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October 1995

Molecular Thermodynamics: Opportunities and Responsibilities

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Abstract

In chemical engineering, most applications of molecular thermodynamics have been based on various forms of the van der Waals theory of fluids augmented by chemical equilibria and by concepts from other, by-now classical, theoretical concepts such as the Flory-Huggins model for polymers and the Debye-Hückel theory for electrolyte solutions. "Extended" van der Waals theory remains a promising method for contributing to the solution of contemporary engineering problems. While modern developments in the theory of fluids are impressive, as yet, they have had only limited impact on engineering practice, in part, because of the widening communication gap between those who do statistical mechanics and those who design and develop chemical processes and products. To realize the large potential utility of molecular thermodynamics, both classical and modern, researchers must not only exhibit more willingness to reduce their work to practice but also to exhibit multidimensionality, i.e., to relate molecular thermodynamics to other chemical engineering disciplines such as mass and heat transfer, nucleation and chemical kinetics. While the future success of molecular thermodynamics will be enhanced by progress in its own narrow domain, the promising possibilities of applied molecular thermodynamics depend crucially on its integration within the wider domain of chemical technology.

I. INTRODUCTION

It has often been pointed out that the special quality of a chemical engineer is versatility, the ability and willingness to use a variety of intellectual concepts and methods toward solving a goal-oriented problem.

While versatility indicates an open mind, able and willing to embrace with courage and imagination whatever discipline or tool may be useful, there is another aspect to versatility that is best described by multidimensionality. An effective chemical engineer is someone who relates his or her special expertise to other areas of concern, someone who may focus on one part of a practical problem but also retains an overall view of where the special area intersects with others. For example, a specialist in heterogeneous catalysis cannot be truly effective unless he or she is also keenly aware of heat and mass transfer in chemical reactors and beyond that, reactor control, corrosion, safety and, inevitably, economics.

My impression of current research in molecular thermodynamics suggests that, in too many cases, there is a deficiency in multidimensionality. It is always difficult--perhaps impossible--to generalize because exceptions can easily be identified, but to the extent that there is a trend, it seems to me that those of us who work in molecular thermodynamics research are not maximizing our opportunities because we are forgetting our responsibilities.

I claim that our major responsibility is first, to identify truly significant problems and second, to reduce our work to practice. I fear that unless we do so, we will become marginalized, that is, perceived as irrelevant to the chemical industry that we are supposed to serve and that directly or indirectly is the source

of support for our efforts. If we lose the confidence of chemical industry, the budget for molecular thermodynamics will rapidly decline at the National Science Foundation and other funding agencies.

Identifying truly significant problems is difficult because communication between industry and university is inadequate and all too often one-sided. Typically, when industrial colleagues come to the Berkeley campus they want to learn what we are doing but, perhaps for proprietary reasons, they are often reluctant to tell us about their important problems. Nevertheless, if we are to realize the unquestioned potential opportunities of molecular thermodynamics, concerted efforts must be made to improve two-way communication. I encourage academics to take every opportunity to meet industrially-oriented colleagues and to ask lots of questions, preferably in the company of a generous supply of beer. To paraphrase President Kennedy: Ask not what the National Science Foundation can do for your academic prestige but ask what you can do at the cutting edge of science toward providing useful and understandable contributions to engineering.

There are many points of view concerning the responsibilities of a chemical engineer who does research in molecular thermodynamics. Certainly I do not claim that my viewpoint is in any way superior but let me state it clearly: With few exceptions, while research by chemical engineers should be at the frontiers of knowledge, research results should be sufficiently developed and reduced to practice so that an engineering-oriented user can understand and apply them without excessive difficulty. My view is that a researcher who claims to be a chemical engineer should not be content to publish only in the Journal of Chemical Physics but must take the time and trouble to show the consequences of his or her research, to show not only how, when and where but also why. In our zeal for new intellectual concepts, tools, and computation techniques, and in our ambition to show our erudition, too many of us in the academic world tend to forget the engineering community that legitimately expects from us the tools for innovative technology.

2.   CONVENTIONAL AND MODERN MOLECULAR THERMODYNAMICS

In this discussion of opportunities and responsibilities, it is useful to distinguish between conventional and modern molecular thermodynamics. Here, conventional refers to the status which prevailed until about 1975, a status which we may call the van der Waals paradigm, concepts and ideas that we find in standard undergraduate textbooks, engineering science based on phenomenological models with little input from statistical thermodynamics. Modern refers to models based, for example, on the integral theory of fluids, density functional theory, sophisticated perturbation methods, fluctuation theory, graph theory, and increasingly, on molecular simulation using high-speed computers.

At present, when molecular-thermodynamic methods are used in chemical engineering practice, they are almost always based on what I have here defined as conventional molecular thermodynamics. Intellectually it is more exciting to work on research in modern thermodynamics but as yet, applications are not plentiful.

Conventional molecular thermodynamics is still remarkably useful for establishing new contributions to chemical engineering. This usefulness is most effective within the framework of multidimensionality, when molecular thermodynamics interfaces with essential non-thermodynamic considerations that make a chemical process commercially attractive.

3.   SOME OPPORTUNITIES IN CONVENTIONAL MOLECULAR THERMODYNAMICS

To illustrate, consider a process developed by C. J. King and coworkers for recovery of valuable carboxylic acids from dilute aqueous solutions (Starr and King 1992). A brute-force method for recovery is

to evaporate all the water but that method is too expensive because of the large enthalpy of vaporization. At first glance, extraction is not promising because carboxylic acids have low solubilities in solvents that are immiscible with water. However, these solubilities are much larger when the solvent is saturated with water as it would be in an extraction process. Table 1 gives solubilities of three carboxylic acids in dry and in water-saturated cyclohexanone.

