Truncation of Virial Equations in PVT Data Reduction

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The danger of generating smoothed PVT data tables from truncated power series obtained by regression analysis of raw data is shown by the derivation of equations that lead to graphical tests for physical correctness. Points of extremum on graphs of $(Z - 1)/P$ vs. P and $(Z - 1)/\rho$ vs. ρ are related to density and pressure virial coefficients, respectively. The variation of curvature with pressure or density provides a graphical criterion for physical correctness, whereas the appropriate pair-potential yields a theoretical criterion. Supporting examples are given with published smoothed values for methane and ethylene.

In experiments involving the densities of fluids (although not all the virial coefficients reported in the literature are derived from truncated series), it is common to use a truncated virial expansion as the equation of state of the fluid, and this truncation can give rise to numerical values which may be interpreted as anomalous physical phenomena if the equation is used in the wrong conditions.

The full virial equations, when written as

$$Z = 1 + B_1\rho + C_1\rho^2 + D_1\rho^3 + \ldots \qquad (1)$$

for the density expansion and as

$$Z = 1 + B_2P + C_2P^2 + D_2P^3 + \ldots \qquad (2)$$

for the pressure expansion, have the following relationships between the second and third virial coefficients:

$$B_1 = RTB_2 \qquad (3)$$

and

$$C_1 = (RT)^2[C_2 + B_2^2] \qquad (4)$$

or

$$C_2 = (C_1 - B_1^2)/(RT)^2 \qquad (5)$$

As the density and pressure approach zero, the higher coefficients may be successively disregarded, and isotherms generated from *either* Equation 1 or 2 will become linear in both $\chi - \rho$ and $\eta - P$ coordinates where

$$\chi = (Z - 1)/\rho \qquad (6)$$

$$\eta = (Z - 1)/P \qquad (7)$$

This is not necessarily so if truncated versions of the equations are used ab initio. The effect of using an expansion which terminates with the linear term in pressure or density has been explored by Scott and Dunlap (6), but they did not consider whether their solution—to include the square terms—removed all the possibilities of error.

If the equation

$$Z = 1 + \beta_1\rho + \gamma_1\rho^2 \qquad (8)$$

is produced by using experimental results to establish β_1 and γ_1, then the numbers generated by Equation 8 will be linear in $\chi - \rho$ coordinates but not in $\eta - P$ coordinates.

Equation 8 gives

$$\eta = (RTZ)^{-1}\left[\beta_1 + \frac{\gamma_1P}{ZRT}\right] \qquad (9)$$

and

$$\frac{d\eta}{dP} = \frac{\gamma_1 - \eta(RT\beta_1 + 2\,\gamma_1P/Z)}{(RTZ)^2 + P(RT\beta_1 + 2\,\gamma_1P/Z)} \qquad (10)$$

Not only is the $\eta - P$ graph a curved line, but it exhibits a minimum value, ρ_m, given by

$$\rho_m = \frac{-\beta_1 + (sgn\,\beta_1)\sqrt{\gamma_1}}{\gamma_1} \qquad (11)$$

ρ_m is not necessarily real: it is shown as a function of γ_1 in Figure 1, for β_1 negative. The graph shows that the condition $\gamma_1 < \beta_1^2$ must also be met if ρ_m is to be positive.

An example of the existence of such a minimum under the conditions ($\beta_1 < 0$, $\gamma_1 < \beta_1^2$) is shown in Figure 2, by use of values for the 263.08K isotherm of methane taken from the work of Roe (5). Roe's data were taken from a Burnett-type apparatus and were analyzed by a scheme which gave negligible values for δ_1 and ϵ_1 in a virial expansion in density truncated at the fourth power. Thus, his results are effectively expressed as a parabola in density, that is, Equation 8; and if it is used to produce a $\eta - P$ plot, a minimum is observed at $\rho_m = 1.99 \times 10^{-3}$ g-mol/cm^3 or $P_m = 38.9$ bar, as predicted by Equation 10. At the next highest experimental isotherm, γ_1 is now greater than β_1^2, and no minimum is found. On

