained to move about fixed lattice sites in a seemingly vibration-type motion.
liquids and gases, on the other hand, the spacing is not as close and the interactions are not as strong, and consequently the molecules have a less constrained motion.

The above discussions should lead to the recognition that the nature of the forces between molecules is important in determining the molecular picture and hence the properties of gases, liquids, and solids. A brief discussion of the Lennard-Jones potential is given in Bird, et al., although a more extensive discussion of intermolecular forces can be found.\[8,9\]

Although the above discussions are of a qualitative nature, some very simple, yet motivating, quantitative examples can be given that illustrate how the molecular picture can directly predict the observed macroscopic properties of matter. The following example, taken from Tabor,\[10\] illustrates the calculation of the internal energy change for sublimation of a crystal.

Example: The connection between molecular structure and macroscopic properties: The internal energy change for sublimation of an ionic solid.

The molecular structure of a NaCl ionic crystal is shown in Figure 4. In the process of sublimation, a change from the crystalline state to the vapor state takes place. Neglecting any subatomic contributions, the internal energy of the crystal is primarily due to the electrical potential energy associated with the configuration of the Na\(^+\) and Cl\(^-\) ions. Considering any ion in the crystal, we note that geometrically there are six nearest neighbors of opposite sign at the distance \(r\) from the ion, 12 neighbors of the same sign at a distance \(\sqrt{3} r\), 8 neighbors of opposite sign at a distance of \(\sqrt{3} r\), etc.

According to Coulomb’s Law, the total potential energy associated with moving each ion to its position relative to the central ion is

\[
U = \frac{1}{2} N \left( -A \frac{e^2}{r} \right)
\]

(2)

Equation (2) represents a sum over pair interactions in the crystal, or “pairwise additivity.” A general representation and discussion of pairwise additivity can also be given where Eq. (2) represents a special case for the NaCl ionic crystal.

In order to finally compute the internal energy change for the sublimation process, the internal energy of the NaCl vapor molecules is needed. Each NaCl molecule is a neutral molecule and, consequently, the total potential energy is obtained by multiplying the electrical potential energy associated with the formation of a single molecule by the total number of molecules, \(N/2\). i.e.

\[
U_{\text{vapor}} = -\frac{1}{2} \frac{N e^2}{r_0}
\]

(3)

where \(r_0\) is the interatomic distance for NaCl in the vapor state.

The internal energy change, per mole, for the sublimation process represents the difference in electrical potential energy between the vapor and solid states, which from Eqs. (2) and (3) is

\[
\Delta U_{\text{sub}} = \frac{1}{2} N e^2 \left( \frac{1.75}{r} - \frac{1}{r_0} \right)
\]

(4)

where \(N\) is the number of ions per mole. Using the values of \(r = (2.82 \times 10^{-8})\) cm and \(r_0 = (3.60 \times 10^{-8})\) cm given by Tabor\[10\] the internal energy change for sublimation of NaCl crystal is calculated from Eq. (4) as 65.3 kcal/mole. An experimental value can be

Figure 3. Characteristic molecular trajectories in gases, liquids, and solids\[3\] corresponding to the molecular arrangements shown in Figure 2.

Figure 4. The NaCl crystal; closed circles represent Na\(^+\) and open circles represent Cl\(^-\). The internal energy of the crystal is obtained by summing the electric potential energy changes in bringing each ion from infinity to its place on the lattice.
estimated from heats of formation data as 54.7 kcal/mole,\(^{13}\) which is in good agreement with the calculated value.

Many other examples of this nature can be used to show the relationship between the molecular-level description of matter and macroscopically observed quantities. For example, Tabor also treats the problem of theoretically predicting the bulk modulus of a crystal from knowledge of the molecular interactions. These examples are very useful in motivating the molecular treatments of transport phenomena that follow in the remaining sections.