Starr and King proposed an economically attractive process outlined in Figure 1: extract acid from water using cyclohexanone as solvent and then strip out water from the water-saturated solvent; stripping is simple because at these conditions, the volatility of water relative to cyclohexanone is well in excess of unity. As water is removed, essentially pure carboxylic acid precipitates as a solid. For process design, Figure 2 shows the necessary phase equilibria. The results shown required a large experimental effort because no molecular thermodynamic model was immediately available for correlating the phase equilibria. Required here is a model for vapor-liquid, liquid-liquid and solid-liquid equilibria in the ternary system carboxylic acid-water-cyclohexanone. At present, we have some crude van der Waals-type models for this case but I expect that, with some effort, we could develop a truly useful model that requires only a few experimental data. Regrettably, Jud King's graduate student never discussed this with me. I was not aware of what he was doing until after his thesis was completed. (In other words, his fugacity was high; he managed to escape.)

RECOVERY OF CARBOXYLIC ACIDS FROM
DILUTE AQUEOUS SOLUTION

(STARR AND KING)

1 - EXTRACT ACID FROM WATER WITH CYCLOHEXANONE.

2 - IN WATER-SATURATED CYCLOHEXANONE, WATER IS HIGHLY VOLATILE BECAUSE ITS ACTIVITY COEFFICIENT IS LARGE.

2 - WATER IS STRIPPED OUT OF THE CYCLOHEXANONE STREAM.

4 - REDUCED WATER CONTENT OF CYCLOHEXANONE LOWERS SOLUBILITY OF CARBOXYLIC ACID.

5 - CARBOXYLIC ACID PRECIPITATES. CLEAN CYCLOHEXANONE IS RECYCLED TO STEP 1.

Fig. 1. Steps for Recovery of Carboxylic Acids

SOLUBILITIES OF CARBOXYLIC ACIDS
IN CYCLOHEXANONE AND IN WATER-SATURATED
CYCLOHEXANONE AT 25 °C

	CONC. OF WATER MOLES/LITER	SOLY. OF ACID MOLES/LITER
FUMARIC ACID	0	0.053
	4.75	0.456
SUCCINIC ACID	0	0.136
	8.32	1.04
ADIPIC ACID	0	0.163
	7.38	1.06

SOLUBILITY IN WATER-SATURATED CYCLOHEXANONE IS ABOUT 6 OR 8 TIMES THAT IN ANHYDROUS CYCLOHEXANONE.

Table 1. Solubilities of Carboxylic Acids

A similar but more difficult example is provided by a low-energy process for production of salt from brine. The classic method is to evaporate water with a triple-effect evaporator but when energy costs are high, a much more economical method is provided by extractive crystallization as suggested by Scott Lynn and coworkers (Weingaertner, Lynn and Hanson 1991). In this process, a water-soluble solvent is added to the brine at room temperature, very much reducing the solubility of salt which precipitates. After the salt crystals are removed, the solvent is regenerated by changing the temperature, perhaps 20 or 30 °C, where the aqueous solution splits into two liquid phases, one rich in water and the other rich in solvent. Figure 3 shows

the essential idea of this process. We can distinguish between two possibilities; in the left side of Figure 3, solvent and water exhibit an upper critical solution temperature while in the right side of Figure 3, solvent and water exhibit a lower critical solution temperature (Ting, Lynn and Prausnitz 1992; Brenner, Anderson, Lynn and Prausnitz 1992).

Fig. 2. Phase Equilibria for Adipic Acid

EXTRACTIVE CRYSTALLIZATION OF

SALTS FROM AQUEOUS SOLUTIONS

TWO TYPES OF PHASE DIAGRAMS FOR WATER/ORGANIC SOLVENT SYSTEMS
SATURATED WITH SALT

FIRST TYPE: n-PROPANOL OR n-BUTANOL

SECOND TYPE: SECONDARY OR TERTIARY AMINE

AT T_C, ORGANIC SOLVENT IS STRONGLY HYDROPHILIC.

AT T_R, ORGANIC SOLVENT IS WEAKLY HYDROPHILIC.

Fig. 3. Crystallization of Salts from Aqueous Solution by Addition of an Organic Solvent

For process design, Scott Lynn requires solid-liquid and liquid-liquid equilibria for a ternary system containing salt, water and an organic solvent. To limit data requirements, a molecular-thermodynamic model would help but, until recently, nothing suitable was available. A good attempt was made by Vera and coworkers (Chaluget et al 1994) and by Zerres (Zerres and Prausnitz 1994) with some, but not complete success. The literature is rich in models for VLE for aqueous salt solutions and there are some molecular-thermodynamic studies on VLE in salt solutions with mixed solvents. But--as we know--it is much more difficult to model LLE than VLE.

It is unlikely that some physical chemist will provide us with a practical procedure for calculating LLE in salt-water-solvent solutions. And we may have to wait many years until computer simulation can help us for obtaining reliable quantitative results for such equilibria. In the meantime, there exists an opportunity for conventional thermodynamics to fill the gap.

4

Recovery of carboxylic acids and production of salts are topics that are not likely to excite graduate students. To arouse the interest of graduate students, it is necessary to add a prefix to molecular thermodynamics. A good one is eco which stands not for economic but for ecologic. An even better prefix is bio.

Woll and Hatton (1989) provide a fine example illustrating application of conventional thermodynamics to biotechnology. They considered the use of reverse micelles as minireactors for enzyme-catalyzed reactions. These reactions require an aqueous environment but often the reactants are only sparingly soluble in water. It has therefore been suggested to form reverse micelles in an organic solvent; the reverse micelle contains the enzyme in a tiny pool of water. Reactants dissolved in the organic solvent diffuse into the reverse micelle and products diffuse out. For design of such reactors, it is necessary to know distribution coefficient K for the enzyme between the reverse micelle and a continuous aqueous phase as indicated in Figure 4. Coefficient K depends on numerous variables, especially on the electric charge of the enzyme which is determined by pH and on concentration S of the anionic surfactant (AOT).

