MOLECULAR ENRICHMENT OF THE CORE CURRICULUM

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The core courses of chemical engineering are properly taught from the viewpoint of continuum physics. Thermodynamics, transport phenomena, and reaction engineering, as they are now presented to students, would be unchanged whether molecules exist or not. This is a strength in that one need never worry about underlying structure or mechanism. But it is also a weakness, for so much of practice in chemical engineering, in the thermal fluid sciences part of mechanical engineering, and in aerothermochemistry rests directly upon molecular insights. It is truly molecular engineering. Without a molecular perspective to complement their continuum perspective, our young graduates will be ill-equipped to be full participants in modern engineering practice.

Building on the courses in physical chemistry, we can enrich our continuum-based core courses in chemical engineering by having students study an auxiliary textbook that discusses the same phenomena and processes, but from a molecular point of view. The molecular discussion can be read at the same time that they read any of our good continuum-based textbooks.

The needed enrichment must not delve into the exotica of quantum and statistical mechanics that is of interest only to the specialist, however; it must engage students and faculty alike at their existing level of understanding. Molecular understanding and practical examples must be compelling and memorable to the engineering student rather than elegant to the theoretical chemist. The molecular perspective on thermodynamics, on transport, and on chemical kinetics may thereby be merged into the four or five semesters now required for the core.

DEFINITIONS AND EXAMPLES

Molecular engineering encompasses those problems wherein a molecular perspective (whether it be computational or merely phenomenological) is an essential part of any optimum design. A number of illustrative examples follow.

Chiral synthesis and separation is an essential part of many problems involving pharmaceuticals, manufactured foodstuffs, agrochemicals, flavors, and fragrances. Chirality can be critical in drug manufacture. For example, one isomer of thalidomide (shown below) is a useful sedative while the other is a potent teratogen that caused thousands of birth defects three decades ago.

How is a stereoselective catalyst designed, or how does one think about separation of chiral molecules? To be sure, Pasteur first separated crystals of d and l tartaric acid by using a pair of tweezers and a microscope, for the salts of the two isomers have macroscopically recognizable differences in crystal morphology. But more usually one thinks about specific complexing agents that geometrically fit the one molecule but not the other. Such catalyst and separation designs are exercises in molecular recognition. Designs frequently depend upon either ab initio or semi-empirical quantum mechani-

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Chemical Engineering Education
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difference is due to the arrangement of the nineteen atoms of the cluster. The understanding and application of clusters is impossible outside of the molecular perspective.

Suppose we are interested in the specific impulse that might be obtained from an electrothermal arcjet thruster using \( \text{H}_2 \) as the propellant. At plasmatemperatures, we need the thermodynamic properties of \( \text{H, H}_2, \text{H}^+, \) and \( e \), for it is necessary to calculate the difference in enthalpy of the expanding gas between the combustion chamber and the exit plane of the nozzle if we are to estimate the thrust. There is no way to measure the heat capacity or entropy of atomic hydrogen or of protons. Rather, we calculate all of the properties using the techniques of molecular physics. With values for all of the properties, we can calculate the equilibrium extent of reaction of

\[
\text{H}_2 \leftrightarrow 2\text{H}
\]

and then the specific enthalpy of the reacting and expanding gas in the nozzle as a function of temperature and pressure. From this, the expected thrust levels for any particular motor design can be deduced. One believes the calculated values of thermodynamic properties in regions not experimentally accessible because in all instances where such comparisons between theory and experiment are possible, agreement is excellent. Without molecular insight, such rational rocket motor design would be impossible.

One of the best ways to grow diamond films is by chemical vapor deposition (CVD). In the high-energy environment of a low-pressure plasma, a large variety of reactive chemical species can exist, and each may play a significant role in the formation and quality of the resulting diamond film. With a feedgas stream of \( \text{H}_2 \) and \( \text{CH}_4 \), reactive species including \( \text{CH}, \text{C}_2, \text{C}_3, \text{C}_2\text{H}_2, \) and \( \text{C}_2\text{H} \) are evident. Different electronic and vibrational states are also evident, and these may not be in equilibrium with the translation/rotation heat bath. How does the concentration of species vary in time and place in the CVD reactor, or with temperature, or with pressure, or with feed-gas composition? How do you even think
about the temperature of such a reacting gas mixture in the presence of an electric field? Such a CVD gas mixture may not be at equilibrium at all, but rather the concentration of the various species may be kinetically determined. All such questions must be addressed from the point of view of molecular engineering, and the optimum design of CVD reactors for diamond deposition depends upon these molecular insights.

Such a listing of examples of molecular engineering could continue, but these few suggest the central importance of molecular insight in engineering design.

**INNOVATION VS. DESIGN**

The manufacturing ability of the United States is being challenged by worthy competitors, particularly in Germany and Japan. The NSF and the entire federal research and development establishment is developing a major initiative designed to help ensure that American industry maintains its international competitiveness. Terms such as “agile manufacturing,” or “21st Century manufacturing,” or “environmentally benign manufacturing” are seen with regularity. Creative innovation and design are central to success in competitive manufacturing. Whether one is substituting an alternative reaction chemistry or optimizing a separation and heat exchange network, there is creative opportunity.