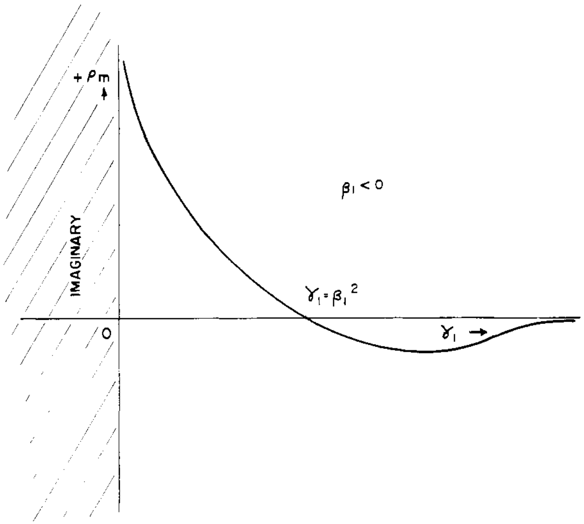

Figure 1. Density corresponding to minimum on $\eta - P$ graph for Equation 8

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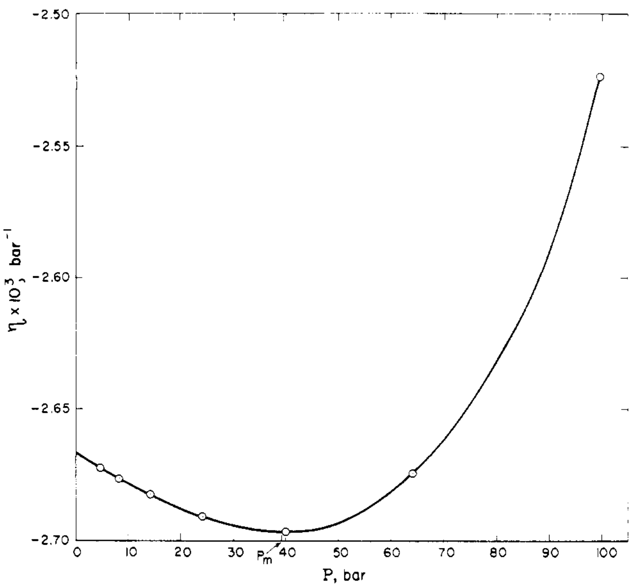

Figure 2. Methane, 263.08K (*5*)

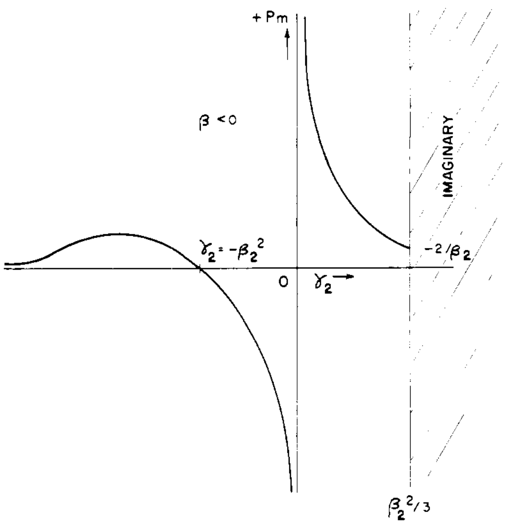

Figure 3. Pressure corresponding to minimum on $\chi - \rho$ graph for Equation 12

isotherms below 263.08K, the minimum is found on the five next lower isotherms, down to 192.64K. Below this, the experiments did not cover the high-density region where the minimum would be found.

If the truncated equation used is

$$Z = 1 + \beta_2 P + \gamma_2 P^2 \tag{12}$$

then the numbers generated by it will be linear in $\eta - P$ coordinates, but not in $\chi - \rho$ coordinates. From Equation 12

$$\chi = RTZ[\beta_2 + RTZ\rho\gamma_2] \tag{13}$$

and

$$\frac{d\chi}{d\rho} = \frac{\beta_2\chi + RT\gamma_2(\rho\chi + 1)\ (3\,\rho\chi + 1)}{(RT)^{-1} - \rho[\beta_2 + 2\,(RT)\gamma_2\rho(\rho\chi + 1)]} \tag{14}$$

This also shows a minimum at

$$P_m = \frac{1}{3}\left[-2\,\frac{\beta_2}{\gamma_2} - \frac{(sgn\,\beta_2)}{|\gamma_2|}\sqrt{\beta_2{}^2 - 3\,\gamma_2}\right] \tag{15}$$

