Equations of State in Engineering and Research

Equations of State in Engineering and Research

Kwang Chu Chao, EDITOR
Purdue University

Robert L. Robinson, Jr., EDITOR
Oklahoma State University

Based on a symposium
sponsored by the Division
of Industrial and Engineering
Chemistry at the 176th
Meeting of the American Chemical
Society, Miami Beach, Florida,
September 11–14. 1978.

ADVANCES IN CHEMISTRY SERIES **182**

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D.C. 1979

Library of Congress CIP Data

Equations of the state of engineering and research.

(Advances in chemistry series; 182 ISSN 0065-2393)

"Based on a symposium sponsored by the Division of Industrial and Engineering Chemistry at the 176th Meeting of the American Chemical Society, Miami Beach, Florida, September 11–14, 1978."

Includes bibliographies and index.

1. Equations of state. 2. Engineering mathematics. I. Chao, Kwang-chu, 1925- . II. Robinson, Robert Louis, 1937- . III. American Chemical Society. Division of Industrial and Engineering Chemistry. IV. Series.

QD1.A355 no. 182 [QC173.3] 540'.8s [541'.042]
ISBN 0-8412-0500-0 79-23696 ADCSAJ 182
1-466 1979

Copyright © 1979

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each article in this volume indicates the copyright owner's consent that reprographic copies of the article may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per copy fee through the Copyright Clearance Center, Inc. for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating new collective works, for resale, or for information storage and retrieval systems.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission, to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto.

PRINTED IN THE UNITED STATES OF AMERICA

Advances in Chemistry Series

FOREWORD

Advances in Chemistry Series was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Volumes in the Advances in Chemistry Series maintain the integrity of the symposia on which they are based; however, verbatim reproductions of previously published papers are not accepted. Papers may include reports of research as well as reviews since symposia may embrace both types of presentation.

CONTENTS

1

Practical Calculations of the Equation of State of Fluids and Fluid Mixtures Using Perturbation Theory and Related Theories

DOUGLAS HENDERSON
IBM Research Laboratory, San Jose, CA 95193

The properties of a fluid are determined largely by short-range repulsive forces. The long-range attractive forces can be considered to be perturbations. Using these concepts, a perturbation theory of fluids is developed. In addition, the relationship of empirical equations of state to the perturbation theory is examined. The major weakness of most empirical equations is the use of the van der Waals free-volume term, $(V\text{–}Nb)^{-1}$*, to represent the contributions of the repulsive forces. Replacement of this term by more satisfactory expressions results in better agreement with experiment.*

The requirements of an equation of state from a theoretical chemist and a chemical engineer are somewhat different. The theoretical chemist desires to understand the origin of the properties of the fluid he is studying and often is less interested in obtaining highly accurate agreement with experimental data. On the other hand, the chemical engineer wants a simple, empirical equation of state which is in close agreement with experimental data. The question of whether this empirical equation of state has any theoretical basis is less interesting.

Because of this apparent divergence of interests and needs, there has been little interaction between theoretical chemists and chemical engineers working on the equation of state of fluids. This is unfortunate because the requirements of the two groups are compatible. No theoretician would claim to understand fully some phenomena if he could not obtain reasonable quantitative agreement with experiment. On the other hand, an empirical equation of state with a weak or even faulty theoretical

0-8412-0500-0/79/33-182-001$07.50/1

basis is no more than an interpolation scheme and is quite useless for extrapolation to thermodynamic states for which experimental data are not available. Presumably chemical engineers would prefer to have some predictive capability and if the results of the theoretician can be expressed in some useful form which is convenient for quick calculation, chemical engineers would be interested.

I assume that this gap between theoretical chemists and chemical engineers exists because, until very recently, theoreticians had little to offer concerning the theory of fluids. However, during the past decade rapid progress has been made in this area and an attempt to bridge this gap now seems appropriate. This is an ambitious task and given the deadlines which are an unavoidable part of any conference, it is not a task that I would claim to accomplish fully here. However, I hope that this chapter will contribute to the bridging of this gap.

I shall attempt to survey recent progress in the theory of dense fluids. I will provide references to all of the major techniques. However, I will emphasize perturbation theory because I feel that this is the technique which is most interesting to chemical engineers. Further, I will show that the perturbation theory can be used in part to justify common empirical equations of state. Many of these equations are well founded in theory. However, we shall see that there is one term which seems to appear in all empirical equations of state. This term has absolutely no theoretical basis and it should be discarded and replaced by a more satisfactory expression.

