

FLUID STRUCTURE FOR SOPHOMORES

J. RICHARD ELLIOTT, JR.
The University of Akron
 Akron, OH 44325-3906

Whenever new fields of technology are developed, they will involve atoms and molecules. Those will have to be manipulated on a large scale, and that will mean that chemical engineering will be involved — inevitably.

Isaac Asimov (1988)

The undergraduate course in chemical engineering thermodynamics continues to present teaching challenges despite its long-term presence in the curriculum. Students often complain that it seems "too esoteric." But it is also a course that can provide opportunities for giving students a strong sense of "manipulating molecules" by illustrating the development of engineering models which address molecular scale interactions. Then students might say that "it was especially good as an introduction to engineering,"—and what a healthy shift in perception that would be. The approach advocated here is to integrate the esoteric principles with the students' inherent intuition so they can see all levels of the modeling process.

This general approach may seem obvious, but introducing fluid structure as a means of reducing the esoteric perception is probably not so obvious. There always seems to be more subject matter than there is time to cover it, and as a result there is a tendency to reduce thermodynamics to its smallest kernel of unique and general concepts (Maxwell's relations and the Gibbs-Duhem equation, for instance). Focusing so much on those concepts, however, would be too esoteric—by themselves, these concepts do not help students understand how liquefaction or distillation works or why polymer blending rarely works. Clearly, there must be some additional relations which demonstrate the utility of the "pure thermodynamics." We faculty recognize these as constitutive relations like equations of state or Gibbs excess functions, and when pressed for time it is tempting to present them macroscopically, as empirical relations that should

basically be accepted on faith. In the discussion below, an alternative strategy is presented which takes advantage of common roots in the molecular perspective to rapidly generate the constitutive relations in a way that highlights some great engineering models and simultaneously leads to the kind of molecular perspective that Asimov envisions.

The common root of constitutive relations is the fluid structure. For solution models, we apply the energy equation (Eq. 1). For the equation of state, we apply the pressure equation (Eq. 2). But in all cases we add up the local quantity (energy or force) weighted by the local density. The local energy or force field around an atom is clear to students from introductory chemistry and physics. The various potential models and the types of molecules they describe are reviewed during the first week of class. But the "fluid structure," which describes the local density, sounds at first like an esoteric concept at its worst. Building an appreciation of fluid structure is a delicate undertaking, but once this appreciation is established, a single framework can be repeatedly applied for rapidly reducing to practical application. Our approach is detailed below.

The concept of fluid structure does for energy what the concept of particle distribution in boxes does for entropy; it provides the connection to the molecular scale. For the treatment of particle distribution in boxes we adapt the presentation of Balzhiser, *et al.*,^[1] at the same time that entropy is introduced. Thus, the students are ready and waiting for a



J. Richard Elliott, Jr., is Associate Professor of Chemical Engineering at the University of Akron. He received his PhD from Pennsylvania State University and his MS from Virginia Polytechnic Institute. His background and interests are primarily in phase equilibria and molecular thermodynamics and related applications. In the spring of 1992, he received the ASEE/Dow Outstanding Young Faculty Award of the North Central Section.

© Copyright ChE Division of ASEE 1993

molecular formulation of the complete problem and are anxious for applications.

The presentation below emphasizes the development of the principles of thermodynamic modeling in four stages. First, a brief introduction to how the fluid structure influences the macroscopic properties is given by the energy equation and the pressure equation. Second, the qualitative features of fluid structure are developed for several examples through simple intuitive arguments. Third, the pressure equation is applied to develop the van der Waals equation of state. And fourth, the energy equation for mixtures is applied to show how mixing rules, the Scatchard-Hildebrand theory, the Van Laar theory, and the Flory-Huggins theory all result from simplifications of the van der Waals equation of state. Local composition theory is then derived from alternative approximations of the fluid structure. In this way, each constitutive relation is related back to intuitively accessible concepts that all students can appreciate, with the result that students can admire the depth of ingenuity involved in engineering models instead of being frustrated by arbitrary equations being pulled from some place known only to a privileged few.

RELATING FLUID STRUCTURE TO MACROSCOPIC PROPERTIES

To apply the relationships for relating changes in properties to C_p , C_v , p , T , V , and their derivatives, we need relationships between p , V , and T . These relationships are dictated by the equation of state. Constructing an equation of state requires considering how the intermolecular forces are affecting the energy and pressure in a fluid. As the fluid becomes dense, we know that the molecules will be closer together on the average and this will give rise to a potential energy contribution and to an increase in the contribution of attractive forces. A common practical implication of this attractive energy is the heat of vaporization of a boiling liquid.