Molecular engineering addresses questions of innovation by stimulating the engineer to think about, say, an alternative separation based on some newly synthesized zeolite with heretofore unavailable pore-size. After the innovation, process design allows its optimization. Both are important—but the senior design class in chemical engineering usually concentrates on process design alone (which has become very logical and analytical).

Computerized design methodologies are a triumph of modern chemical engineering. But in contrast, molecular engineering gives the student more opportunity to be imaginative. It gives the chemical engineer an opportunity not unlike that afforded to an architect who imagines the form of a building and then performs structural design calculations (just as in the chemical engineer’s process design) to judge whether that imaginative design is economically buildable.

Modeling and tools such as ASPEN are important and powerful components of the curriculum. But they will never invent AVLIS or a stereoselective separation or a nanoparticle manufacturing scheme. After the innovation has occurred, conventional teaching allows the practitioner to pursue the important, but subsequent, tasks of simulation, modeling, optimization, and control. That initial innovation, however, is the point where molecular insight is so important. It is not a panacea, and it is not a sufficient condition for innovation. But it does broaden one’s scope and opportunities.

Some curricula require a year of physical chemistry where some insights into partition functions, energy levels, kinetic theory, and molecular dynamics is learned. However, ABET requires only one semester of physical chemistry (which is largely classical thermodynamics in most courses). Whether the study of molecular physics in physical chemistry is required or elective, it is to be applauded—but it remains a subject apart from the mainstream (like technical writing, or the German language) and the student never integrates modern molecular physics into his or her engineering Weltanschauung (philosophical world-view). That now-missing integration is the goal of molecular enrichment of the core curriculum.

**SOLUTION**

Teaching and learning molecular engineering, like other subjects in the core curriculum, are not difficult if the sophisticated research-oriented aspects of the subject are abandoned. For example, starting with a thought experiment with a collection of a half-dozen, labeled molecules, one immediately visualizes the most probable distribution of molecules among energy levels, with the distribution driven to its most probably state by no other mechanism than simple chance.\(^1\) Then, with the same Lagrangian technique of undetermined multipliers learned in calculus or in thermodynamics when calculating reaction equilibria, the student immediately derives the Boltzmann distribution; he/she gains immediate insight into why so many macroscopic phenomena (equilibrium constant, rate coefficient, vapor pressure, etc.) depend on exp(-energy/RT).

Molecular insight also provides a powerful pedagogical tool in that it enables linkage between otherwise (seemingly) disparate macroscopic phenomena and processes. For example, it can be seen that the same intermolecular collision frequency that governs the chemical reaction rate also governs thermal conductivity. As a pedagogical tool, molecular engineering is compelling, provided only that sophisticated molecular physics is avoided.

Similarly, single particle partition functions are easy to understand as compared to ensemble ideas. To be sure, there are troubling consequences when
real gases are studied, but sensible treatment is possible and nothing has to be unlearned by those very few students who later will wish to become expert in statistical thermodynamics.

The Maxwell-Boltzmann distribution of molecular speeds is easily obtained from the most probable distribution of energy, which itself was easily obtained (as we saw) from simple thought-experiments with a few labeled molecules. With the MB distribution, all the concepts of kinetic theory of average speed, mean free path, and collision frequency may be immediately shown. Similarly, and of more interest to students, each of the transport properties can be calculated and collision theories of chemical kinetics can be developed.[1] Compelling comparisons of all such theories with experiment make it real and believable to the students. With this kinetic theory, it is natural to realize that chemical reaction does not occur in one step as we typically write an overall stoichiometric change, e.g.,

\[ \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr} \]

Rather, reaction occurs by a complex array of usually bimolecular encounters which together constitute the reaction mechanism, which for the hydrogen/bromine flame is

- \[ \text{Br}_2 \rightarrow 2 \text{Br} \]
- \[ \text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H} \]
- \[ \text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br} \]
- \[ \text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br} \]
- \[ \text{Br} + \text{Br} \rightarrow \text{Br}_2 \]

The rate of each of these molecular events of the mechanism depends on its particular reactant collision frequency, the relative energy involved in the collision, the energy states of each colliding reactant, and the relative geometry of the colliding reactants at the moment of impact. Reaction occurs only in collisions that occur with an above-some-minimum threshold energy, and even then only in collisions that occur with certain geometric orientation. Finally, the macroscopic (or observed) rate of the overall stoichiometric change is some sort of a complex average of these many different microscopic events. And, under a variety of assumptions, this averaging can be calculated, and comparisons with experiment may be made.

It is pedagogically essential to present numerous comparisons with experiment and to present many case studies and practice problems to inspire and provide exercise for the students in their development of new skills.[1]

CONCLUSION

You may invent a laser-based process for isotope separation, or be concerned with fundamental problems in combustion leading to greater fuel efficiencies and less pollution, or be concerned with ion implantation for the development of new alloys of new and unusually doped materials of interest in electronics, or require some property of matter that may be unknown or unmeasurable. From whatever perspective, however, a molecular view is essential, and a purely traditional or classical perspective unacceptably slows invention, hinders creativity, and frustrates original design.

This enrichment of the chemical engineering core curriculum will have served its purpose if its attitudes can be internalized. That is, long after the student has forgotten just exactly how this or that particular argument or calculation goes, he or she will nonetheless instinctively think about any problem in terms of what the molecules must be doing. That is the real, bottom-line goal of molecular enrichment of our core curriculum.

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REFERENCES


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OXYGEN MASS TRANSFER

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