Some General Considerations

The basic result in statistical mechanics is that the probability of a system being in a state specified by an energy E_i is proportional to the Boltzmann factor $\exp\{-\beta E_i\}$, where $\beta = 1/kT$. With this result, thermodynamic properties may be specified. For example, the thermodynamic energy is

$$U = \frac{\sum_i E_i \exp\{-\beta E_i\}}{\sum_i \exp\{-\beta E_i\}}$$

$$= -\frac{\partial \ln Z_N}{\partial \beta}, \tag{1}$$

where

$$Z_N = \exp\{-\beta A\}$$

$$= \sum_i \exp\{-\beta E_i\} \tag{2}$$

is called the partition function and A is the Helmholtz free energy (i.e., $A = U - TS$). With exception of a few fluids, such as helium and hydrogen, the energy levels E_i form a continuum and the sum in Equation 2 can be replaced by an integral. Thus, for a system of N molecules

$$Z_N = \frac{1}{h^s N!} \int \exp\{-\beta \mathcal{H}\}\, dp_s\, dq_s \tag{3}$$

where the p's and q's are the generalized momenta and coordinates, s is the number of degrees of freedom, and $\mathcal{H}$ is the Hamiltonian of the system. The factor h^s arises from the volume associated with quantum states in phase space and the factor $N!$ appears because the molecules in a fluid are indistinguishable.

Generally the molecules of the fluid will have internal degrees of freedom. If these internal degrees of freedom are independent of the density of the fluid (as is often the case) they make no contribution to the equation of state and can be ignored. Since I am interested only in presenting general principles, I will ignore the contribution of internal degrees of freedom and assume that

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \Phi(r_1, \ldots r_N) \tag{4}$$

where Φ is the potential energy of the molecules and depends only upon the positions of the center of mass. The theory of fluids in which internal degrees of freedom contribute to the equation of state is still under development. Using Equation 4, the partition function becomes

$$Z_N = \frac{\lambda^{-3N}}{N!} \int \exp\{-\beta\Phi\} d\mathbf{r}_1 \ldots d\mathbf{r}_N \tag{5}$$

where $\lambda = h/(2\pi mkT)^{1/2}$.

To make further progress the form of Φ must be specified. Generally the potential energy will contain terms involving the coordinates of pairs, triplets, quadruplets, etc., of molecules. A few calculations of the equation of state of a fluid with such a general form for Φ have been made. However, the common practice is to assume pair-wise additivity:

$$\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i<j} u(r_{ij}) \tag{6}$$

In this case, $u(r)$ is not the correct pair interaction but some effective pair interaction which simulates the multibody terms.

Often

$$u(r) = \epsilon\varphi(r/\sigma) \tag{7}$$

where φ is some universal function which is applicable to a wide class of substances. Substitution of Equation 7 into Equation 5 leads to the law of corresponding states which states that for such substances the thermodynamic functions are also universal functions that are scaled by appropriate combinations of ϵ and σ. Thus,

$$P^* = \mathrm{f}(\rho^*, T^*) \tag{8}$$

where $P^* = P\sigma^3/\epsilon$, $\rho^* = \rho\sigma^3$, and $T^* = kT/\epsilon$ are the reduced pressure, density, and temperature.

The above form of the law of corresponding states may seem unsuitable for a chemical engineer since it seems to require the determination of $u(r)$ for the fluid of interest. However, if the temperature and density of the fluid at some fundamental state (e.g. the critical point or the triple point) are known, then ϵ and σ may be determined using the law of corresponding states. For example,

$$\begin{aligned} \epsilon &= c_1\, T_c \\ \sigma^3 &= c_2\, V_c \end{aligned} \tag{9}$$

where T_c and V_c are the critical temperature and volume and c_1 and c_2 are universal constants. Thus, an equivalent statement of the law of corresponding states is

$$P/P_c = \mathrm{g}(V/V_c, T/T_c) \tag{10}$$

where P_c is the critical pressure.

One useful test of the law of corresponding states is the invariance of certain dimensionless terms: e.g., for many fluids

$$z_c = P_cV_c/NkT_c \simeq 0.291 \tag{11}$$

As we would expect, there are deviations from Equation 11 for fluids with internal degrees of freedom.

