

# FROM MOLECULAR THEORY TO THERMODYNAMIC MODELS

## Part I. Pure Fluids

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**T**HERMODYNAMICS AND physical properties are central to the practice of chemical engineering. This is evident from the fact that 70 to 90% of both investment and energy operating costs in a typical chemical plant involves the separations and purifications equipment which are designed largely on the basis of phase equilibrium. Further, the complete flow sheet of a chemical plant may depend on whether an azeotrope or two liquid phases are formed somewhere in the process. With the availability of modern process simulators it is usually the uncertainty in thermodynamic behavior, rather than the design algorithms or calculational complexity, which presents the biggest difficulty in accurate process design.

Because of their importance in process design, many thermodynamic and physical properties models have been developed. Indeed, there are more than 100 variations of the van der Waals equation of state in addition to numerous other equations of state and activity coefficient models. A problem that arises in teaching thermodynamics to chemical engineering students is providing a coherent scientific (rather than

merely empirical) basis for these models. A related problem is introducing students to the use of molecular theory for the development of thermodynamic models. This paper presents a framework which allows one to identify the molecular level assumptions underlying many thermodynamic models. We then continue on to test these assumptions using theory and computer simulation and to show how we can make better assumptions which lead to improved models. Here we consider only pure fluids and their equations of state; in Part 2 (to be published in the next issue of *CEE*) we will consider mixtures and activity coefficient models.

### SIMPLIFIED STATISTICAL MECHANICS: The Generalized van der Waals Partition Function

The molecular theory from which one can derive thermodynamic models is statistical mechanics. For the case in which the temperature  $T$ , volume  $V$ , and number of particles  $N$  are the independent variables, the canonical partition function

$$Q(N, V, T) = \sum_i^{\text{states}} e^{-E_i(N, V)/kT} \quad (1)$$



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He was cochair of the Chemical Engineering Faculty Summer School of the ASEE in 1982, and was originator and chair of the 1988 Chemical Engineering Education in a Changing Environment Conference, held for the purpose of introducing new technology examples into standard undergraduate courses. He has served on the Editorial Advisory Board of the *AIChE Journal*, Industrial and Engineering Chemistry Fundamentals, and the University of Delaware Press. He is an ABET/AIChE chemical engineering accreditation visitor and is on the AIChE subcommittee for New Technology Educational Materials.

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is the starting point for our work [1]. Here the sum is over all the quantum states of  $N$  molecules in a volume  $V$ ,  $k$  is Boltzmann's constant,  $T$  is temperature, and  $E_i$  is the energy of the system in the  $i^{\text{th}}$  quantum state. Once we know the partition function, all other thermodynamic properties can be computed as follows

$$A(N, V, T) = kT \ln Q(N, V, T) \quad (2)$$

$$P = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T, N} \quad E = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V, N} \quad (3)$$

$$S = kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V, N} - k \ln Q \quad (4a)$$

$$C_V = 2kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V, N} + kT^2 \left( \frac{\partial^2 \ln Q}{\partial T^2} \right)_{V, N} \quad (4b)$$

etc.

Eq. 2, which relates the Helmholtz free energy to  $N$ ,  $V$ , and  $T$ , is one of the fundamental equations of state in the sense of Gibbs; from it all other thermodynamic properties of a fluid can be obtained without any other information, as is evident from the equations above.

Identifying each quantum state of an assembly of molecules is at present an impossible task except for special cases such as the ideal gas. For the case of relatively simple molecules (for the moment excluding long chain hydrocarbons or polymers) the total energy of an assembly of molecules can be separated into translational ( $t$ ), rotational ( $r$ ), vibrational ( $v$ ), electronic ( $e$ ), and interaction ( $i$ ) energies, each of which is independent of the others. Further, except for the interaction energy term, each of the contributions is a sum of the energies of the individual molecules. Therefore, for a pure fluid of  $N$  identical molecules we have

$$\begin{aligned} Q(N, V, T) &= \sum e^{-(E_t + E_r + E_v + E_e + E_i)/kT} \\ &= \left( \sum e^{-E_t/kT} \right) \left( \sum e^{-E_r/kT} \right) \left( \sum e^{-E_v/kT} \right) \left( \sum e^{-E_e/kT} \right) \left( \sum e^{-E_i/kT} \right) \\ &= \frac{1}{N!} (q_t(T))^N (q_r(T))^N (q_v(T))^N (q_e(T))^N \frac{Z(N, V, T)}{V^N} \end{aligned} \quad (5)$$

Here  $q_r$ ,  $q_v$ , and  $q_e$  are the single particle rotational, vibrational, and electronic partition functions which are only a function of temperature. Also,  $q_t = (2\pi mkT/h^2)^{3/2} V$  is the single particle translational partition function where  $m$  is the particle mass and  $h$  is

Planck's constant.