**B. Transport Phenomena from Elementary Kinetic Theory**

A simple, but elegant, treatment of the transport properties of gases can be shown through the elementary kinetic theory of gases. The so-called phenomenological laws of transport phenomena (Fick's Law of Diffusion, Fourier's Law of Heat Conduction, and Newton's Law of Viscosity) are also derived through the elementary kinetic theory of gases. Consequently, this is a very useful introductory theory in establishing a firm physical foundation for discussing the phenomenological laws.

In general, mass, momentum, and energy can be transferred by a substance through random motions and interactions of its constituent molecules. This transfer takes place even in the absence of any overall or bulk-material motion. An everyday example is the rapid sensation of odors in a closed room, without drafts, at locations many meters away from the source of their emission. Here, random molecular motion is the driving force for a macroscopic transfer of material.\(^1\)

The phenomenon of macroscopic transfer as the result of random molecular motion is illustrated in Figure 5, which shows molecules of two different types, depicted as open and closed circles. The left-hand side of the plane at \(z = 0\) is more concentrated in open circles than in closed, although the total number of circles is equivalent on both sides of the plane. One of the basic hypotheses of the elementary kinetic theory of gases is that a gas is comprised of molecules in constant random motion. Although this randomness is in all directions, for the sake of simplicity we will consider only one dimension. For example, consider random molecular motion in the \(z\)-direction, as shown by the arrows randomly affixed to each molecule in Figure 5. This could be accomplished by a series of coin tosses where a "heads" corresponds to an arrow pointing to the right, and a "tails" results in an arrow pointing to the left.

Over a small interval of time, several molecules will be transferred from the left-half to the right-half plane, and vice-versa, owing to random molecular motion, with the total number of molecules on either side of the plane remaining essentially unchanged (no overall motion). Because of the imbalance in concentrations, the several molecules transferred from the left-half to the right-half plane are predominantly open circles, whereas the several molecules transferred from the right-half to the left-half plane are predominantly closed circles. Thus, there will be a net transfer of open circles from a more concentrated region of open circles to a lower concentrated region of open circles. Likewise, the closed circles also are transferred from a region of high concentration of closed circles to a region of lower concentration of closed circles. Random molecular motion statistically tends to equalize concentration differences that exist in a system. The macroscopic observation is a net transfer of a molecular property in a direction from a high property concentration to a low concentration.

In addition to molecules being characterized as a certain type or species, molecules also possess the properties of momentum and energy. Since momentum is a vector quantity, there are three scalar components of momentum that are considered as separate properties. Gradients in the concentration of these properties (\(x\), \(y\), or \(z\) momentum/volume and energy/volume) will also result in a transfer of those properties through the system by random molecular motions.

There are many excellent quantitative developments of the elementary kinetic theory of gases that follow from the above qualitative description. A very concise quantitative treatment of the elementary

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\(^1\) By macroscopic, we mean an observation made over a statistically large group of molecules.
kinetic theory of gases is given by Hirschfelder, et al. Other elementary transport theories for liquids and solids can also be discussed, e.g., the Eyering theory of transport phenomena in liquids.

C. Phase Space and Liouville's Equation

The purpose of this section is to develop the so-called Liouville equation, which is the starting point in the derivation of the transport equations and associated flux relations (see Section E below).

There are several introductory and clearly written developments of the Liouville equation that can be consulted for this section of the course,\textsuperscript{12-14} and only some highlights will be given here.

In this section and the remaining sections, we consider only molecules of a single type or species; the transport phenomena of multicomponent systems is beyond the scope of an introductory, one-semester course.

The first part of this section of material discusses the concepts of phase points and phase space. The phase point represents the collection of all momentum and position variables of the molecules in the system at any time. As the molecules move according to Newton's Second Law of Motion, the phase point moves through a multidimensional space consisting of the momentum and position coordinates of all the molecules in the system. I have used simple cartesian coordinates in an undergraduate class. However, some instructors may wish to introduce the concept of generalized coordinates and Hamiltonian equations of motion.