Computer Simulations and Integral Equations

I would like to turn to the question of the calculation of the partition function. There are three methods of obtaining Z_N and the thermodynamic properties. I will consider two of these methods in this section and the third in the next section. The first method is computer simulation. In this method a set of about 100 molecules in a box with periodic boundary conditions (to minimize surface effects) is considered and either the time or statistical evolution of the system followed. A detailed review (*1*) is available so I will not consider this method in detail. The method involves large computations and will not become a routine tool in chemical engineering. However, it is completely general: to date it is the only technique generally applicable to molecules with internal degrees of freedom. Further, it provides (in principle) complete information about the system, including the *h*-body distribution functions,

$$g(\mathbf{r}_1, \ldots, \mathbf{r}_h) = V^h \frac{\int \exp\{-\beta\Phi\} d\mathbf{r}_{h+1} \ldots d\mathbf{r}_N}{\int \exp\{-\beta\Phi\} d\mathbf{r}_1 \ldots d\mathbf{r}_N} \qquad (12)$$

as well as the thermodynamic functions. Computer simulations do not give Z_N directly. However, derivatives of Z_N are obtained and Z_N can be obtained by integration over a series of states. The only limits on the computer simulation method are our ingenuity in programming the computer and our ability to cope with the numerical data. The later limitation is nontrivial and prevents detailed consideration of four- and higher-body distribution functions. Finally, we may regard the computer simulation methods as either an experimental or a theoretical tool. Generally speaking it is used as an experimental tool for providing data with which theoretical calculations may be compared. Apart from statistical problems and the question of whether the box contains a sufficiently large number of molecules, the method is exact. The results of some computer simulations of hard spheres are given in Figure 1.

The second method is the integral equation method. In this approach some approximate integral equation for the radial distribution function, $g(r)$, is formulated and solved. For the simple molecules without internal degrees of freedom which I am considering, the radial distribution function (RDF) is the pair ($h = 2$) distribution function (PDF) defined by Equation 12. The integral equation method involves much less computer usage than do the computer simulations but still involves enough to make its use as a routine chemical-engineering tool unlikely.

However, in certain cases where these integral equations yield analytical solutions, the method will be interesting to chemical engineers. For instance, Wertheim (*2, 3*) and Thiele (*4*) have solved the Percus–Yevick (PY) equation for the hard-sphere potential, where

$$u(r) = \begin{cases} \infty, r < d \\ 0, r > d \end{cases} \qquad (13)$$

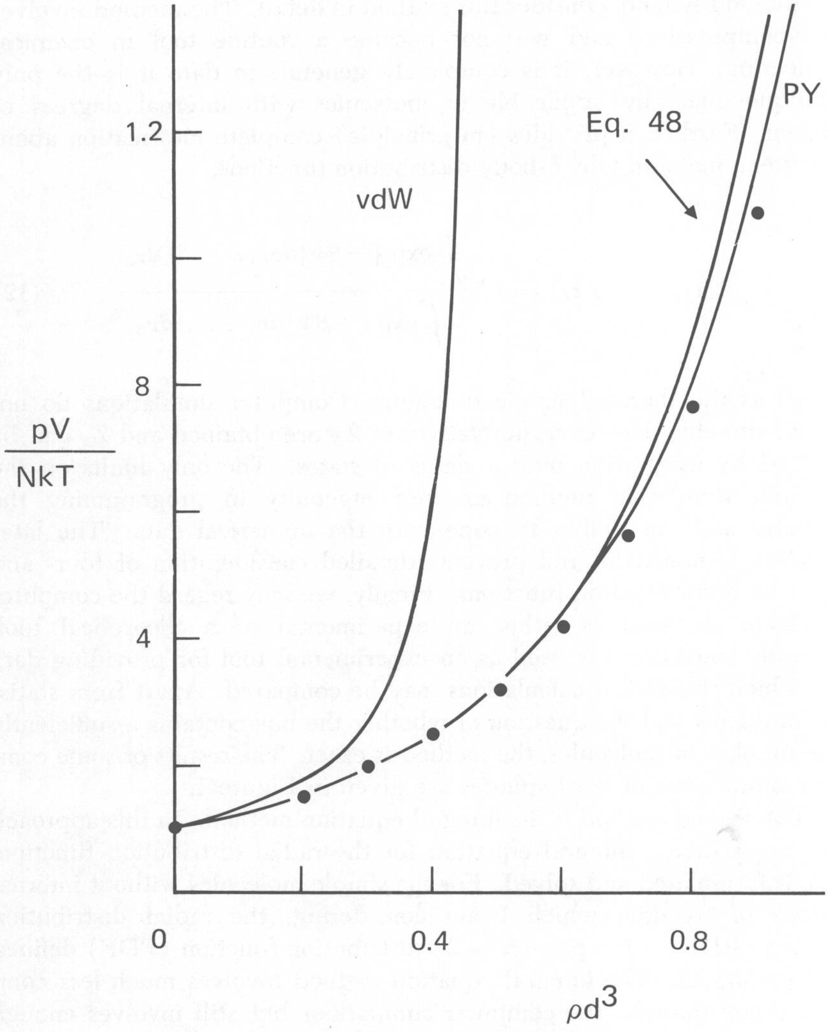

Figure 1. Equation of state of the hard-sphere fluid. The points give computer simulation results and curves give the results of three approximations.