Of special interest is the last term, the configuration integral, which arises from the interactions between molecules. For spherical molecules in a volume element of macroscopic dimensions, classical mechanics can be used (thereby replacing summations with integrations)

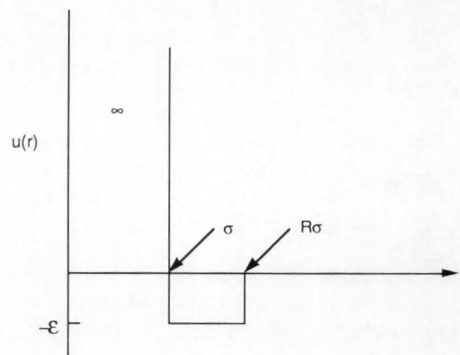
$$Z = \int \dots \int e^{-u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/kT} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (6)$$

where  $u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  is the interaction energy when a molecule is located between position vectors  $\mathbf{r}_1$  and  $\mathbf{r}_1 + d\mathbf{r}_1$ , a second molecule between position vectors  $\mathbf{r}_2$  and  $\mathbf{r}_2 + d\mathbf{r}_2$ , etc., and the integrals are over all values of the position vectors within the volume  $V$ . It is only the configurational integral  $Z$  which depends upon the interactions among the molecules and therefore, from Eqs. 3 and 4, it is the derivative of  $Z$  with respect to temperature that gives information about the average interaction energy among the molecules. We refer to this average total interaction energy as the configurational energy  $E^{\text{CONF}}$ .

To proceed further we need to make some statement about the interactions between the molecules. We will assume that the interaction energy for the assembly of molecules in any particular configuration can be computed as the sum of the interaction energies between all possible pairs of molecules (*i.e.*, the pairwise additivity assumption) so that

$$u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i > j} u(r_{ij}) \quad (7)$$

#### SQUARE-WELL POTENTIAL



**FIGURE 1. The square-well potential with an unpenetrable hard wall at  $r = \sigma$ .**

and for the purpose of illustration here, we will consider two molecules to interact with the square-well potential of Figure 1

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

though other potential models may be used [2]. This very simplified model does have the essential features of a real interaction; it has a repulsive region ( $r < \sigma$ ), an attractive region ( $\sigma \leq r \leq R\sigma$ ), and vanishes at large separations.

The average total interaction or configurational energy,  $E^{\text{CONF}}$ , for a fluid of square-well molecules can be gotten from a simple analysis. If  $N_c(\rho, T)$  represents the coordination number, that is the average number of molecules in the well of a central molecule at the density  $\rho$  and temperature  $T$ , then the interaction energy of that molecule with all others is  $-N_c(\rho, T)\epsilon$ . Since there are  $N$  choices for the central molecule, the total interaction energy is

$$E^{\text{CONF}} = \frac{-NN_c(\rho, T)\epsilon}{2} \quad (9)$$

where the factor of 2 accounts for the fact that each interaction is counted twice as each member of the interacting pair is considered to be the central molecule.

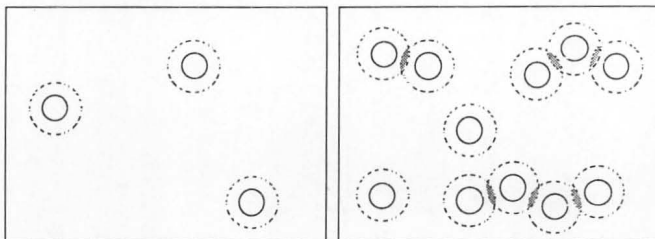
To proceed further it is useful to relate the configurational energy to the configuration integral using Eqs. 3 and 5 as follows

$$\ln Z(\rho, T) = \ln Z(\rho, T = \infty) + \int_{T=\infty}^T \frac{E^{\text{CONF}}}{kT^2} dT$$

or

$$\frac{Z(\rho, T)}{V^N} = \frac{V_f^N(\rho)}{V^N} \exp\left(-\frac{N\phi}{2kT}\right) \quad (10)$$