Next, the concept of an ensemble of phase points is introduced. Each phase point or member of the ensemble initially consists of the same total number of molecules, same total momentum, and same total energy. There are, however, a number of different ways or realizations in distributing the initial positions and momenta of the molecules in order to achieve the same total values in energy and momentum (macroscopically indistinguishable systems). The collection of these realizations can be visualized as a "cloud" of phase points at any time. A number density function is introduced to quantify the "cloud" that moves through multidimensional space.

An analogy can immediately be drawn between the number density function for the phase points and the ordinary mass density function introduced in the first undergraduate transport course in fluid mechanics. In fact, the Liouville equation simply represents a conservation equation for the phase points as they move through multidimensional space.

I have used Figure 2.1 in Bird, et al., as a start-
assumed "natural" behavior of the phase point number density function that it tends to zero as the position and momentum variables of the molecules tend to infinite values.

The configurational part of the reduced Liouville equation is useful in the development of equations of state and thermodynamic properties of gases, liquids, and solids. This equation can be derived as outlined by Hirschfelder, et al., and is recognized by statistical thermodynamicists as the "Integral Equation" for lower-ordered configurational distribution functions (see Section F below).

E. The General Equations of Change

It is the purpose of this section of the course to develop the transport equations (or mass, momentum, and energy conservation equations) from first principles. Although many introductory texts on kinetic theory and transport phenomena derive the transport equations beginning with the so-called Boltzmann transport equation (Section F below), following Irving and Kirkwood\[15\] we prefer to adopt a general approach and derive the transport equations directly from the Liouville equation developed in Section C. The resulting "General Equations of Change" are applicable to all types of flows, including laminar, turbulent, and shock flows, thus forming an important basis for understanding current and future developments in transport phenomena.

As mentioned in the previous section, the normalized phase point number density function $\rho_N$ can be interpreted as a probability density function, i.e., $\rho_N dr_N dp^N$ is proportional to the probability of finding a phase point in a multidimensional region between $(r^N, p^N)$ and $(r^N + dr^N, p^N + dp^N)$ at any time. Just as one defines the mean, variance, and other moments of probability density functions, we can also examine these quantities with respect to the phase point (probability) density function. More specifically, the averaging can be performed directly with the Liouville equation leading to the so-called transport equations. The transport equations thus represent the behavior of the various moments of the density function $\rho_N$. These moments are defined more specifically below. Since the Liouville equation is a conservation equation, the transport equations also represent conservation equations for the various moments of the density function.

Following Irving and Kirkwood, the average or expectation value of any dynamical variable $\alpha(r^N, p^N)$ that does not depend explicitly on time is introduced as

$$E[\alpha] = \frac{1}{N!} \int \alpha(r^N, p^N) f_N(r^N, p^N, t) dr^N dp^N$$

where $f_N(r^N, p^N, t) = N! \rho_N(r^N, p^N, t)$ is the phase point density function for indistinguishable molecules.

A judicious choice of $\alpha$ leads to the definitions of the average mass (or number) density, average momentum, and average energy for the fluid as follows:\[15\]

1) Average Total Mass Density, $E[\alpha] = \rho(r, t)$

$$\alpha = m \sum_{k=1}^{N} \delta(r_k - r)$$

2) Average Total Momentum Density, $E[\alpha] = \rho(r, \mathbf{v}(r, t))$

$$\alpha = m \sum_{k=1}^{N} p_k \delta(r_k - r)$$

3) Average Total Energy Density, $E[\alpha] = U(r, t)$

$$\alpha = \frac{1}{2m} \sum_{k=1}^{N} p_k^2 \delta(r_k - r) + \frac{1}{2} \sum_{j=1}^{N} \sum_{j=1}^{N} \theta_0 \delta(r_j - r)$$

Note that the first term in Eq. (8) represents the kinetic energy contribution, and the second term represents the intermolecular potential energy contribution.