PARTITIONING OF A PROTEIN BETWEEN
WATER AND REVERSED MICELLES
(FROM T. A. HATTON)
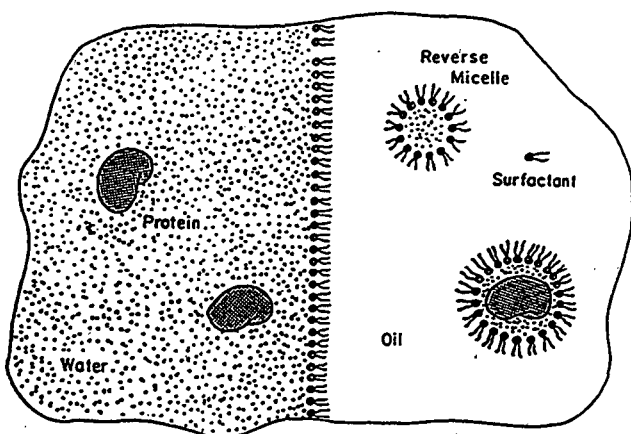
FOR RECOVERY, PURIFICATION OF TARGET PROTEINS

OR FOR MINIREACTORS FOR ENZYME-CATALYZED
REACTIONS:

REACTANTS ———→ PRODUCTS
(ENZYME)

REACTANTS AND PRODUCTS HAVE ONLY
VERY LOW SOLUBILITY IN WATER BUT
ENZYME NEEDS WATER FOR CATALYTIC
ACTIVITY.

Fig. 4. Reverse Micelles Provide an Aqueous
Mini-environment for Proteins

CONSTANTS FROM DATA REGRESSION
GIVE REASONABLE VALUES OF
PHYSICAL PARAMETERS

Regressed coefficients for the correlation of protein partition coefficient with pH and surfactant concentration
$\ln K = A + B(pH) + [C + D(pH)] \ln S^*$

	Ribonuclease	Concanavalin
A	4.43	11.42
B	-0.061	-1.054
C	-2.84	-5.50
D	0.585	-1.158

* Units of S are moles/dm³

Estimated parameter values for thermodynamic partitioning model

	Ribonuclease	Concanavalin
pI	7.8	7.2
$\Delta\psi$ [mV]	68	68
N_x	100	100
ΔG^o [kJ/mole]	-29.4	-41.9
α	-1.0	-1.64
n_o	1.72	2.84
ϵ	-0.59	-0.70

UNDERLINED PARAMETERS WERE
SPECIFIED FROM INDEPENDENT DATA.
OTHERS WERE OBTAINED FROM
REGRESSED CONSTANTS A, B, C & D.

Table 2. Correlation of Protein Partition
Coefficients

Woll and Hatton presented an analysis using conventional molecular thermodynamics augmented by relations from electrochemistry. After a series of reasonable simplifying assumptions, they derived a simple equation giving ln K as a linear function of pH, shown in Figure 5. Some experimental data are shown in Figure 6. Table 2, showing constants A, B, C and D from data regression, shows that these constants

are not mere fitting parameters but correspond at least approximately to their physical significance as given in their definitions.

SIMPLE MOLECULAR-THERMODYNAMIC THEORY

FOR PARTITION COEFFICIENT K

(WOLL AND HATTON)

$$\ln K = A + B\,(pH) + [C + D\,(pH)]\,\ln S$$

$$A = -\,[\Delta G^0 - \alpha\, F\, \Delta\psi\,(pI)]/RT - [n_0 - \epsilon\,\alpha\,(pI)]\,\ln N$$

$$B = -\,(\alpha\, F\, \Delta\psi)/RT - \epsilon\,\alpha\,\ln N$$

$$C = n_0 - \epsilon\,\alpha\,(pI) \qquad\qquad D = \epsilon\,\alpha$$

S =	SURFACTANT CONCENTRATION
ΔG^0 =	STANDARD-STATE ΔG FOR PROTEIN TRANSFER IN ABSENCE OF ELECTRIC-CHARGE EFFECTS
F =	FARADAY'S CONSTANT
pI =	PROTEIN ISOELECTRIC POINT
n_0 =	NO. OF EMPTY MICELLES REQUIRED AT pH = pI
N =	AGGREGATION NUMBER OF MICELLE
α =	PROPORTIONALITY FACTOR RELATING PROTEIN CHARGE TO pH (FROM PROTEIN TITRATION DATA)
$\Delta\psi$ =	ELECTROSTATIC POTENTIAL DIFFERENCE BETWEEN MICELLE AND BULK SOLUTION
ϵ =	CHANGE IN MICELLE SIZE PER UNIT CHARGE

Effect of pH and surfactant concentration on the solubilization of concanavalin in reversed micelle solutions. Solid lines are from the correlation established from a regression using data points denoted by the filled symbols. [● 0.025 M, ■ 0.05 M, ▼ 0.10 M, ♦ 0.20 M AOT]

AOT is the ionic surfactant

Fig. 5. Partition Coefficient for Protein Depends on Numerous Variables

Fig. 6. Partition Coefficient for Protein Depends Strongly on pH

The remarkable feature of this work is that an extremely complex physical situation has been described by a simple equation. Of course the result is not rigorous; of course it is approximate. But it is not arbitrary, blind empiricism. It is useful for interpreting data and for extrapolation to other systems where data may be sketchy or nonexistent.

A final example is given by the work of R. C. Reid 22 years ago (Reid 1973). I cite this work here because it illustrates how conventional thermodynamics can be used to contribute to an important practical subject that also requires other, nonthermodynamic, sciences.

Reid was interested in understanding explosions which can occur when a liquid is suddenly contacted with another liquid or solid at a much higher temperature. Very rapid heat transfer can superheat the liquid far above its boiling point at the prevailing pressure. Explosion can occur if the superheated temperature exceeds a limit which can be calculated from stability theory. Reid measured this limit in a column filled with a dense host liquid shown in Figure 7. In the bottom of the column, the liquid of interest is injected in the form of tiny drops. A temperature gradient is maintained in the column. As the droplet rises, its temperature increases and eventually explodes. The explosion is observed visually as a function of temperature and pressure.