But how can we make a quantitative connection between molecular forces and macroscopic properties? The key is to consider the average number of molecules at each distance from the center of an average molecule. To get the internal energy, multiply this average number of molecules by the amount of intermolecular energy at that distance and integrate over all distances. As for the pressure, the complete statistical mechanical derivation is beyond the scope of this introduction, but appreciation of the relevant terms can be gained by highlighting the similarity between the energy equation and the pressure equation and the relation between the potential

Students often complain that [thermodynamics] is "too esoteric." But it is also a course that can provide opportunities for giving students a strong sense of "manipulating molecules" by illustrating the development of models which address molecular scale interactions.

and the force. These considerations give rise to the energy equation and the pressure equation, and most importantly, to the definition of this "average number of molecules." The average number of molecules at a particular distance from an average molecule is given by the "radial distribution function" ("g").

The Energy Equation

$$\frac{U - U^{id}}{NkT} = \frac{\rho}{2kT} \int_0^{\infty} u g 4\pi r^2 dr \quad (1)$$

The Pressure Equation

$$Z = \frac{p}{\rho kT} = 1 - \frac{\rho}{6kT} \int_0^{\infty} r \left(\frac{\partial u}{\partial r} \right) g 4\pi r^2 dr \quad (2)$$

where

- g \equiv radial distribution function (rdf)
- Z \equiv compressibility factor
- ρ \equiv N/V is the number density
- k \equiv Boltzmann's constant
- u \equiv intermolecular potential function
- N \equiv number of atoms
- V \equiv total volume
- U^{id} \equiv internal energy of the ideal gas

AN INTUITIVE METHOD OF INTRODUCING FLUID STRUCTURE

The fluid structure described by the rdf can be initially introduced by considering two simple examples that can be solved exactly: the low density hard sphere fluid and the body centered cubic crystal. These provide the two limits of density, and the other examples can be considered as variations. The other examples are the high-density hard-sphere fluid, the low-density square-well fluid, and the high-density square-well fluid.

As a prelude to a general description of fluid structure, it may be helpful to review the structure of crystal lattices like those in body centered cubic (bcc) metals. Such lattices possess long-range order via repetitive arrangements of the unit cell in three dimensions. As an example, we can compare the structure of a body-centered cubic crystal to that of a face-centered cubic crystal. A specific arrangement of

atoms gives a single value for the density, and it correlates with many of the macroscopic properties of the material (*e.g.*, strength, ductility). Having an idea of such a specific structure for a solid provides the basis for contrast to the structure of a fluid.

The structure arising from the distribution of atoms in bcc crystals is fairly easy to understand, but how can we address the distribution of atoms in a fluid? For a fluid, the positions of the atoms around a central atom are less well-defined than in a crystal. To get started on a generally applicable description of fluid structure, think about the simplest fluid—an ideal gas.

Consider a fluid of point particles surrounding a central particle. What is the number of particles in a neighborhood surrounding the central particle? Since they are point particles, they do not influence one another. This means that the number of neighbors is proportional to the size of the neighborhood.

$$dN_V = \frac{N}{V} dV \quad (3)$$

where dN_V is the number of particles in the volume element.

Recalling that $\rho \equiv N/V$,

$$dN_V = \rho dV \quad (4)$$

If we would like to know the number of particles within some spherical neighborhood of our central particle, then

$$dV = 4\pi r^2 dr \quad (5)$$

where r is the radial distance from our central particle, and

$$N_c = \int_0^{R_0} dN_V = \int_0^{R_0} \rho 4\pi r^2 dr \quad (6)$$

where R_0 defines the size of our spherical neighborhood, and N_c is the number of particles in the neighborhood (also known as the coordination number).

Now consider the case of atoms which have a finite size. In this case the number of particles within a given neighborhood is strongly influenced by the size of the neighborhood. If the range of the neighborhood is less than two atomic radii, or one atomic diameter, then the number of particles in the neighborhood is zero (not counting the central particle). Outside the range of one atomic diameter we do not know exactly how the number of particles changes. We can express these insights mathematically, however, by introducing a "weighting factor" which is a function of the radial distance. The weighting factor takes on a value of zero for ranges less than two atomic radii, and for larger ranges we will consider its behavior undetermined as yet.