The transport equations can now be derived using the simple paradigm of multiplying the Liouville equation by each of the defining relations for $\alpha$ and integrating over all phase space. Since there are some similarities in each derivation, this process can be facilitated by first considering the conservation equation for $\alpha$.\[9, 15\] Generally, finding time to derive the energy balance equation has been difficult. For the purposes of this introductory course it is sufficient to derive the mass and momentum conservation equations and merely present the results for the energy conservation equation.

Finally, it should be noted that in the derivation of the transport equations, use is made of the integral relationship involving the derivative of the Dirac delta function\[16, 17\]

$$\int g(x) \delta^{(n)}(x - x_0) dx = (-1)^n g^{(n)}(x_0)$$

where $\delta^{(n)}$ denotes the $n^{\text{th}}$ derivative of $\delta$ with respect to $x$ and, similarly, $g^{(n)}(x_0)$ is the $n^{\text{th}}$ derivative of $g$ with respect to $x$ evaluated at $x_0$. The derivation of Eq. (15) can be easily obtained by using one of the limiting definitions of the delta function (a generalized function) e.g., the limit of a normal or Gaussian density function as the variance tends to zero.

F. Transport Properties and Solutions to the Reduced Liouville Equation

The general equations of change derived in the previous section contained expressions for the property flux vectors representing the transfer of a property relative to the mass average velocity of the
fluid. It was shown that these expressions contain lower-order density functions whose behavior is dictated by the corresponding reduced forms of the Liouville equation introduced in Section C.

It is the goal of this section to show that various types of solutions to the reduced Liouville equation result in a form of the transport equations known as the Navier-Stokes equations. This derivation can be rigorously accomplished for dilute gases which, by definition, have at most only two molecule encounters; three or more molecule interactions are neglected. Consequently, the reduced Liouville equation derived in Section E can be truncated at order two for a dilute gas. From this truncated equation a very simple derivation of the so-called Boltzmann transport equation can be given.\(^{18}\) Note that some discussion on the geometry and dynamics of a binary molecular collision is necessary in the development of the Boltzmann equation.

Having derived the Boltzmann transport equation, scaling and dimensional analyses are performed.\(^{19}\) The Knudsen number, the ratio of a characteristic molecular length scale (such as the gas mean free path) to a characteristic macroscopic length scale, is introduced as an important dimensionless group for the Boltzmann transport equation.

By considering the two extremes (i.e., very small and very large Knudsen numbers), various approximate analytical solutions to the Boltzmann equation can be outlined. Unfortunately, there is not sufficient time in a one-semester course to cover these solutions in great detail. Typically, I have outlined the Chapman-Enskog solution to the Boltzmann equation, asymptotically valid at very small Knudsen numbers. This discussion includes the Boltzmann H-Theorem, the first-order perturbation expansion, and the general forms of the solutions. The overall presentation is sufficient to obtain the celebrated Navier-Stokes equation and the energy transport equation encountered in the students’ previous courses on transport phenomena. Newton’s Law of Viscosity and Fourier’s Law of Heat Conduction are shown to naturally arise in the Chapman-Enskog solution method. The expressions for the coefficients of viscosity and heat conduction are also obtained. However, it is shown that further resolution of these expressions is needed (via solutions to a set of finite integral equations) in order to perform actual numerical calculations. Typically, there is not sufficient time to cover the solution to these specific integral equations, nor is it necessary at this level, and the final results can be presented without proof.

The above discussions and presentations are also sufficient for demonstrating the connection between thermodynamics and transport phenomena. It is readily shown that, under local equilibrium conditions, the normal component of the pressure tensor in a dilute gas is the thermodynamic pressure. For fluids that are far removed from local equilibrium, it is doubtful that the thermodynamic pressure can be utilized in a transport equation. Nonetheless, a general framework has been established for evaluating the pressure tensor in both equilibrium and nonequilibrium fluids; similar analyses can be applied to the evaluation of the internal energy.