Using his and other experimental explosion data, Reid prepared the reduced pressure-versus reduced temperature plot shown in Figure 8. The line is calculated from the Redlich-Kwong equation of state; for a given pressure, the superheated temperature limit is given by the spinodal line shown schematically in Figure 9. The spinodal line separates the metastable from the unstable region. When heating a liquid at fixed pressure, the temperature rises rapidly; when the temperature enters the unstable region, an explosion is likely.

CALCULATED AND OBSERVED
SUPERHEAT-LIMIT TEMPERATURES

BUBBLE-COLUMN FOR MEASURING

SUPERHEAT-LIMIT TEMPERATURES

(FROM R. C. REID 1973)
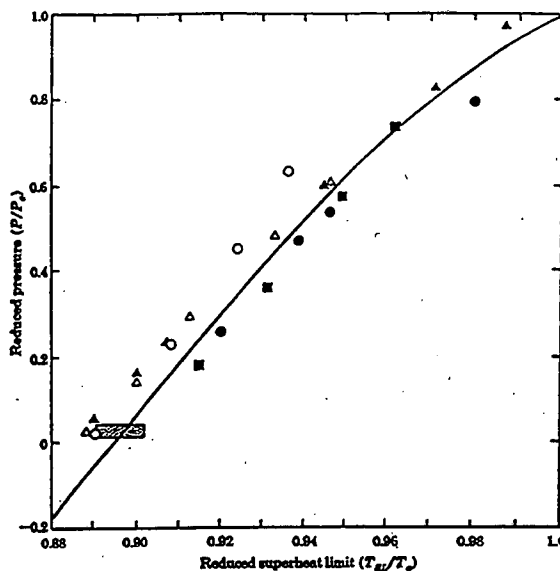
In bubble-column experiments, reduced superheat-limit temperatures (T_{sL}/T_c) correlate with reduced pressure (P/P_c). The rectangle encompasses data from many experiments with different liquids at a pressure of one atmosphere. The solid line is calculated from thermodynamic stability theory using the Redlich-Kwong equation of state.

O = cyclohexane
△ = n-pentane ● = n-hexane
■ = n-heptane ▲ = dichloro-
difluoromethane

(FROM R. C. REID 1973)

Fig. 7. Reid's Apparatus for Measuring Explosive Conditions Due to Superheating

Fig. 8. Correlation of Limiting Superheat Temperatures Based on Stability Theory and the Redlich-Kwong Equation of State

The results in Figure 8 do not alone constitute a theory of explosions due to rapid heat transfer. To establish that theory, other sciences, notably nucleation theory, are required. However, molecular thermodynamics--in this case, very simple molecular thermodynamics--can make a contribution. Bob Reid did this work in response to stimuli from colleagues outside the thermodynamic community. He had heard about explosions of liquified natural gas spilled onto the ocean from tankers and asked himself how his expertise in thermodynamics might help better to understand and control this phenomenon. Thanks, in part to Bob Reid, such explosions are now very rare. I cite this example to illustrate what I mean by opportunity and responsibility.

4. SOME OPPORTUNITIES IN MODERN MOLECULAR THERMODYNAMICS

Social philosophers tell us that we live in a post-industrial society where "industrial" refers essentially to manufacturing. Post-industrial does not say that we no longer manufacture anything but rather that we think about the problems of industry using new ideas and methods, taken from a variety of areas such as psychology, anthropology, linguistics, political science and increasingly, feminism. In an analogous way, molecular thermodynamics now is in a post-van der Waals era. That does not mean that methods based on the van der Waals concept are no longer useful but rather that molecular thermodynamics is now increasingly using ideas and tools from a variety of advanced concepts in chemical physics, mathematics and computer simulations.

Theories and correlations based on van der Waals-type ideas are best described by words like phenomenological and mean field. A van der Waals fluid is represented by a crude mechanical picture, by a photograph taken with poor focus, where structural details are not visible. By contrast, statistical mechanics takes structure very seriously; modern results from statistical thermodynamics are usually based on detailed structural information, typically given by distribution functions which, essentially, tell us where atoms are located in space. The modern picture of a fluid therefore comes from a sharply focused photograph.

The most useful analytic tool for calculating fluid structure is the Ornstein-Zernike equation which can give distribution functions for a variety of molecular assemblies as a function of temperature, density, composition and intermolecular (or intergroup) potentials. Once we have the required potentials and distribution functions, we can calculate thermodynamic properties using well-established integrals. In modern molecular thermodynamics, primary emphasis is not on macroscopic properties but on structure and on intermolecular (or intergroup) forces as expressed through potentials. Once structure and forces are quantitatively known, thermodynamic properties follow in a manner that is usually straightforward although it may be tedious. ·

A practical illustration of modern molecular thermodynamics comes from recent work in polymer solutions. For example, Chiew has applied the Ornstein-Zernike equation to a system of sticky spheres; because each sphere has two sticky spots, an assembly of sticky spheres can form chains. Using sophisticated mathematics, Chiew (1990) derived a relatively simple equation of state for non-attracting chains of spheres

$$z = \frac{Pv}{RT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \left(\frac{r-1}{r}\right)\left[\frac{1+ \eta/2}{(1 - \eta)^2}\right] \tag{1}$$

where reduced density $\eta = \frac{\pi}{6}\rho\sigma^3$; ρ is the number density of spheres; σ is the sphere diameter; and r is the number of spheres in the chain.

In Eq. (1), the first term is the well-known Carhahan-Starling equation; the second term accounts for chain formation; when r = 1, the second term disappears. Chiew's result has been generalized to mixtures of non-attracting chains. Song et al added a perturbation term to take into account forces of attraction between chains; it is then possible to generate complex phase diagrams for polymer solutions where temperature is plotted against composition for fixed pressure and/or polymer molecular weight. Figure 10 shows one example for a system with both lower and upper critical solution temperatures (Song, Lambert and Prausnitz 1994).