Here, for convenience, we have defined  $Z(\rho, T = \infty) = V_f^N(\rho)$ , where  $Z(\rho, T = \infty)$  is the configurational integral at infinite temperature when only hard core



**FIGURE 2. Free volume as total volume less the volume around each molecule from which the center of another molecule is excluded: (a) low density; (b) high density including overlap of excluded volume regions.**

forces are important;  $V_f$  is referred to as the free volume. For the square-well fluid  $Z(\rho, T = \infty)$  is the configuration integral for hard spheres since only the infinite repulsive energy, not the finite attractive energy, is important at  $T = \infty$ . The second term

$$\phi = \frac{-2kT}{N} \int_{T=\infty}^T \frac{E^{\text{CONF}}}{kT^2} dT \quad (11)$$

which for the square-well fluid is

$$\phi = \epsilon T \int_{T=\infty}^T \frac{N_c}{T^2} dT = -\epsilon T \int_{1/T=\infty}^{1/T} N_c d\left(\frac{1}{T}\right) \quad (12)$$

is the free energy change accompanying a change from  $T = \infty$  to the temperature of interest,  $T$ . We will refer to  $\phi$  as the mean potential. Combining all of the above, we have

$$Q = (q_t q_r q_v q_e)^N Z(N, V, T) = \frac{1}{N!} (q_r q_v q_e)^N \left( q_t \frac{V_f}{V} \exp(-\phi / 2kT) \right)^N = \frac{1}{N!} (q_{\text{int}})^N (q_{\text{ext}})^N \quad (13)$$

where we have grouped the short wavelength rotational and vibrational motions and the electronic energy term into the internal partition function  $q_{\text{int}}$ , and the long wavelength translational motions into an external partition function  $q_{\text{ext}}$ . Eq. (13), in which the partition function has been separated into an internal part, a hard-core part ( $V_f$  or  $Z$ ), and an interaction part ( $\phi$ ), will be referred to as the generalized van der Waals partition function [3].

In Eq. (13) the internal partition function,  $q_{\text{int}}$ , is a function of temperature but not volume and as such does not affect the equation of state, though it is important when computing values of the ideal gas energy, entropy, and heat capacity. The hard core part,  $V_f$  or  $Z$ , will lead to a repulsive or configurational term in the equation of state, while the mean potential  $\phi$  will lead to the interaction or residual term, as will be seen shortly.

### Application of Generalized van der Waals Theory to Equations of State

With this background, we can examine the equations of state commonly used by engineers in terms of the assumptions that have been made about the free volume  $V_f$  and the mean potential  $\phi$ . For example, though not explicitly stated this way, van der Waals used the literal interpretation of the free volume as the volume accessible to the center of a new molecule of diameter  $\sigma$  when put into a volume  $V$  occupied by  $N$  similar molecules. As shown in Figure 2a, this results in  $V_f = V - N\beta$  with  $\beta = 2\pi\sigma^3/3$ ,

where the excluded volume  $N\beta$  is equal to one-half the volume of  $N$  spheres of radius  $\sigma$ . (The factor of one-half arises from considering each molecule of the pair to contribute one-half of the excluded volume.) In essence, van der Waals also assumed that the coordination number is a linear function of density and independent of temperature, *i.e.*,  $N_c = c\rho$ , where  $c$  is a constant. We then have that  $\phi = -N_c\epsilon = -c\rho\epsilon$ , and

$$Z(N, V, T) = (V - N\beta)^N \exp\left(\frac{NN_c\epsilon}{2kT}\right) = \left[(V - N\beta) \exp\left(\frac{c\rho\epsilon}{2kT}\right)\right]^N \quad (14a)$$

from which we obtain

$$P = kT \left(\frac{\partial \ln Q}{\partial V}\right)_T = \frac{NkT}{V - N\beta} + \frac{cN^2\epsilon}{2V^2} = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2} \quad (14b)$$

where  $\underline{V} = V/(N/N_a)$  is the molar volume,  $b = N_a\beta$ ,  $a = -cN_a^2\epsilon/2$  and  $N_a$  is Avogadro's number. Consequently, we can now understand the molecular basis for the van der Waals equation of state in terms of the assumptions made about the coordination number and the free volume. Further, we can also relate the

parameters in this equation of state to the intermolecular potential function parameters.