Then we may write

$$N_C = \rho \int_0^{R_0} g(r) 4\pi r^2 dr \quad g = \begin{cases} 0 & r < \sigma \\ ? & r \geq \sigma \end{cases} \quad (7)$$

where $g(r)$ is our "weighting factor" referred to as the radial distribution function (rdf). This radial distribution function provides the quantitative description of what we refer to as "fluid structure."

As a first approximation, we might assume that atoms outside the range of two atomic radii do not influence each other. Then the number of particles in a given volume element goes back to being proportional to the size of the volume element, and the rdf has a value of one for all r greater than one diameter. The approximation that atoms outside the atomic diameter do not influence each other is reasonable at low density (see Figure 1).

Far from the low density limit, we approach close-packing. The ultimate in close-packing is a crystal lattice. It is necessary to clarify what is meant by the rdf of a lattice, as opposed to its crystal structure. The rdf of a bcc lattice can be deduced from knowledge of N_c vs. neighborhood size using some elementary ge-

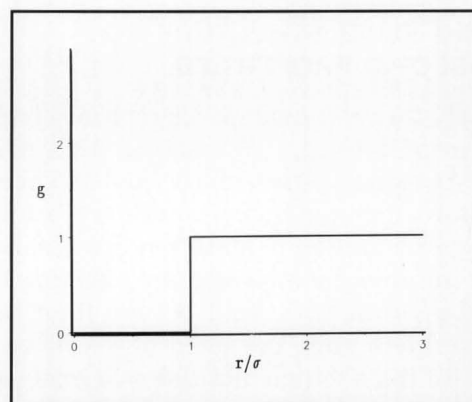


Figure 1. The radial distribution function vs. radial distance for a hard sphere fluid at low density.

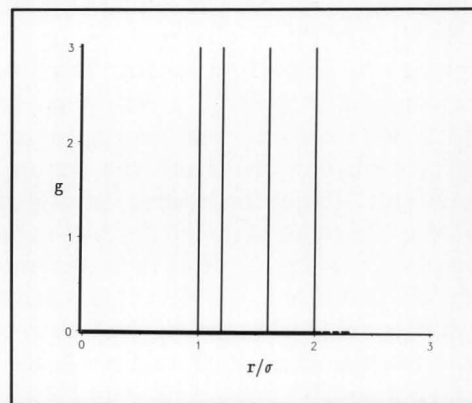


Figure 2. The radial distribution function vs. radial distance for a body centered cubic crystal.

ometry and applying Eq. 7.

If we assume that the atoms in a crystal are located in specific sites and that no atoms are out of their sites, then g must be zero everywhere except at a site. For a body centered cubic crystal, these sites are at

$$r = \{\sigma, 1.15\sigma, 1.6\sigma, \dots\}$$

For instance, the location of the second shell at 1.15σ is given directly from the length of the side of the unit cell. Since the atoms are assumed to be only at specific distances, the rdf looks like a series of spikes (see Figure 2).

The distribution of atoms in a substance is most conveniently referred to as its "structure." The structures of the low density hard sphere and the bcc crystal clarify what is meant by the rdf and how we represent it. Next, we can develop some insight about the high density hard sphere fluid. Its behavior is something of a hybrid between the low density fluid and the solid lattice. Similar to the low density case, when atoms are too far away to influence each other, the rdf approaches unity because the increase in neighbors becomes proportional to the size of the

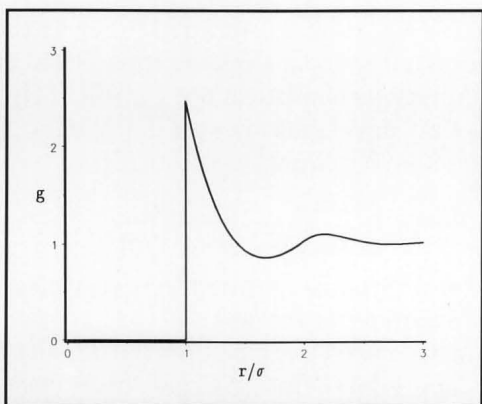
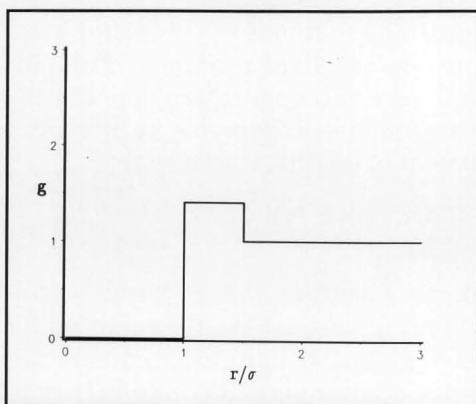
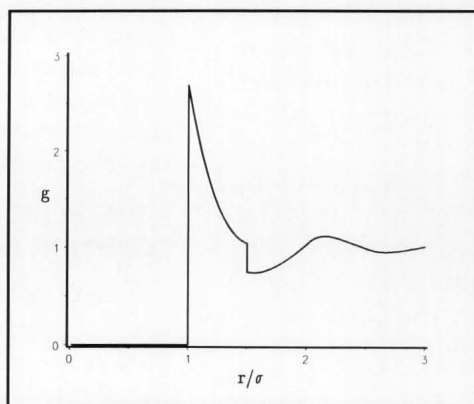