In addition to the Chiew-Song theory, there are several other similar theories for polymer solutions, notably those based on Wertheim's SAFT theory (Wertheim 1987; and, for example, Chapman et al 1990; Ghonasgi and Chapman 1994; Chen, Economou and Radosz 1992). These theories can represent all the observed phase diagrams for solutions and blends of polymers, copolymers and solvents but good quantitative agreement with experiment requires empirical modifications. Nevertheless, perturbed chain-of-spheres theories, based on structure, provide a big improvement over the conventional 50-year-old Flory-Huggins equation and the perturbed hard-chain theories of the 1970's.

Another example based on the Ornstein-Zernike equation is provided by recent work of Ford and Glandt (1994) who were concerned with sorption of a fluid in a porous medium, shown schematically in Figure 11. Dark circles represent solid particles and light circles represent fluid molecules. The void spaces represent the pores. The structure of the solid particles is frozen but the fluid molecules are free to move. In this idealized case, parameter ϵ is the depth of a square-well potential for interaction for molecule-molecule and molecule-particle interactions and d is the diameter of a particle equal to that of a molecule. The Ornstein-Zernike equation is used to establish the structure of the matrix and then the chemical potential of the fluid is obtained as a function of fluid number density. Under some conditions, the same chemical potential is obtained for two values of that density, producing a phase diagram shown in Figure 12. A horizontal line drawn at some fixed temperature and fixed number density of particles gives the compositions of two coexisting phases. The top line corresponds to 100% pores; the top line therefore gives phase equilibria for the bulk fluid.

EFFECT OF PRESSURE ON THE PHASE
DIAGRAM FOR A 3-MER/300-MER MIXTURE

CALCULATION OF SUPERHEAT-LIMIT
TEMPERATURES

(AFTER R. C. REID, 1976)

ISOTHERM T_1

ISOTHERM T_2

PRESSURE

P_1

CONNODAL

SPINODAL

VOLUME

FOR PRESSURE P_1, THE EQUIL. TEMP. IS T_1.
BUT THE SUPERHEAT-LIMIT TEMP. IS T_2.

$$T_2 > T_1$$

AT P_1 AND T_2, $\left(\frac{\delta^2 P}{\delta v^2}\right)_T = 0$.

T_{c1} AND P_{c1} ARE CRITICAL TEMPERATURE AND PRESSURE OF SOLVENT 1 ; ϕ_2 IS THE SEGMENT FRACTION OF POLYMER 2.

AT LOW PRESSURE, PHASE BEHAVIOR IS OF THE "HOUR-GLASS" TYPE. AT HIGH PRESSURE, THE SYSTEM SHOWS AN UPPER CRITICAL SOLUTION TEMPERATURE AND A LOWER CRITICAL SOLUTION TEMPERATURE.

ϵ AND σ ARE SEGMENT PARAMETERS.
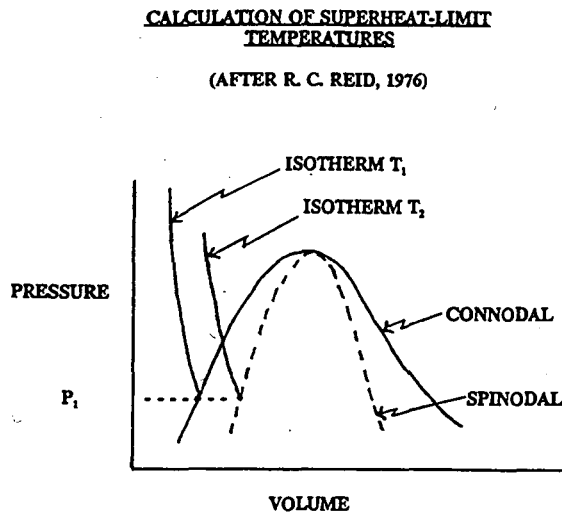BECAUSE $k_{12} = 0$, $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$.

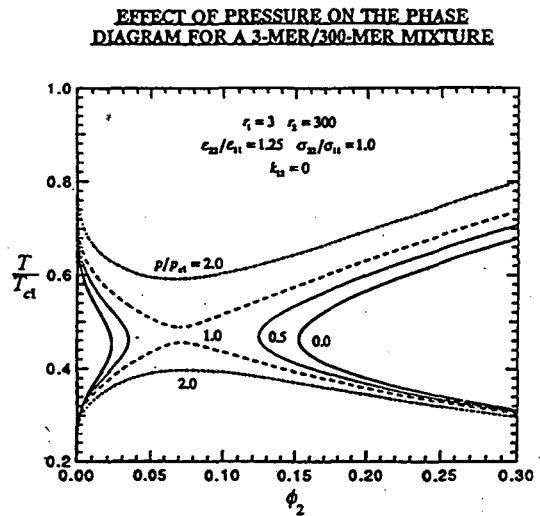Fig. 9. Superheat-Limit Temperatures from Stability Theory

Fig. 10. Phase Diagram for a Binary Polymer-Solvent System Showing Upper and Lower Critical Solution Temperatures

Figure 12 gives information on condensation of a sorbed fluid in a porous medium. The maximum of each curve gives a critical temperature; condensation is not possible above that temperature but below that temperature condensation can occur, depending on fluid density. The critical temperature declines as the number density of frozen particles rises, i.e., as the porosity falls.

While this work by Ford and Glandt is for a highly idealized situation, it represents an impressive achievement that indicates the power of modern molecular thermodynamics. It is an intellectual tour de force obtained with elegant mathematics. It is difficult to imagine that similar results could have been obtained with van der Waals-type thermodynamics. Regrettably, Ford and Glandt did not yet show calculations for more realistic systems nor did they yet compare their results with experiment. Hopefully they will do so, consistent with my definition of opportunity and responsibility.