Other equations of state can be analyzed in a similar manner. Table 1 contains the free volume and coordination number models imbedded in some other equations of state. Clearly different assumptions have been made for the free volume and coordination number in each of the equations in the table, and many others are possible. We can now ask which, if any, of the models in Table 1 is correct?

### Use of Theory and Computer Simulation to Test Molecular Assumptions

We now need to answer the question raised at the end of the last section. From statistical mechanics we know quite a bit about the free volume; the simple van der Waals model is correct only in one dimension. In three dimensions it underpredicts the free volume at moderate and high densities because of the overlapping of the excluded volume regions shown in Figure 2b. However, the Carnahan-Starling expression [9]

TABLE 1  
Free Volume and Coordination Number Approximations  
in Several Equations of State

Equation of State		$V_f$	$N_c$
• van der Waals	$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2}$	$V - Nb$	$c\rho$
• Redlich-Kwong [4]	$P = \frac{RT}{\underline{V} - b} - \frac{a/\sqrt{T}}{\underline{V}(\underline{V} + b)}$	$V - Nb$	$\frac{C_1}{\sqrt{T}} \ln(1 + \beta\rho)$
• Redlich-Kwong-Soave [5]	$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b)}$	$V - Nb$	$C_2(T) \ln(1 + \beta\rho)$
• Peng-Robinson [6]	$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)}$	$V - Nb$	$C_3(T) \ln \left[ \frac{1 + (1 + \sqrt{2})\beta\rho}{1 + (1 - \sqrt{2})\beta\rho} \right]$
• Widom, <i>et al.</i> [7]	$P = \frac{RT}{\underline{V}} \left[ \frac{1 + \eta^2 + \eta^2 - \eta^3}{(1 - \eta)^3} \right] - \frac{a(T)}{\underline{V}^2}$	$V \exp \left[ \frac{\eta(3\eta - 4)}{(1 - \eta)^2} \right]$	$C(T)\rho$
• Alder, <i>et al.</i> [8]	$P = \frac{RT}{\underline{V}} \left[ \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right] - \sum \sum A_{nm} \left( \frac{\epsilon}{kT} \right)^n (\rho\sigma^3)^m$	$V \exp \left[ \frac{\eta(3\eta - 4)}{(1 - \eta)^2} \right]$	$2 \sum \sum nA_{nm} \left( \frac{\epsilon}{kT} \right)^{n-1} \left( \frac{\rho\sigma^3}{\sqrt{2}} \right)^m$
• Lattice Gas Models	$\frac{PV}{RT} = \left[ \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right] - \frac{N_m V_0 (e^{\epsilon/2kT} - 1)}{[V + V_0 (e^{\epsilon/2kT} - 1)]}$	$V \exp \left[ \frac{\eta(3\eta - 4)}{(1 - \eta)^2} \right]$	$\frac{N_m V_0 e^{\epsilon/2kT}}{V + V_0 [e^{\epsilon/2kT} - 1]}$
	$= \left[ \frac{N + 0.77b}{N - 0.42b} \right] - \frac{N_m V_0 (e^{\epsilon/2kT} - 1)}{V [V + V_0 (e^{\epsilon/2kT} - 1)]}$	$\frac{(V - 0.42Nb)^{2.8333}}{V^{1.8333}}$	$\frac{N_m V_0 e^{\epsilon/2kT}}{V + V_0 [e^{\epsilon/2kT} - 1]}$

$$\frac{V_f}{V} = \exp \left[ \frac{3(3\eta - 4)}{(1 - \eta)^2} \right] \quad (15)$$

with  $\eta = \beta\rho/4$  is in almost exact agreement with computer simulation data for hard spheres, while, as can be seen from Figure 3, the simpler equation of Kim, Lin, and Chao [10]