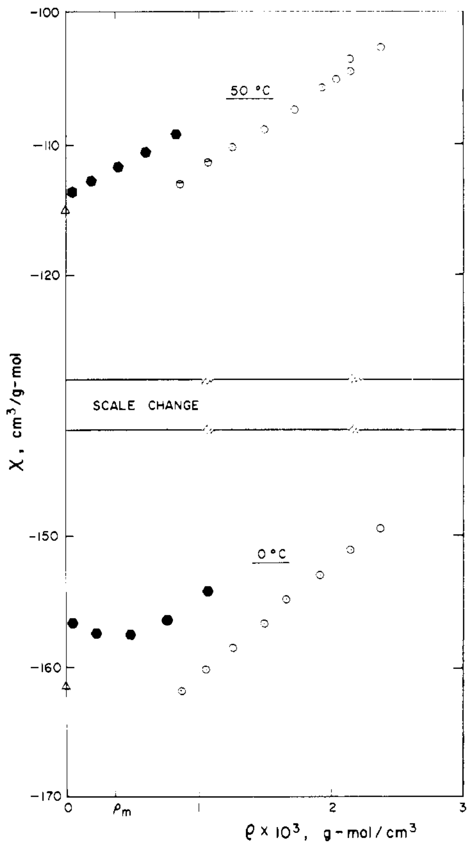

Figure 4. Ethylene
⊙ (*4*)
● (*7*)
△ (*1*)

with

$$\rho_m = P_m/Z_m RT \tag{16}$$

The region within which the minimum is real and positive is now, for negative β_2, either where $\gamma_2 < -\beta_2{}^2$ or where $0 < \gamma_2 < \beta_2{}^2/3$, as shown in Figure 3.

The dangers of using the "opposite" system of parameters can be illustrated in Figure 4, which shows a $\chi - \rho$ plot of the 0°C results of Michels and Geldermans (*4*), Butcher and Dadson (*1*), and Thomas and Zander (*7*) for ethylene. The difference between the second virial coefficients of the first two pairs of experimenters for both ethylene and carbon dioxide is a well-known problem. The addition of the Thomas and Zander values to the graph, although agreeing with neither, suggests a possible explanation, since the upward curve is characteristic of adsorption effects, and a simple downward displacement of the Thomas and Zander curve (i.e., an assumption of a systematic error in temperature) would suggest that the Butcher and Dadson work also suffers from adsorption problems. Adsorption errors *accumulate* in the Burnett-type apparatus of ref. *1* and *7*. The 50°C isotherm shows the Thomas and Zander results to be almost the same distance away from the Michels and Geldermans results as at 0°C and to be almost collinear. Since this isotherm is well above the critical temperature (9.5°C), no adsorption effects would be expected, and this graph strengthens the hypothesis.

Closer study shows this reasoning to be in error. The table of PVT values given by Thomas and Zander, from which the graphs were drawn, are not experimental results but are smoothed values derived from an equation similar to 12. The minimum at 0°C is therefore not a physical phenomenon but an artifact of the data-handling process. If we use the values given by Thomas and Zander for 0°C of

$$\beta_2 = -6.974 \times 10^{-3}\ \text{atm}^{-1} \tag{17}$$

and

$$\gamma_2 = -6.310 \times 10^{-5}\ \text{atm}^{-2} \tag{18}$$

then Equation 15 predicts a pressure minimum of 7.91 bar, to which corresponds $\rho_m = 3.71 \times 10^{-4}$ mol cm^{-3}, which is close to that found. At 50°C, the values are

$$\beta_2 = -4.286 \times 10^{-3}\ \text{atm}^{-1} \tag{19}$$

and

$$\gamma_2 = -1.200 \times 10^{-5}\ \text{atm}^{-2} \tag{20}$$

which gives a value of $P_m = -33.7$ bar, and the graphed points, being well away from the physically unreal minimum, show little curvature.

Thus, the hypothesis of adsorption is not proven, and the experimental conflict is not resolved although the estimate of C_1 of Thomas and Zander extracted from Figure 4 at 0°C is negative which is unexpected for a simple, nonpolar molecule near the critical temperature (*3*). A basic difference between Figures 2 and 4 is the increasing curvature of the data of Thomas and Zander with decreasing density.