Figure 3. Radial distribution function vs. radial distance for a hard sphere fluid at high density ($N\sigma^3/V = 0.60$).



(a)



(b)

Figure 4. The radial distribution function vs. radial distance for a square-well fluid ($kT/\epsilon = 3.0$) (a) at low density, and (b) at high density ($N\sigma^3/V = 0.60$).

neighborhood. Near the atomic diameter, however, the central atom influences its neighbors to position themselves in "layers" in an effort to approach the close packing of a lattice. Thus the value of the rdf is large, very close to one atomic diameter. Because liquids lack the long-range order of crystals, the influence of the central atom on its neighbors is not as well defined as in a crystal, and we get smeared peaks and valleys instead of spikes (see Figure 3).

As a final case, consider the influence of attractive forces on surrounding neighbors. The range within the atomic diameter is still off-limits, and the value of the rdf there is still zero. But what about the rdf at low density for the range where the attractive potential is significant? We would expect some favoritism for atoms inside the attractive range since that will release energy, but overlap would still be off limits and there would be no influence outside the range of the potential at low density.

For the square-well potential, the changes with radial distance are very distinct:

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma < r < R_0 \\ 0 & R_0 < r \end{cases} \quad (8)$$

The impact of the attractive force then becomes clearly recognizable (see Figure 4a). As for the rdf at high density, we expect packing effects to dominate because attaining a high density is primarily affected by efficient packing. At intermediate densities, the rdf will be some hybrid of the high and low density limits (Figure 4b).

Qualitative description of these sample fluid structures is about as far as intuition can carry us. A mathematical formalization of these intuitive concepts is presented in several texts^[2,3] but the difficulty of such a rigorous treatment is beyond the scope of our introductory presentation. For our purposes, we would simply like to understand that something called "fluid structure" exists and that it is described in detail by the "radial distribution function."

VAN DER WAALS EQUATION OF STATE

Having laid the foundation for intuitively considering fluid structure and its impact on mac-

roscopic properties, the derivations of every theory from equations of state to local composition theory can follow in rapid sequence. These derivations can serve to illustrate model development and simultaneously demonstrate the utility of the "pure thermodynamics." One of the most successful and useful equation of state has been the van der Waals equation. Even the most popular engineering equations currently used are only minor variations on the theme originated by van der Waals. The beauty of his argument is that detailed knowledge of the rdf is not necessary—only the kind of general knowledge of its existence as described in the preceding section. As pointed out by Abbott,^[4] we can assume that van der Waals started with the pressure equation and reasoned that the integral could be broken into two parts:

$$\frac{p}{\rho kT} = 1 - \frac{\rho}{6kT} \int_0^{\sigma} r \left(\frac{\partial u}{\partial r} \right) g 4\pi r^2 dr - \frac{\rho}{6kT} \int_{\sigma}^{\infty} r \left(\frac{\partial u}{\partial r} \right) g 4\pi r^2 dr \quad (9)$$

Each integral can now be analyzed separately. Mathematically, analysis of the first integral is difficult because $g = 0$ except at $r = s$, and the derivative of the potential is zero except at $r = s$, where it becomes a Dirac delta function. This leads to the result

$$-\frac{\rho}{6kT} \int_0^{\sigma} r \left(\frac{\partial u}{\partial r} \right) g 4\pi r^2 dr = \frac{2\pi g(\sigma)}{3} \rho \sigma^3 \quad (10)$$

We have already recognized that $g(\sigma)$ increases with density, but we need a simple analytical function which can be used to provide a numerical representation of this increase. One of the simplest functions leads to

$$-\frac{\rho}{6kT} \int_0^{\sigma} r \left(\frac{\partial u}{\partial r} \right) g 4\pi r^2 dr \approx \frac{bp}{(1-b\rho)} \quad (11)$$

where $b \approx$ close-packed volume. This is the function which van der Waals suggested. It should be noted that Eq. 11 suggests that $p \rightarrow \infty$ near the close-packed density and that this helps to understand how engineering models of such divergences are often developed.