FLUID IN A POROUS MEDIUM
(FORD AND GLANDT 1994)

PHASE EQUILIBRIA FOR A FLUID f IN
CONTACT WITH A POROUS MEDIUM
(FORD AND GLANDT 1994)
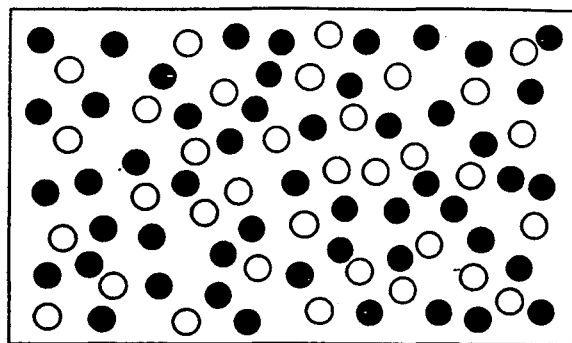
● IMMOBILE SOLID PARTICLES

○ FLUID MOLECULES

VOID SPACE REPRESENTS PORES

THE STRUCTURE (RADIAL DISTRIBUTION FUNCTIONS) IS OBTAINED FROM THE ORNSTEIN-ZERNIKE EQUATION AS A FUNCTION OF FLUID DENSITY, PARTICLE DENSITY AND INTERACTION ENERGIES.

FROM THE STRUCTURE, THE CHEMICAL POTENTIAL OF THE FLUID IS FOUND.
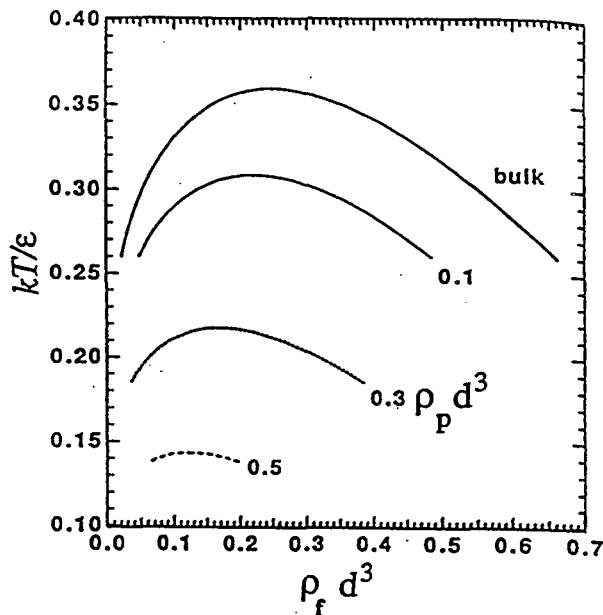
ρ_f = NUMBER DENSITY OF FLUID f
ρ_p = NUMBER DENSITY OF SOLID PARTICLES
$d_f = d_p$ = DIAMETER d
$\epsilon_{fp} = \epsilon_{ff}$ = INTERACTION ENERGY ϵ

Fig. 11. Idealized Picture of a Porous Medium

Fig. 12. Phase Diagram for a Fluid Confined to a Porous Medium

5.   MOLECULAR SIMULATION

A major opportunity for molecular thermodynamics is provided by molecular simulation using ever-more-powerful computers. One significant application of simulations is to give quantitative answers to questions that cannot be answered experimentally.

An example is provided by the simulation calculations of Smit and coworkers (Siepmann, Karaborni and Smit 1993) who studied the critical properties of paraffins as a function of carbon number N_c.

Because paraffins become thermally unstable at temperatures above 650K, it is difficult, perhaps impossible, to measure critical properties of paraffins with $N_c > 10$. However, for correlating phase behavior of heavy petroleum using standard equations of state it is necessary to have good estimates of these properties.

Using the Gibbs-ensemble technique, Smit and coworkers calculated coexistence diagrams for normal paraffins to $N_c = 48$, as shown in Figure 13. These diagrams provide estimates of critical temperature and critical density; when these estimates are compared with limited experimental results, the results are, in part, surprising. Simulation calculations show that the critical temperature rises monotonically with N_c but Figure 14 shows that the critical density does not; the critical density unexpectedly goes through a maximum near $N_c = 8$. Based on experimental evidence alone, there was some question about the validity of the maximum because there is disagreement in the trend of the data; the data of Teja and coworkers (Anselme, Gude and Teja 1990) show a maximum but those of Steele (Steele, quoted by Tsonopoulous and Tan 1993) do not. Molecular simulation calculations have settled the disagreement: the maximum in Figure 14 is real.
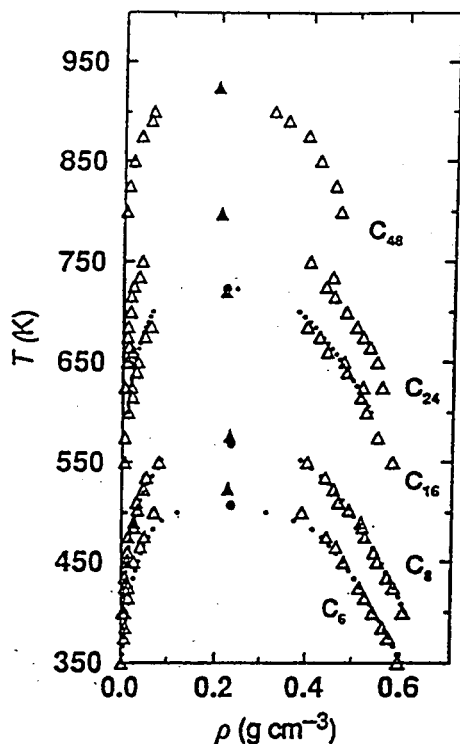
Vapor-liquid curves for various alkanes, plotted as temperature T against density ρ. Simulations are represented by open triangles and the critical point by a large filled triangle. The experimental results are represented by black dots. The experimental critical points are represented by large filled circles.