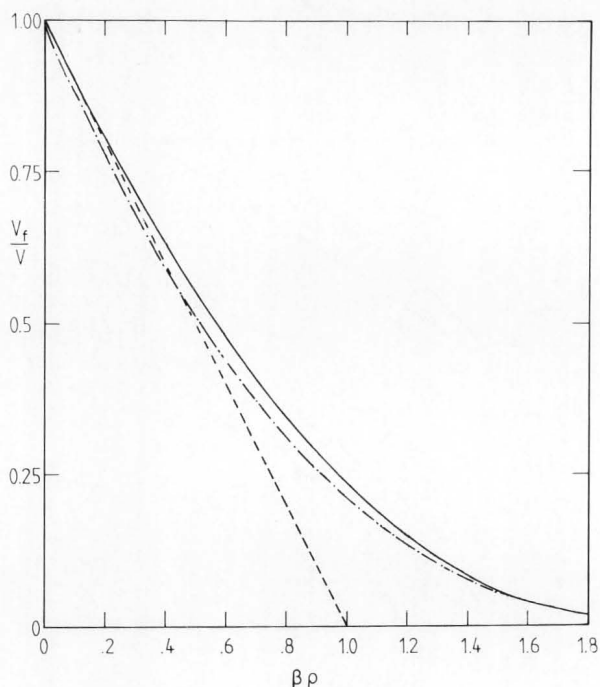
$$\frac{V_f}{V} = \left( \frac{V - 0.42N\beta}{V} \right)^{2.8333} \quad (16)$$

is in very good agreement with Eq. (15) and has the advantage of still producing cubic equations of state when combined with some coordination number models.

Choosing among the coordination number models is more difficult. At low density the exact result for the square well fluid is

$$\lim_{\rho \rightarrow 0} N_c = \frac{4\pi}{3} \rho \sigma^3 e^{\epsilon/kT} (R^3 - 1) \quad (17)$$

so that at low density the coordination number is a linear function of density, as is predicted by all the models in Table 1, though none has the same temperature dependence. At higher densities, we do not have coordination number information from theory, al-



**FIGURE 3. Free volume as a function of reduced density: — represents the Carnahan and Starling equation (Eq. 15) and the result of computer simulation; --- is the van der Waals model; and — · — is the Kim-Lin-Chao result (Eq. 16).**

**TABLE 2**  
**Absolute Average Deviation in the Compressibility Factor of the Square-Well Fluid Predicted by Various Equations of State**

Equation of State	aad Z
van der Waals	8.380
Peng-Robinson	2.159
Redlich-Kwong	1.332
Alder, <i>et al</i>	0.380
Aim-Nezbeda [13]	0.418
Aim-Nezbeda + 3 body	0.323
Ponce-Renon [14]	0.378
Equation (19)	0.240

though we can obtain such information from computer simulation methods such as Monte Carlo or molecular dynamics [11]. In brief, by considering many different configurations of molecules in a volume element which exist only in the memory of a computer, these simulation methods can be used to obtain average values for all mechanical variables such as energy, pressure, and the coordination number for any chosen intermolecular potential. Coordination number values so obtained for the square-well fluid [12] are plotted in Figure 4a as a function of dimensionless temperature  $\epsilon/kT$  and density  $\rho\sigma^3$ . In Figure 4b we have drawn curves for some of the coordination number models of Table 1.

There are a number of things to be seen from these figures. First, unlike the van der Waals assumption, the coordination number is a function of both temperature and density, and the density dependence is non-linear. Second, the density dependence is smooth, except at the lowest simulation temperature. When we examined the location of the molecules at these conditions we found that the fluid had separated into regions of high density and others of low density; that is, a phase separation had occurred. (Since we did not impose a gravitational field in our simulations, the separation was not of a low density vapor above a high density liquid, but rather of vapor and liquid regions interdispersed as would occur in a phase separation on the space shuttle.) The last and most important observation is that none of the coordination number models in common equations of state are in agreement with the simulation data.