As for the second integral, this basically represents the attractive force at each distance times the number of particles at that distance integrated over all distance. As an example, consider what happens to this integral when u is given by the square-well potential (with $R_0 = 1.5\sigma$). Then

$$\frac{\rho}{6kT} \int_{\sigma}^{\infty} r \left(\frac{\partial u}{\partial r} \right) g 4\pi r^2 dr = \left(\frac{\rho \sigma^3 \epsilon}{6kT} \right) \left(\int_1^{\infty} x \left(\frac{\partial u}{\partial x} \right) g 4\pi x^2 dx \right) \quad (12)$$

where $x \equiv r/\sigma$. The integral on the right-hand side is

independent of the particular substance of interest because the only way of distinguishing different substances in the square-well potential is by different values of σ and ϵ . By factoring the σ and ϵ out of the integral, we obtain a dimensionless integral which can be applied universally to any substance multiplied by a dimensionless constant which accounts for the substance dependent values of ϵ and σ . Van der Waals did not have quantitative information available about g ; therefore he made the approximation that the value of this integral was some constant independent of T and ρ for all substances. This may seem somewhat crude since we know that g changes significantly with respect to density, but the way that g oscillates about unity leads to a weak density dependence for the integral. When this universal constant is factored in with σ^3 and ϵ , a single substance-dependent constant is obtained

$$a \equiv \frac{\sigma^3 \epsilon}{6} \int_1^{\infty} x \left(\frac{\partial u}{\partial x} / \epsilon \right) g 4\pi x^2 dx \quad (13)$$

The resulting equation of state is

$$Z = 1 + \frac{bp}{(1-b\rho)} - \frac{ap}{kT} = \frac{1}{(1-b\rho)} - \frac{ap}{kT} \quad (14)$$

When this equation is compared to currently popular equations, it is clear that the theoretical basis of modern equations of state is not significantly different from that developed by van der Waals. For example, the Soave^[5] equation is

$$Z = 1 + \frac{bp}{(1-b\rho)} - \frac{ap}{kT} \frac{\alpha}{(1+b\rho)} \quad (15)$$

where $\alpha = \alpha(T)$ is an empirically determined temperature-dependent function.

The function used to correct for the density dependence is $1/(1+b\rho)$. The principal difference is the modification of the temperature and density dependence of the attractive term, but this modification is based on experience and empiricism more than any theoretical insight. The methods of these empirical developments provide excellent examples of the interplay between theory and application, and discussion of these developments can provide keen insight into the development of engineering models.

FROM FLUID STRUCTURE TO SOLUTION THEORY

The development of solution theory closely parallels the development of van der Waals' equation for pure fluids. The final equations presented here are familiar to the reader, but the ease of relation back to the molecular perspective may be simpler than imagined at first thought. We begin with the van der Waals equation for pure fluids and consider how to

adapt it to mixtures. Essentially, all that is necessary is to define "a" and "b" for a mixture. Since "b" provides a crude representation of the close-packed volume, it is not unreasonable to crudely approximate it by a molar average. To determine the composition dependence of the "a" parameter, the energy equation can provide guidance. For mixtures, the energy equation is given by exactly the same method of adding energies times interactions that was applied for pure fluids

$$\left(\frac{U-U^{\text{id}}}{NkT}\right) = \frac{\rho}{2} \sum \sum x_i x_j \int \frac{u_{i,j}}{kT} g_{ij} 4\pi r^2 dr \quad (16)$$

The only term that may seem mysterious is the factor of one-half in front. This factor arises because we imagine summing all the interactions by going from one atom to the next. But the j - i interaction is really the same as the i - j interaction, so we would be double counting if we did not divide by 2. Applying classical thermodynamics to the van der Waals equation gives

$$\left(\frac{U-U^{\text{id}}}{NkT}\right) = \frac{-ap}{kT} = \frac{-a}{vkT} \quad (17)$$

where $v = 1/\rho$ is the more traditional manner of representing the density term. Comparing Eq. (17) to Eq. (16) shows that

$$a = \frac{1}{2} \sum \sum x_i x_j \int u_{ij} g_{ij} 4\pi r^2 dr \quad (18)$$

when $x_i \rightarrow 1$,

$$a_{ii} = \frac{1}{2} \int u_{ii} g_{ii} 4\pi r^2 dr \quad (19)$$

Assuming g_{ij} is weakly dependent on composition, we obtain

$$a = \sum \sum x_i x_j a_{ij} \quad (20)$$

where the cross-term, a_{ij} , is traditionally approximated by

$$a_{ij} = \sqrt{a_i a_j} \quad (21)$$

Expressions for free energy and fugacity via the equation of state can then be quickly developed by the usual methods.