(FROM SIEPMANN et al)

Fig. 13. Calculated and Observed Phase Diagram for Normal Alkanes. Calculations from Molecular Simulations
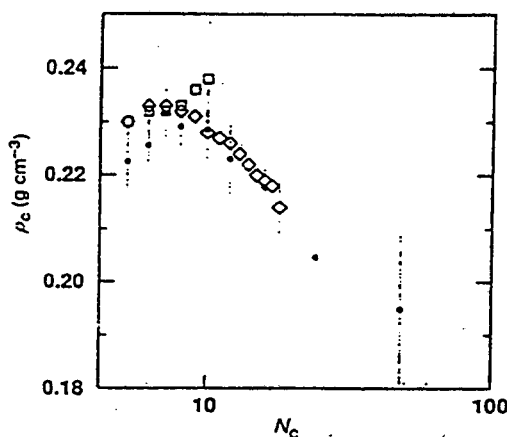
Critical densities of the normal alkanes (ρ_c) as a function of carbon number (N_c). The experimental data of Anselme et al are represented by diamonds, the data of Steele by squares and the results from the simulations by filled circles.

(FROM SIEPMANN et al)

Fig. 14. Calculated and Observed Critical Densities of Normal Alkanes. Calculations from Molecular Simulations

While molecular simulation can give us guidance concerning thermodynamic properties for common engineering calculations, it is perhaps most useful when it provides a connection with material science. Molecular simulation can give structural details that are not accessible by classical van der Waals models. To illustrate, consider some recent work by Snurr, Bell and Theodorou (1993) on sorption of p-xylene in a zeolite (silicalite).

There are two structures of silicalite, called otho and para; these structures are known quantitatively from X-ray diffraction experiments. Snurr et al calculated sorption isotherms for p-xylene for both structures

at 70 °C, shown in Figure 15. Also shown in that figure are some experimental results by Olson which indicate a step function in sorption.

There has been considerable speculation concerning the step function observed 14 years ago. Is there perhaps a condensation effect? Snurr's calculations suggest that there is no condensation but a change in silicalite structure when each unit cell in the zeolite contains about 4 molecules of p-xylene.

Snurr's work illustrates that, while molecular simulation can often provide useful answers, simulation alone cannot solve all our problems. In this case, simulation calculations support the conclusion that silicalite is not an inert matrix for sorbing hydrocarbon solutes but experiences a phase change in response to some critical value of sorption. However, a reliable numerical value of that critical sorption must be determined experimentally. Similarly, the two structures of silicalite were obtained from experimental measurements. Molecular simulation is a powerful tool, but it is only that, not a magic drug for curing all ailments.

Given the wide range of applicability of both old and new tools, of both conventional and modern thermodynamics, the opportunities for molecular thermodynamics are wide open, especially if we can find the courage and the financial support to tackle new problems in new areas, in industries other than petroleum-related industries which have dominated such a large part of chemical engineering thermodynamics. It is difficult to obtain financial support for research in new areas of application because, unlike in the petroleum industry, molecular thermodynamicists are not well known in industries concerned with, for example, pharmaceuticals, foods, textiles, metals, electronics and so on. To obtain support from industry or from government, we must first show that we have something useful to contribute; in other words, we must bear the burden of proof.

It is this burden of proof which constitutes for me the responsibilities of molecular thermodynamics. We have the intellectual power and the versatility characteristic of chemical engineering to tackle new problems successfully. But are we willing to complete the job, that is to reduce our work to practice? Are we willing to devote the time and effort to do what is now called "technology transfer" My sense of responsibility is that we must make a greater effort to communicate less with each other but more with those in process and product design who can benefit from what we have to offer. If we fail in meeting that responsibility, we will become irrelevant and the world will treat us accordingly.

6.   CONCLUSION

I would like to conclude with a happy example of technology transfer, an example where research in molecular thermodynamics, perhaps unexpectedly, opened a new area of application, well removed from those in the petroleum and petrochemical industries. I refer to the work of Chang and Randolph (1989) who measured the solubility of β-carotene in supercritical ethylene, shown in Figure 16. β-Carotene, found in vegetables, may be useful as a drug for treating cancer; its solubility is a highly nonlinear function of pressure in the vicinity of ethylene's critical point; ethylene may, therefore, provide a useful process for supercritical fluid extraction. That was hardly news in 1989; many similar results had been reported previously. However, Chang and Randolph also observed that, because a rapid drop in pressure produces high rates of nucleation, supercritical ethylene can be used to prepare very fine solid particles of β-carotene, as shown in Figure 17. When a wide size distribution of β-carotene particles is dissolved in ethylene at high pressures, and the pressure is suddenly reduced, a narrow size distribution of tiny particles is obtained. It is precisely this narrow distribution of very small particles which the pharmaceutical industry wants for efficient drug-delivery systems. While it is difficult to obtain such narrow distributions by crystallization from cooling a liquid solution, it is simple to do so by rapidly decreasing the pressure in a dense-gas solution.

Using a gas to precipitate a solid has also found application in the polymer industry's prevailing search for new and better materials. To illustrate, Figure 18 shows experimental phase boundaries for a

12

dilute solution of polyamide-8 in dimethyl sulfoxide (DMSO) and carbon dioxide (Yeo, Debenedetti, Radosz and Schmidt 1993). At low pressures, we have two phases: a vapor rich in carbon dioxide and a liquid rich in DMSO with dissolved polymer. As the pressure rises, polymer precipitates and we have three phases: vapor, liquid and solid. At still higher pressures vapor and liquid merge; we then have two phases: fluid and solid.

