

# Phase Equilibrium of Butane

Jonathan D. Hauenstein

Fundamental equations of state are the state-of-the-art in high accuracy thermodynamic property description of fluids. These equations of state are functions of temperature and density which allow for all thermodynamic quantities of interest to be expressed through combinations of partial derivatives and equality constraints. In this example, we utilize the equations of state for butane to compute its critical temperature  $T_c$  (K) and critical density  $\rho_c$  (kg/m<sup>3</sup>) for liquid-vapor phase equilibrium using the homotopy-based approach developed in [4, Alg. 4].

Let  $T$  be the temperature,  $\rho_l$  and  $\rho_v$  be the density in the liquid and vapor phase, respectively, and  $P$  be the pressure which is a function of temperature and density. Densities  $\rho_l$  and  $\rho_v$  are called *spinodal* densities for the liquid and vapor phase, respectively, for a given temperature  $T$  if

$$(1) \quad \frac{\partial P(T, \rho_l)}{\partial \rho} = \frac{\partial P(T, \rho_v)}{\partial \rho} = 0.$$

Spinodal densities are easily computed for low temperatures, i.e., when  $T \ll T_c$ . At the critical temperature  $T_c$ , the spinodal densities for the liquid and vapor phases are equal, namely  $\rho_c$ . Hence, given a temperature  $T^* < T_c$  with spinodal densities  $\rho_l(T^*) \neq \rho_v(T^*)$ , we can utilize the following homotopy to compute  $T_c$  and  $\rho_c$ :

$$(2) \quad H(T, \rho_l, \rho_v; s) = \begin{bmatrix} \frac{\partial P(T, \rho_l)}{\partial \rho} \\ \frac{\partial P(T, \rho_v)}{\partial \rho} \\ (\rho_l - \rho_v) - s(\rho_l(T^*) - \rho_v(T^*)) \end{bmatrix} = 0.$$

The homotopy (2) starts at  $s = 1$  with start point  $(T^*, \rho_l(T^*), \rho_v(T^*))$  and forces the spinodal densities to be equal at  $s = 0$  yielding the endpoint  $(T_c, \rho_c, \rho_c)$ . Other numerical approaches have difficulty near the critical temperature due to ill-conditioning partially arising from the fact that  $(T_c, \rho_c, \rho_c)$  lies on the positive-dimensional set of so-called trivial solutions

$$\left\{ (T, \rho, \rho) \mid \frac{\partial P(T, \rho)}{\partial \rho} = 0 \right\}.$$

By using adaptive precision algorithms [1, 2, 3] and endgames in `Bertini`, we can accurately compute the critical temperature  $T_c$  and critical density  $\rho_c$  as shown in [4]. We demonstrate this with butane for which  $\frac{\partial P(T, \rho_v)}{\partial \rho}$  is not polynomial. Nonetheless, we can still utilize a user-defined homotopy in `Bertini` that tracks in affine space as presented in `inputPhaseEquilibrium`. We additionally provide the start point in `startPhaseEquilibrium` which corresponds with  $T^* = 300$  K. Executing `PhaseEquilibrium.sh` tracks the solution path to (2). In our test, the following is the corresponding data list in `main_data`:

```
Solution 0 (path number 0)
Estimated condition number: 1.180094054166440e+17
Function residual: 2.58681964737661e-14
Latest Newton residual: 1.36551830251988e-11
T value at final sample point: 1.525878906250000e-06
Maximum precision utilized: 64
T value of first precision increase: 2.441406250000000e-05
Accuracy estimate, internal coordinates (difference of last two endpoint estimates): 8.258740913369421e-12
```

```

Accuracy estimate, user's coordinates (after dehomogenization, if applicable): 8.258740913369421e-12
Cycle number: 1
0.425758765786680772381e3 0.00000000000000000000e0
0.215473397418730659936e3 0.00000000000000000000e0
0.215473397418730685804e3 0.00000000000000000000e0
Paths with the same endpoint, to the prescribed tolerance:
Multiplicity: 1

```

We see evidence of the ill-conditioning with the condition number being  $\approx 1.18 \cdot 10^{17}$  and observe that adaptive precision algorithms [1, 2, 3] utilized 64-bit precision to accurately compute the solution  $T_c \approx 425.759$  and  $\rho_c \approx 215.473$  which matches with results for butane in [5, Table V].

## REFERENCES

- [1] D.J. Bates, J.D. Hauenstein, and A.J. Sommese. Efficient path tracking methods. *Numer. Algor.*, 58(4), 451–459, 2011.
- [2] D.J. Bates, J.D. Hauenstein, A.J. Sommese, and C.W. Wampler. Adaptive multiprecision path tracking. *SIAM J. Numer. Anal.*, 46(2), 722–746, 2008.
- [3] D.J. Bates, J.D. Hauenstein, A.J. Sommese, and C.W. Wampler. Stepsize control for adaptive multiprecision path tracking. *Contemp. Math.*, 496, 21–31, 2009.
- [4] H. Sidky, A.C. Liddell, Jr., D. Mehta, J.D. Hauenstein, and J. Whitmer. An algebraic geometric method for calculating phase equilibria from fundamental equations of state. *Ind. Eng. Chem. Res.*, 55(43), 11363–11370, 2016.
- [5] R. Span and W. Wagner. Equations of State for Technical Applications. II. Results for Nonpolar Fluids. *Int. J. Thermophys.*, 24(1), 41–109, 2003.