They showed that

$$A/NkT = 3 \ln \lambda - 1 + \ln \rho - \ln (1 - \eta) + \frac{3}{2} \eta \frac{2 - \eta}{(1 - \eta)^2} \tag{14}$$

and

$$P/\rho kT = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \tag{15}$$

where $\eta = \pi \rho d^3/6$. Equation 15 is compared with computer simulations in Figure 1. They showed further that the Laplace transform of $g(r)$ is given by

$$\begin{aligned} G(s) &= \int_1^\infty x g(x) \exp(-sx)\, dx \\ &= \frac{sL(s)}{12\eta[L(s) + \exp(s)S(s)]} \end{aligned} \tag{16}$$

where $x = r/\sigma$,

$$L(s) = 12\eta[1 + 2\eta + (1 + \eta/2)s] \tag{17}$$

and

$$S(s) = -12\eta(1 + 2\eta) + 18\eta^2 s + 6\eta(1 - \eta)s^2 + (1 - \eta)^2 s^3 \tag{18}$$

Smith and Henderson (*5*) have inverted $G(s)$ analytically for $1 \leq x \leq 5$. For the hard-sphere potential, these PY results for A, P, and $g(r)$ are in good agreement with computer simulations.

A second case of potential interest to chemical engineers is Waisman's solution (*6*) of the mean sperical approximation (MSA) integral equation for the case where

$$u(r) = \begin{cases} \infty, r < \sigma \\ -\epsilon \exp\{-z(x - 1)\}/x, r > \sigma \end{cases} \tag{19}$$

and $x = r/\sigma$. Waisman's solution is implicit and involves the solution of six nonlinear equations. However, Henderson (*7*) has shown recently that a good parametrization of Waisman's solution is given by

$$\begin{aligned} A/NkT = A_0/NkT - \beta\epsilon v_1/2 - (\beta\epsilon)^2 v_2/4 - \\ (\beta\epsilon)^3 v_3/6 - (\beta\epsilon)^4 v_4/8 \end{aligned} \tag{20}$$

where A_o is given by Equation 14,

$$v_1 = \frac{2z\mathrm{L}(z)}{\mathrm{e}^{-z}\mathrm{L}(z) + \mathrm{S}(z)} \tag{21}$$

$$v_2 \simeq \frac{12}{z}\,\eta(1-\eta)^{12c} \tag{22}$$

$$v_3 \simeq \frac{144(2 - 3\mathrm{e}^{-z}/2)}{\mathrm{z}^3}\,\eta^2(1-\eta)^{19c} \tag{23}$$

$$v_4 \simeq \frac{1728(11/2 - 8\mathrm{e}^{-z} + 3e^{-2z})}{\mathrm{z}^5}\,\eta^3(1-\eta)^{26.3c} \tag{24}$$

and

$$c = \frac{(1.25 - 0.35\,e^{-z^3/24})}{z^3}\,[-4 + 2z^2 + 4(1+z)\,e^{-z}] \tag{25}$$

Equation 21 gives the exact result for v_1 in the MSA. The expressions for v_2, v_3, and v_4 are parametrizations. Equation 21 is analytical and quite easy to use. For most cases, v_2, v_3, and v_4 are small when compared with v_1 so that it is best to use Equation 21 for v_1 rather than some approximation. However, if one wishes, simplifications can be obtained from an expansion of Equation 21 in powers of ρ and z. One possibility is

$$v_1 \simeq 24\eta\,\frac{1+z}{z^2}\left[1 + \frac{77z^2}{10(1+z)(7+2z)}\,\eta\right] \tag{26}$$

Except for $z \to \infty$, most of the contribution to v_1 comes from the first term. The limit $z \to \infty$ is mainly of mathematical interest. In most situations of physical interest z is small.

We refer to the literature (*1*) for a discussion of the derivation of the various integral equations and for details regarding their solution (usually numerical) for other cases.

Perturbation Theory

Perturbation theory is the oldest of the three methods. We will see that it dates back to van der Waals. However, its utility was not appreciated by theorists until the last decade.