The phase boundaries in Figure 18 are commercially interesting because, depending on the selected temperature and pressure, the polymer can precipitate in different morphologies, having different mechanical and optical properties. The morphology obtained depends also on kinetic and hydrodynamic factors (e.g., stirring) but the phase diagram provides an essential first step for designing a process to yield a material of specified properties.
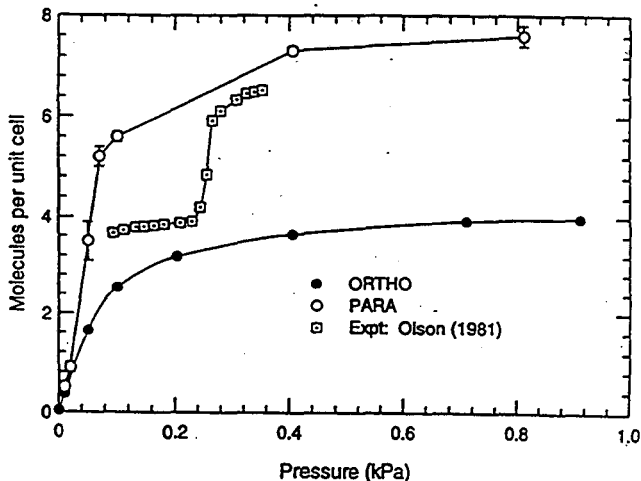

SORPTION OF P-XYLENE IN PARA AND
ORTHO-SILICALITE (ZEOLITE) AT 70 °C. CIRCLES
ARE SIMULATION CALCULATIONS BY SHURR ET AL (1993).
SQUARES SHOW STEP-WISE SORPTION MEASURED
BY OLSON (1981).

Fig. 15. Observed and Calculated Sorption of
p-Xylene. Calculations from Molecular Simulations
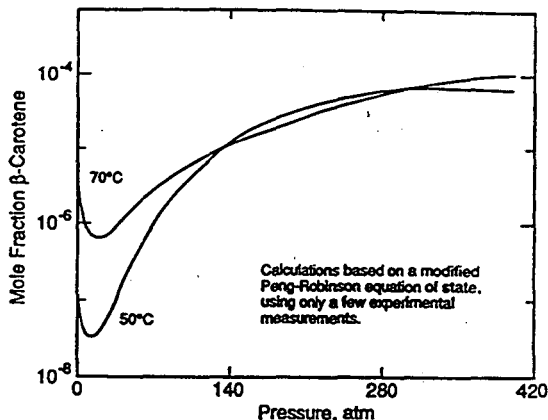
SOLUBILITY OF β-CAROTENE IN
SUPERCRITICAL ETHYLENE
(From Chang and Randolph)

Fig. 16. Supercritical Extraction of β-Carotene.
Solubility is a Strong Function of Pressure
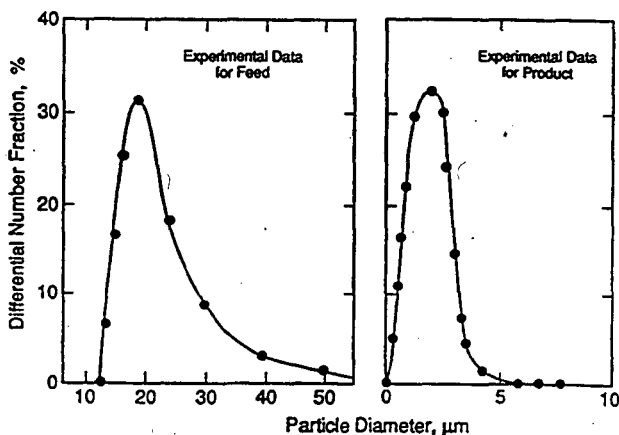
CRYSTALLIZATION OF β-CAROTENE FROM SUPERCRITICAL
ETHYLENE. PRODUCT HAS MUCH SMALLER PARTICLE
SIZE AND MORE NARROW SIZE DISTRIBUTION
(From Chang and Randolph)

Fig. 17. Supercritical Solvent Can Produce
Small Crystals with Narrow Size Distribution

OBSERVED PRECIPITATION OF POLYAMIDE-8 FROM A
SOLUTION IN DIMETHYLSULFOXIDE USING
ANTI-SOLVENT CARBON DIOXIDE
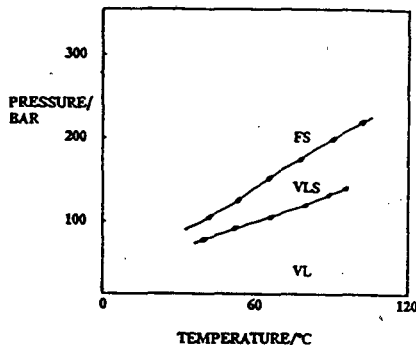
DATA ARE FOR A SOLUTION CONTAINING
12.2 Wt% DMSO (POLYMER-FREE BASIS) AND
0.1 OR 1 Wt% POLYMER. LINES ARE NOT CALCULATED
BUT SERVE TO GUIDE THE EYE.

FS = FLUID-SOLID   VLS = VAPOR-LIQUID-SOLID
VL = VAPOR-LIQUID

(AFTER YEO, DEBENEDETTI, RADOSZ & SCHMIDT, 1993)

Fig. 18. Experimental Phase Diagram for a Polymer-
Solution/Anti-Solvent System

Figures 17 and 18 suggest that new frontiers for molecular thermodynamics are not only within our view but within our grasp. The history of science and technology has shown convincingly that, for any discipline, growth is rarely at the center; it is almost always at the periphery where one discipline intersects with another.

My Berkeley colleagues in the history and philosophy of science tell me that the effective value of new knowledge in one area lies not in the new knowledge itself but in its relation to other knowledge in other areas. For example, impressive recent advances in medicine are due not primarily to new medical knowledge but to application of advances in physics (e.g., x-rays plus computers = tomography) or analytical chemistry (electrophoresis, mass spectrometry and chromatography = powerful diagnostics) to medical problems. We live in an intellectually-interrelated world where isolation of knowledge brings an end to progress. The essence of that idea was well summarized more than 100 years ago by H. J. MacKinder [Proc. Royal Geogr. Soc. 9 141 (1887)] when he wrote "Knowledge is one. Its division into subjects is a concession to human weakness." We must strive to overcome that weakness, lest molecular thermodynamics become an arcane subject that gathers dust on library shelves.

For those who work in molecular thermodynamics, opportunities and responsibilities are inseparable. They converge in our privilege and in our task to communicate with an ever-widening world of technology and to show that world how much we can do.

Acknowledgment

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