Turning our attention to Gibbs excess models for liquids, we find that we already have all of the theoretical foundation laid for many of the models. All that is required is some specific approximations and simplifications for the specific application being considered. A brief outline of the derivation of regular solution theory and Flory-Huggins theory from the van der Waals equation follows.

The Gibbs excess energy of a van der Waals mixture may be derived by considering the Gibbs departure functions of the overall mixture and the indi-

vidual components in turn

$$\frac{G-G^{\text{id}}}{NkT} = \ln\left(\frac{p(v-b)}{kT}\right) - \frac{a}{vkT} + \frac{pv}{kT} - 1 \quad (22)$$

and applying

$$G^E = (G-G^{\text{id}}) - \sum x_i (G_i^o - G_i^{\text{id}}) - \sum x_i \ln(x_i) \quad (23)$$

yields

$$\begin{aligned} \frac{G^E}{NkT} = & - \sum x_i \ln\left(\frac{v-b}{v_i-b_i}\right) \\ & - \left(\frac{a}{vkT} - \sum x_i \frac{a_i}{v_i kT}\right) + \frac{p}{kT} (v - \sum x_i v_i) \end{aligned} \quad (24)$$

A common approximation when developing solution theories for liquids is to assume that $v = \sum x_i v_{ii}$. While this is often inaccurate relative to volume estimates for non-ideal solutions, it is accurate enough for free energy estimates because the excess volume makes a small contribution to the excess free energy. This eliminates the last term in the above equation. Following Flory,^[6] we may assume that for liquids

$$v_i - b_i \sim v_i \quad (25)$$

which implies that the void fraction is roughly a universal constant for all liquids (65% is generally quite reasonable). Then,

$$\frac{v-b}{v_i-b_i} = \frac{x_i}{\Phi_i} \quad (26)$$

where

$$\Phi_i \equiv \frac{x_i v_i}{\sum x_i v_i}$$

This result is referred to as the *Flory-Huggins term*. Noting that this term is independent of temperature and applying classical thermodynamics to the free energy shows that this term describes the excess entropy of mixing and the remaining terms describe the excess internal energy. Summarizing:

$$\frac{G^E}{NkT} = \sum x_i \ln\left(\frac{\Phi_i}{x_i}\right) - \frac{U^E}{NkT} \quad (27)$$

Returning to the van der Waals theory, the internal energy may be written as

$$\left(\frac{U-U^{\text{id}}}{NkT}\right) = - \frac{\sum \sum x_i x_j a_{ij}}{kT \sum x_i v_i} \quad (28)$$

For the pure fluid, taking the limit as $x_i \rightarrow 1$, we recover

$$\left(\frac{U-U^{\text{id}}}{NkT}\right)_i \rightarrow \frac{-a_i}{v_i kT} \Rightarrow \left(\frac{U-U^{\text{id}}}{NkT}\right)_{\text{id soln}} = - \sum \frac{x_i a_{ij}}{v_i kT} \quad (29)$$

For a binary mixture, subtracting the ideal solution

result to get the excess energy gives

$$\frac{U^E}{NkT} = \frac{x_1 a_{11}}{v_1 kT} + \frac{x_2 a_{22}}{v_2 kT} - \frac{(x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22})}{kT(x_1 v_1 + x_2 v_2)} \quad (30)$$