In perturbation theory we assume that we have full knowledge of some reference system (or unperturbed system) whose properties we will denote by a subscript 0. We may have obtained this knowledge by means of some computer simulations or from the solution of some integral equation. Usually, this reference system is taken to be the hard-sphere fluid, where

$$u_0(r) = \begin{cases} \infty, & \mathrm{r} < \mathrm{d} \\ 0, & \mathrm{r} > \mathrm{d} \end{cases} \tag{27}$$

We assume that, to some approximation, the pair potential is $u_0(r)$ and a small perturbation. The simplest case is

$$u(r) = u_0(r) + \epsilon w(r) \tag{28}$$

If the free energy is expanded in powers of ϵ, we have

$$\frac{A - A_0}{NkT} = \sum_{n=1}^{\infty} (\beta\epsilon)^n A_n/NkT \tag{29}$$

where

$$A_1/NkT = \frac{1}{2} \rho \int w(r) \mathrm{g}_0(r)\, d\mathbf{r} \tag{30}$$

and $\mathrm{g}_0(r)$ is the RDF of the reference system. The higher-order A_n involves integrals over higher-order distribution functions.

If the reference system is the hard-sphere system, A_0 may be calculated from Equation 14. Carnahan and Starling (*8*) have proposed a slight modification of Equation 14 which is slightly more accurate. Using the Carnahan and Starling expression is certainly recommended; however, I wish to give the following warning. The analogue of the Carnahan and Starling equation of state becomes very inaccurate for a mixture of hard spheres when one of the components in the mixture is very large whereas the analogue of Equation 14 remains accurate. In as much as the Carnahan and Starling-type expression is in better agreement with computer simulations for hard-sphere mixtures for diameter ratios at least as large as 3:1, it is probable that this deficiency probably is irrelevant to any practical calculation. However, one should be wary not only to avoid application of the Carnahan and Starling-type expression for extremely large diameter ratios but to examine carefully any predictions based on the use of this expression in situations in which it has not been studied in detail. For a hard-sphere reference fluid, $\mathrm{g}_0(r)$ and thus A_1, can be obtained either from the PY hard-sphere results (*5*) or from computer simulations (*9, 10*). For most cases, A_1 must be obtained by numerical integration. However, if

$$w(r) = -\epsilon \exp\{-z(x-1)\}/x \tag{31}$$

where $x = r/\sigma$ and the PY $g_0(r)$ are used, Equation 16 may be used to yield

$$A_1 NkT = -\frac{z\mathrm{L}(z)}{\mathrm{e}^{-z}\mathrm{L}(z) + \mathrm{S}(z)} \tag{32}$$

The similarity to Equation 21 is not accidental.

If a hard-sphere reference fluid is used, the second-order term has the form

$$A_2/NkT = -\pi\rho d^3 \int_1^\infty r^2[w(rd)]^2 g_0(r)\,dr + \int_1^\infty \int_1^\infty w(r_1 d)\,w(r_2 d)\; F_0(r_1, r_2)\; dr_1\, dr_2 \tag{33}$$

Barker and Henderson (*10*) have given a convenient parametrization of $F_0(r_1, r_2)$ for the hard-sphere reference fluid.

So far all we have is formalism. One could argue that there is no reason to believe that Equation 29 is useful except at high temperatures, where $\beta\epsilon$ is small. The utility of perturbation theory even at temperatures as low as the triple point, was first pointed out a decade ago by Barker and Henderson (*11*) who argued that the relevant parameter in determining the convergence of Equation 29 was not the smallness of $\beta\epsilon$ but the smallness of the effect of the perturbation on the structure of the fluid. They noted that A_1 gives the effect of $w(r)$ on the thermodynamic properties in the absence of any changes in structure and that A_2 gives the effect of changes in structure. At high densities such changes in structure are suppressed because the molecules are packed tightly. Therefore, A_2 is small compared with A_1 (as is observed by direct calculation of A_1 and A_2). The higher-order A_n are even smaller and, as Barker and Henderson suggested, can be neglected in most calculations.

At lower densities, particularly near the critical point, changes in structure are easier and the convergence of the perturbation expansion is slower. But even there, second-order perturbation theory gives quite reasonable results.

All of this makes sense as long as $u(r)$ is the hard-sphere potential plus $\epsilon w(r)$. Unfortunately, the potentials which occur in real applications are not of this form. Nevertheless, following Barker and Henderson (*12*), we can write

$$u(r) = u_0(r) + \epsilon w(r) \tag{34}$$

where $u_0(r)$ and $w(r)$ are the positive and negative parts of $u(r)$. Thus, we can use Equations 29 and 30. However, we now have an unfamiliar reference fluid. Fortunately, for most applications $u_0(r)$ is very steep