Thus, we find that the equations of state commonly used in chemical engineering are reasonably satisfactory, not because they are fundamentally correct but rather as a result of a cancellation of errors between the free volume (repulsive) and mean potential

(largely attractive) terms. Further, since the expressions used for the mean potential or residual term in the common cubic equations have been empirically chosen to give reasonably accurate results when combined with the van der Waals free volume term, this also means that it would not be very productive to try to develop better equations of state by improving only the free volume term (*i.e.*, replacing the van der Waals term with the Carnahan-Starling or Kim-Lin-Chao expressions) while leaving the mean potential term unchanged, or vice versa. Both need to be improved.

The coordination number behavior found in our simulations (except within the two-phase region) can be described by a simple lattice gas model in which the likelihood of two neighboring sites being occupied is proportional to the Boltzmann factor of  $\epsilon/2kT$  which leads to [12]

$$N_c = \frac{N_m V_0 e^{\epsilon/2kT}}{V + V_0 (e^{\epsilon/2kT} - 1)} \quad (18)$$

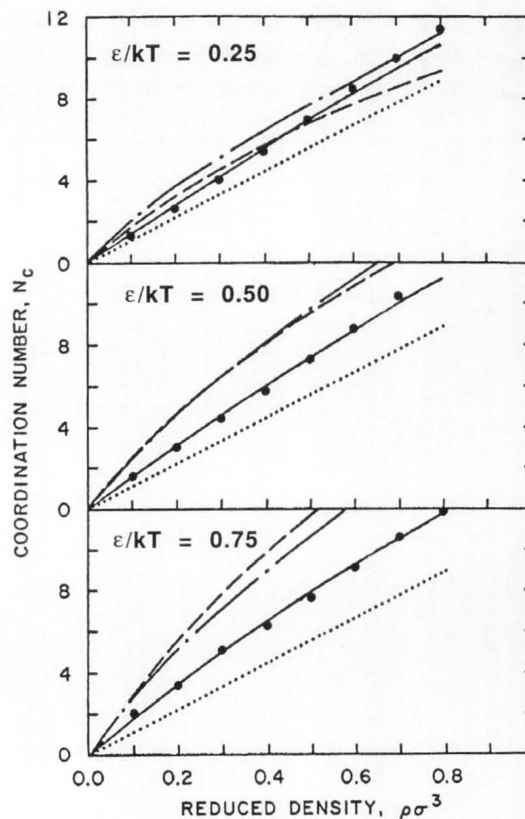
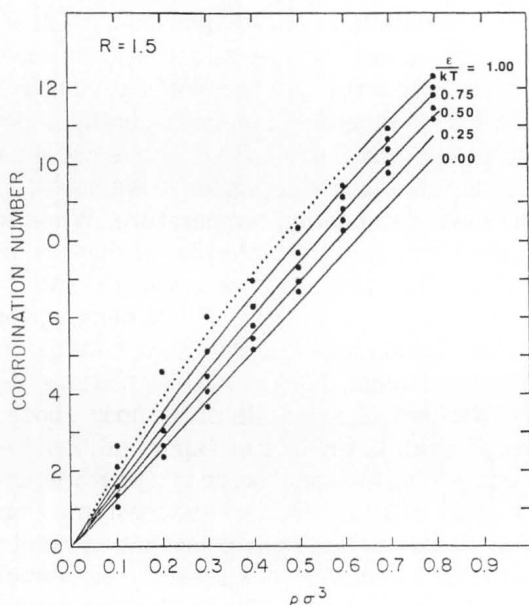
where  $V_0 = N\sigma^3/\sqrt{2}$  is the close-packed volume and  $N_m$  is the coordination number at close packing (18 when  $R$  in the square-well potential is equal to 1.5). The success of this simple, theoretically-based model in describing the square-well fluid is evident from Figure 4b.

Using Eq. (18) in the generalized van der Waals partition function together with the Carnahan-Star-

ling free volume expression (Eq. 15) leads to the relatively simple equation of state

$$\frac{PV}{RT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^2} - \frac{N_m V_0 (e^{\epsilon/2kT} - 1)}{[V + V_0 (e^{\epsilon/2kT} - 1)]} \quad (19)$$

In Table 2 the results of this and other equations of state for the square-well fluid are compared. We see from that table that the empirical equations (vdW, PR, and RK) are, in fact, not very good for describing this fluid. Better is the twenty-three term Alder *et al.* [6] equation which is a double power series expansion in temperature and density, with parameters that had been fit to their simulation data. The best equation, however, is Eq. (19) which has no adjustable parameters! That is, once the parameters in the potential model have been fixed, there is nothing left to adjust in Eq. (19) to fit the simulation data. The success of this relatively simple, theoretically-based equation over the empirical equations of state is the first example of the advantage of using the generalized van der