A homework assignment can also be given that ties together thermodynamic and transport properties for dilute gases: experimental values of the second virial coefficients for a variety of dilute gases are used to determine the corresponding Lennard-Jones force constants.\(^{18}\) The Lennard-Jones constants determined in this manner are, subsequently, used to predict the viscosity coefficients of each gas according to the Chapman-Enskog formula.

Some instructors may wish to present other solutions to the Boltzmann transport equation, such as Grad’s 13-moment method; some recent reviews on solutions to the Boltzmann transport equation are given by Cercignani\(^{19}\) and by Dorfman and van Beijeren.\(^{20}\) A condensed discussion of the Chapman-Enskog method is given by McQuarrie\(^{21}\) and a readable discussion is given by Vincenti and Kruger.\(^{22}\)

\section*{G. An Introduction to Molecular Dynamic Computations}

Given the dramatic advances in the scientific and engineering computational abilities provided by supercomputers and other machines, it is highly likely that many problems in transport phenomena will, in the future, be solved at the molecular level. It should be clear from the above discussions that the numerous approximations involved in actually resolving the transport equations limits the usefulness of the results for performing engineering calculations for a variety of different systems, other than systems of dilute gases. Although extending the usefulness of the statistical mechanical development of transport phenomena is a subject of current engineering and scientific research, molecular dynamics computations provide a fundamentally simple and rigorous means of studying transport phenomena for almost all classical fluids.\(^7\)

There are many books and review articles on the molecular dynamics method. No attempt is made

\(^7\) For a review of nonclassical or quantum mechanical methods for molecular dynamics, see Kosloff.\(^{20}\)
here to review the literature in this area. Rather, some suggested discussions and topics are given that are useful as further expositions of the topics covered in the previous sections. It is important that the students understand the basis and salient features of the molecular dynamics method and see the usefulness of the method in predicting equilibrium or nonequilibrium properties of matter.

A recent text by Heermann discusses a number of important aspects of the molecular dynamics method, including finite difference schemes for solving the equations of motion for the molecules, periodic boundary conditions and minimum image convention, types of ensembles, and averaging methods for determining macroscopic properties. Heermann also lists a number of computer programs associated with the molecular dynamics method. For example, a clearly presented computer program listing is given for microcanonical (constant energy) ensemble equilibrium molecular dynamics. This program can be readily installed on a mainframe computer or network system. As an enlightening homework assignment, the students can be asked to determine the equilibrium pair correlation function for a Lennard-Jones fluid discussed in Section D above. Comparisons between dilute gases, dense gases, and liquids can be made, as well as the study of other types of intermolecular potentials and equations of state.

Instructors may also wish to present other types of molecular dynamics methods or applications, including nonequilibrium molecular dynamics methods. Because of the conceptually simple basis of molecular dynamics, instructors can have a great degree of flexibility (and fun!) in bringing their own interests into developing this part of the course.

CONCLUDING REMARKS

In general, I have found this course suitable as an upper-level chemical engineering elective course. A final student project is substituted in place of a final exam. The students can select any project that illustrates a molecular interpretation of the macroscopic properties of matter. Ideally, these topics should be taken from areas not fully treated in the lecture material, such as molecular design in solids, multicomponent systems, and other molecular dynamic or Monte Carlo simulation methods. Specific applications or potential applications to systems of interest to chemical engineering and related disciplines should be emphasized in the students' projects. These additional topics could also be developed in a second-semester course where greater emphasis could be placed on molecular level engineering design of materials and processes.

Although the lecture material is taken from a number of different sources (a course text is currently in preparation), any introductory book on statistical mechanics or statistical physics, some of which are given in the references, should be used as a required supplementary text for the course. These texts can provide a source of homework problems and can be used as a basis for the development of some of the material suggested above.

REFERENCES