Surprisingly, the Michels and Geldermans results, if plotted in $\eta - P$ coordinates, exhibit curvature as though they had been smoothed by a truncated density expansion (Figure 5).

It would be helpful for the experimenter if some indication could be given as to where these spurious minima are likely to be found. No general rule can be given, but their occurrence can be predicted for a Lennard-Jones gas, which is a useful approximation to many real fluids. Using the second and third virial coefficients of a Lennard-Jones (*12*, *6*) gas (*2*), the range of $T^* = (Tk/\epsilon)$, for which ρ_m of Figure 1 is real and positive, is determined together with the analogous range of P_m, Figure 3. The approximate relationship $(\epsilon/k) = 0.77\ T_c$ converts T^* to reduced temperature, T_R, with the final results represented by Figure 6. An example will demonstrate the use of Figure 6. For a reduced temperature range of 0.7–1.50, PVT data reduced by Equation 8 will exhibit a real minimum in $\eta - P$ coordinates. Figure 6 should provide a rough guide for nonpolar, nonspherical molecules but could be most misleading for associated polar compounds.

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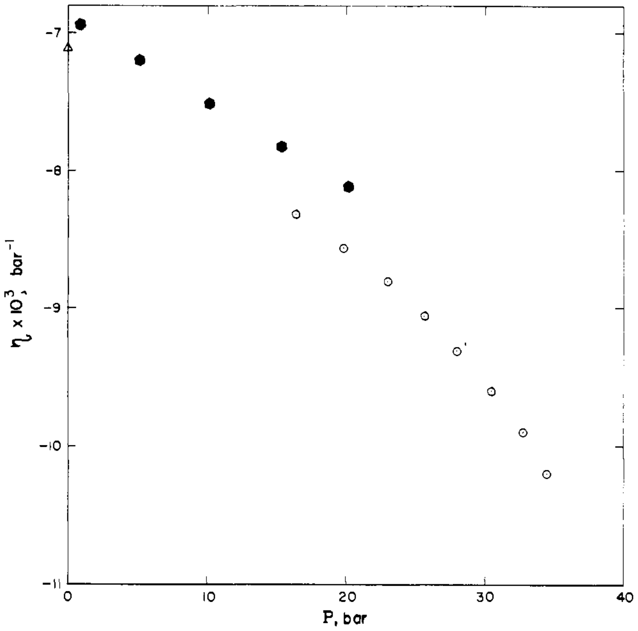

Figure 5. Ethylene, 0°C
⊙ (*4*)
● (*7*)
△ (*1*)

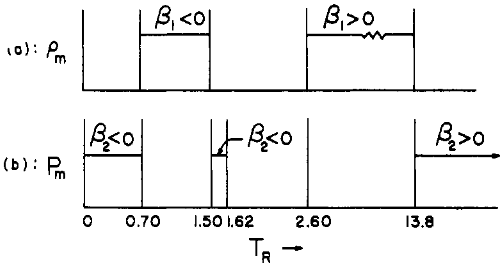

Figure 6. Reduced temperature range for positive, real values of (a) ρ_m in $\eta - P$ coordinates and (b) P_m in $\chi - \dot{\rho}$ coordinates for Lennard-Jones gas

Literature Cited

(1) Butcher, E. G., Dadson, R. S., *Proc. Roy. Soc. (London)*, **A277**, 448 (1963).
(2) Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Molecular Theory of Gases and Liquids," pp 1114–17, Wiley, New York, N.Y., 1954.
(3) Mason, E. A., Spurling, T. H., "The Virial Equation of State," Topic 10, Vol 2, *Int. Encyclo. of Phys. Chem. and Chem. Phys.*, p 14, Pergamon Press, London, England, 1969.
(4) Michels, A., Geldermans, M., *Physica*, **9**, 967 (1942).
(5) Roe, D., PhD thesis, Imperial College, London, England, 1972.
(6) Scott, R. L., Dunlap, R. D., *J. Phys. Chem.*, **66**, 639 (1962).
(7) Thomas, W., Zander, M., *Z. Angew Phys.*, **20**, 417 (1966).

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