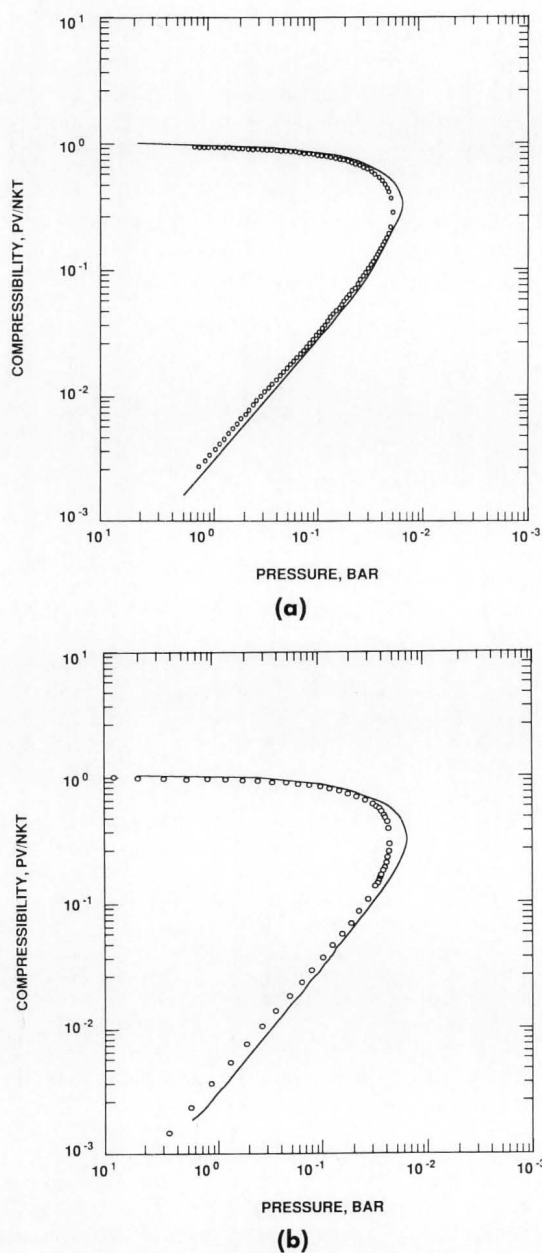
**FIGURE 4. Coordination number of the square-well fluid as a function of reduced temperature and density. In all cases the points  $\cdot$  are the result of Monte Carlo simulation and the solid lines are the result of Eq. (18).**

(a) All simulation results including the two-phase region at the lowest temperature ( $\epsilon/kT = 1$ ); extent of two phase region is indicated by the dotted line;

(b) predictions of various equations including the van der Waals (...), Redlich-Kwong (---) and Peng-Robinson (-·-) models.

Waals theory as a basis for developing thermodynamic models.

Of course engineers are interested in the equation of state for real fluids, not merely models such as the square-well fluid. We show in Figures 5a and 5b how well Eq. (19) does in describing the phase behavior of argon and methane. Of even more concern to chemical engineers is the behavior of more complicated molecules which are not spherical, and chain molecules such as hydrocarbons and polymers.



**FIGURE 5.** The compressibility of (a) argon and (b) methane. The points are experimental data for the two-phase or saturation envelope, and the line results from Eq. (19).