Applying $a_{12} = \sqrt{a_{11} a_{22}}$,

$$\begin{aligned} \frac{U^E}{NkT} &= \frac{x_1 x_2 v_1 v_2}{kT(x_1 v_1 + x_2 v_2)} \left(\frac{a_{11}}{v_1^2} + \frac{a_{22}}{v_2^2} - 2 \frac{\sqrt{a_{11}} \sqrt{a_{22}}}{v_1 v_2} \right) \\ &= \frac{x_1 x_2 v_1 v_2}{kT(x_1 v_1 + x_2 v_2)} \left(\frac{\sqrt{a_{11}}}{v_1} - \frac{\sqrt{a_{22}}}{v_2} \right)^2 \\ \frac{U^E}{NkT} &= \frac{(\delta_1 - \delta_2)^2}{kT} \Phi_1 \Phi_2 (x_1 v_{11} + x_2 v_{22}) \end{aligned} \quad (31)$$

where

$$\delta_i \equiv \frac{\sqrt{a_{ii}}}{v_i}$$

Substituting

$$\frac{G^E}{NkT} = \sum x_i \ln \left(\frac{\Phi_i}{x_i} \right) - \frac{(\delta_1 - \delta_2)^2}{kT} \Phi_1 \Phi_2 (x_1 v_1 + x_2 v_2) \quad (32)$$

If we choose to neglect the Flory-Huggins term, Scatchard-Hildebrand theory is obtained. The Van Laar equation may easily be derived from the Scatchard-Hildebrand form. If we choose to approximate $(\delta_1 - \delta_2)^2$ by an adjustable parameter κ , then the full Flory-Huggins theory is obtained. If we retain all of the above terms, then the theory of Blanks and Prausnitz^[7] is obtained. The development of these solution models can be interspersed with examples of retrograde condensation, azeotrope formation, distillation, and polymer mixing/blending to impress even the most skeptical application-oriented student. And the conciseness of each theoretical development makes the investment small enough to maintain interest at every step.

LOCAL COMPOSITION THEORY

There is one last class of solution theories which requires coverage even though the attention of the student has been pressed close to its limit by this stage in the course. Fortunately, the foundation for development of this theory has been laid in the form of the energy equation for mixtures and the derivation can quickly proceed as a slight modification of the previously developed solution theories. While it is difficult to motivate this further development *a priori*, it is a necessity if students are to understand the basis of the very popular and versatile UNIFAC model.^[8] The value of this investment can be reinforced by an application-oriented project which dem-

onstrates the power of the UNIFAC model.

The modification required to develop local composition theory is to realize that in developing the van der Waals mixing rules, we made a key assumption about the radial distribution function in a mixture. Briefly, we assumed that g_{ij} was independent of composition. That assumption is accurate when the components of the mixture are roughly the same size, but it becomes more questionable when their diameter ratio is greater than 1.5. Consider the differences in packing that would occur when a few very large spheres were surrounded by tiny ones *vs.* a few tiny spheres dispersed among large ones.

To develop a more accurate representation of local composition effects, we seek a description of the excess internal energy which is at least "more flexible" than that assumed by van der Waals. By more flexible, we mean to recognize that predicting complicated local composition effects may be more difficult than predicting a_{ij} . The more flexible expression we seek should be capable of at least correlating the local composition effects even if predicting them seems too difficult.

We can relate the energetics of the mixture directly to the local compositions by recalling that the intermolecular energy is a short-range function. The square-well potential is especially useful for making this point. These local compositions can then be multiplied by the energy associated with each type of interaction to obtain the total energy from the energy equation. We can define a local mole fraction by

$$\begin{aligned} x_{ij} &\equiv N_{ij} / Nc_j \\ N_{ij} &= \text{number of } i \text{ atoms around a } j \text{ atom} \\ Nc_j &= \sum_i N_{ij} \end{aligned}$$

The local mole fraction can be related to the bulk mole fraction by

$$x_{ij} = x_i \frac{N}{V} \frac{\sigma_{ij}^3}{Nc_j} \int_0^{R_{ij}} g_{ij} 4\pi r_{ij}^2 dr_{ij} \quad (33)$$

where

$$\begin{aligned} r_{ij} &= \frac{r}{\sigma_{ij}} \\ R_{ij} &= \text{"neighborhood" where intermolecular} \\ &\quad \text{energy is significant} \end{aligned}$$

Further, we can write

$$\frac{x_{ij}}{x_j} = \frac{Nc_j N_i \sigma_{ij}^3 \int g_{ij} 4\pi r_{ij}^2 dr_{ij}}{Nc_j N_j \sigma_{jj}^3 \int g_{jj} 4\pi r_{jj}^2 dr_{jj}} \equiv \frac{x_i}{x_j} \Lambda_{ij} \quad (34)$$