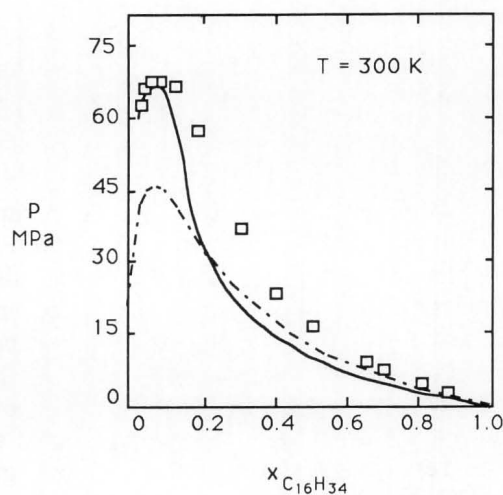
### Extension to Chain Molecules

While, in principle, the generalization of the discussion above to nonspherical, and especially to chain molecules, is very difficult, a very clever approximate formulation was presented by Prausnitz and co-workers [15,16] more than a decade ago in the form of the perturbed hard chain theory (PHCT). In brief, this model considers a chain molecule to behave like a chain of  $m$  spherical beads, each of which interacts with the square-well potential. A difficulty in evaluating the partition function of a chain molecule is that some of its rotations and vibrations are unaffected by the presence of neighboring beads, and can therefore be treated as in Eq. (5), while others (the long wave length motions) are hindered. Following a suggestion of Prigogine [17], these latter degrees of freedom are assumed to have the same density dependence as the translational degrees of freedom. Letting  $C$  be the external degree of freedom parameter (which is unity for atomic fluids) we have

$$\frac{Z(\rho, T)}{V^N} = \left[ \frac{V_f}{V} \exp\left(\frac{-\phi}{2kT}\right) \right]^{CN} \quad (20)$$

That is, a chain molecule is considered to have  $(C-1)/3$  rotational or vibrational modes which are behaving as 3-dimensional translations, where  $C$  is taken to be an adjustable parameter.

The free volume for this fluid of chains is described



**FIGURE 6.** Bubble points of mixtures of methane and hexadecane at 300 K. The points are the experimental data of ref. 16, the solid line is the result of the simplified perturbed hard chain theory and the dashed line results from the Soave-Redlich-Kwong equation. The calculations, reported in ref. 16, are predictions in that no adjustable parameters were fit to the experimental data.

by the Canahan-Starling term with  $\eta = m\beta\rho/4$ ; here we will replace the 23-term Alder expansion of Table 1 used in the original PHCT with our new single term expression of Eq. (18). The resulting equation for this simplified perturbed hard chain theory [18] is

$$\frac{PV}{RT} = \frac{1 + (4C - 3)\eta + (3 - 2C)\eta^2 - \eta^3}{(1 - \eta)^3} - \frac{CN_m V_0 (e^{\epsilon/2kT} - 1)}{V + V_0 (e^{\epsilon/2kT} - 1)} \quad (21)$$

This relatively simple, three-parameter ( $\epsilon$ ,  $C$ , and  $b$  or  $V_0$ ) equation of state has been remarkably successful in describing the properties of pure fluids, especially for large molecules, as shown in reference 18, and even more successful in predicting the properties of nonpolar mixtures of molecules of very different size. This is shown in Figure 6, for the mixture of  $\text{CH}_4 + \text{C}_{16}\text{H}_{34}$  [16] where the predictions (no adjusted parameters) of the simplified perturbed hard chain theory are found to be more accurate than those of the Soave-Redlich-Kwong equation [5].

The success of the simplified perturbed hard chain equation is another example of the value of developing thermodynamic models from theory, rather than merely choosing algebraic functions or a power series expansion with parameters fit to experimental data or using power series expansions. Note that if we use the simpler Kim-Lin-Chao expression (Eqn. 16) for the free volume, we obtain an even more simplified perturbed hard chain equation

$$\frac{PV}{RT} = \frac{V + b(1.19C - 0.42)}{V - 0.42b} - \frac{CN_m V_0 (e^{\epsilon/2kT} - 1)}{V + V_0 (e^{\epsilon/2kT} - 1)} \quad (22)$$

The properties of this three-parameter cubic equation of state have not yet been thoroughly studied.

## CONCLUSIONS

We leave the reader first with some new equations of state to explore. More importantly, however, we also leave him or her with a formulation which allows one to understand the molecular level assumptions in the equations of state now being used and a proper theoretical basis for developing new ones. We have also shown that many of the equations of state now in use do not have a good basis in theory. In fact, each consists of repulsive and interaction (or configurational and residual) terms which are incorrect, but which have been empirically chosen so that when they are combined, reasonable results are obtained. Thus there is much room for improvement and further research.

In the next paper we will consider the extension of the generalized van der Waals partition function to mixtures, which allows us to understand and test the

basis for activity coefficient models and equation of state mixing rules.

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