Noting

$$\sum_i x_{ij} = 1 = \frac{\sum x_i \Lambda_{ij} x_{ij}}{x_j} = \frac{x_{ij}}{x_j \sum x_i \Lambda_{ij}} \quad (35)$$

$$\Rightarrow \frac{x_j}{x_{ij}} = \sum x_i \Lambda_{ij} \quad (36)$$

Therefore

$$x_{ij} = \frac{x_i \Lambda_{ij}}{\sum_k x_k \Lambda_{kj}} \quad (37)$$

Substituting into the energy equation gives

$$\frac{U^E}{NkT} = \frac{1}{2kT} \sum x_j Nc_j \sum \frac{x_i \Lambda_{ij} (\epsilon_{ij} - \epsilon_{jj})}{\sum x_k \Lambda_{kj}} \quad (38)$$

In our previous development of solution theories, U^E was assumed to be independent of temperature. In local composition theory, it is more convenient to assume some temperature dependence of Λ_{ij} . In particular

$$\Lambda_{ij} = \left(\frac{v_j}{v_i} \right) \exp \left[\frac{(\epsilon_{ij} - \epsilon_{jj})}{kT} \right] \quad (39)$$

gives

$$\frac{G^E}{NkT} = \frac{C}{kT} + \sum \frac{x_j}{kT} \ln(\sum x_i \Lambda_{ij}) \quad (40)$$

where C is the temperature-independent integration constant obtained from integrating the internal energy with respect to temperature. If we set $C = 0$, we obtain the Wilson^[9] equation. If we use the Flory-Huggins theory to describe the integration constant, we obtain essentially the UNIFAC expressions. Several applications showing the predictive capability of UNIFAC can then be exemplified to reinforce the utility of having made this extension. This also provides another opportunity to illustrate the interplay between theoretical development, empiricism, and application that is so essential to engineering. Attention should be called to the number of adjustable parameters inherent in the UNIFAC model and the distinction between correlation and prediction. This also provides the necessary background for considering Sandler's^[10] award lectures without the necessity of canonical partition functions.

CONCLUSION

All of this may seem like more theory than chemical engineering sophomores can absorb. Nevertheless, we have been incorporating this material into our sophomore course for the past two years and student evaluations show surprisingly few complaints. In fact, our evaluations last year were the highest obtained over the past six years. We feel that

the key to this success is the immediate reduction of each theory to practice. Our engineering students are as pragmatic as any engineering students, but presentation of the above theoretical developments consumes only about seven lectures out of fifty-nine. The remaining lectures are devoted almost entirely to sample applications demonstrating the utility of each theory.

But there may still be some doubt on the part of thermodynamics instructors about whether this is all worthwhile. To respond, we may consider Asimov's quote given at the beginning of this paper. How close are we chemical engineers to the "manipulation of molecules on a large scale"? In reality, we teach precious little about the connections between the molecular scale and continuum scale. We occasionally hear arguments that the molecular scale and the statistical mechanics which connect it to larger scales are the domain of chemistry, not engineering. But our students do apply theories like UNIFAC. This means that they currently apply the theories blindly, like computer operators.

What we should be teaching our students is the general engineering approach to understanding a physical situation, modeling, empiricizing, and reducing to practice. Through the concept of fluid structure, we can achieve all this and maintain constant focus on the fundamental sources of energy and entropy.

REFERENCES

1. Balzhiser, R.E., M.R. Samuels, and J.D. Eliassen, *Chemical Engineering Thermodynamics: The Study of Energy, Entropy, and Equilibrium*, Prentice-Hall, New York (1972)
2. McQuarrie, D.A., *Statistical Mechanics*, Harper and Row, New York (1976)
3. Hansen, J.P., and I.R. McDonald, *Theory of Simple Liquids*, 2nd ed., Academic Press, New York (1986)
4. Abbott, M.M., "Thirteen Ways of Looking at the van der Waals Equation," *Chem. Eng. Prog.*, **85**(2), 25 (1989)
5. Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972)
6. Flory, P.J., "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca (1943)
7. Blanks, R.F., and J.M. Prausnitz, "Thermodynamics of Polymer Solubility in Polar and Nonpolar Systems," *Ind. Eng. Chem. Funds*, **3**, 1 (1964)
8. Fredenslund, A., R.L. Jones, and J.M. Prausnitz, "Group Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," *AIChE J.*, **21**, 1086 (1975)
9. Wilson, G.M., "Vapor-Liquid Equilibrium: IX. A New Expression for the Excess Free Energy of Mixing," *J.A.C.S.*, **86**, 127 (1964)
10. Sandler, S.I., "From Molecular Theory to Thermodynamic Models," *Chem. Eng. Ed.*, **24**(2), 80 (1990) □