Evolution of Equations of State

A Physics-Driven Perspective

Graduate Lecture Notes

Advanced Chemical Engineering Thermodynamics

M.Sc. and Ph.D. programmes in Chemical, Mechanical,
Petroleum, Energy and Materials Engineering

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Every equation of state in this course was created because the previous one neglected a piece of physics that mattered. The sequence from the ideal gas law to modern molecular and electrolyte models is therefore not a catalogue of formulas but a single argument, in which each step identifies a specific physical omission and repairs it at a specific mathematical cost.

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Contents

How to use these notes

Scope and prerequisites

These notes accompany a graduate lecture module on equations of state (EOS) for students in chemical, mechanical, petroleum, energy and materials engineering. They assume a first course in classical thermodynamics: the first and second laws, Maxwell relations, the ideal gas law, and the equality of chemical potentials as the criterion for phase equilibrium. They do not assume prior exposure to statistical mechanics; the small amount required is developed where it is needed, in Chapter 5.

The organising argument

The material is deliberately not organised as a catalogue of equations. It is organised as a single argument with thirteen steps. Each step has the same internal structure, and every chapter answers the same six questions in the same order:

1. What engineering or scientific problem existed?
2. Why did the preceding equation of state fail to solve it?
3. What new piece of physics was introduced?
4. How was the mathematics modified to carry that physics?
5. What limitations remain after the modification?
6. What did those remaining limitations motivate next?

A student who can answer these six questions for each of the thirteen chapters understands the subject. A student who has memorised thirteen equations does not.

Typographic conventions

- **Key idea** boxes (navy) state the central result of a section in one or two sentences. They are the minimum that should be retained.
- **Physics introduced** boxes (amber) isolate the new physical content of each model. Amber is used consistently throughout the notes, the slides and the figures to mark the physics being added at that point in the argument.
- **Limitations** boxes (rust) state what the model still cannot do. These boxes motivate the following chapter and should be read as part of the narrative, not as caveats.
- **Student handout** boxes (grey) close each chapter with a summary, the key equations, a concept map, practice questions and recommended references.
- **Worked example** boxes (teal) contain fully solved calculations. All numerical values in these boxes were computed with the accompanying Python routines rather than read from charts, so intermediate digits are reproducible.

Notation

Symbol	Meaning	Symbol	Meaning
P	pressure	Z	compressibility factor PV/RT
T	absolute temperature	$T_\mathrm{r}, P_\mathrm{r}, V_\mathrm{r}$	reduced T/T_c, P/P_c, V/V_c
V	molar volume	ω	Pitzer acentric factor
ρ	molar density, $1/V$	a	attraction parameter
R	$8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$	b	co-volume parameter
f, φ	fugacity, fugacity coefficient	$\alpha(T)$	alpha function
μ	chemical potential	B_2, B_3	second, third virial coefficients
K_i	y_i/x_i, equilibrium ratio	$u(r)$	pair potential
A^res	residual Helmholtz energy	m, σ, ε	SAFT segment parameters

Two symbols collide in the classical literature. The dimensionless groups of the cubic equations, $A = aP/R^2T^2$ and $B = bP/RT$, share letters with the virial coefficients. In these notes the virial coefficients always carry a numerical subscript, B_2 and B_3, and the dimensionless cubic groups never do.

Computational companion

Every numerical result quoted in these notes, including all worked examples and every curve in every figure, was generated by the Python routines distributed with the package. Students are expected to reproduce and extend them. Reading an equation of state is not the same as being able to solve one, and the cubic root selection, the fugacity evaluation and the saturation solver are where most practical errors occur.

Chapter 1

Why do we need an equation of state?

1.1 Historical background

Classical thermodynamics, as assembled by Clausius, Kelvin and finally Gibbs between roughly 1850 and 1878, is a theory of *relations*. The first and second laws produce exact differential statements linking internal energy, enthalpy, entropy and the Gibbs energy, and the Maxwell relations convert derivatives of one property into derivatives of another. What the laws conspicuously do not provide is substance-specific information: they give $(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P$, but not V for carbon dioxide at 320 K and 80 bar. Gibbs made the structure explicit in *On the Equilibrium of Heterogeneous Substances* (1876–1878): all equilibrium behavior follows from a single fundamental relation, and supplying that relation is an experimental and molecular problem, not a thermodynamic one.

The volumetric part of the fundamental relation is the part that can be measured with a pressure gauge and a thermometer, and it acquired a name of its own. The empirical thread runs from Boyle in 1662, through Charles in the 1780s and Gay-Lussac in 1802, Avogadro's hypothesis of 1811, and their combination by Clapeyron in 1834. Regnault's mid-century precision measurements then established that real gases do not obey that formula, and Andrews' 1869 experiments on carbon dioxide showed that the deviation is not a small correction but the entire physics of condensation. Van der Waals' thesis of 1873 was the first successful attempt at a single algebraic relation covering both gas and liquid.

The industrial demand arrived later and was decisive. High-pressure ammonia synthesis, in commercial operation from 1913, ran at pressures of the order of 200 bar, where the ideal gas law is quantitatively useless; cryogenic air separation, gas processing and refining extended the requirement across the whole (P,T) plane. From the 1960s, computer-based process simulation turned the equation of state from a chart in a handbook into a subroutine executed millions of times per flowsheet convergence.

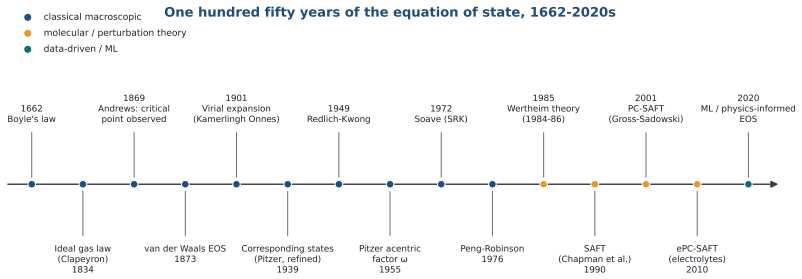

Figure 1.1: Chronology of the models developed in these notes, from Boyle's 1662 measurements to machine-learning equations of state. Navy marks the classical era, amber the molecular-theory era, teal the data-driven era.

1.2 Physical motivation: the closure problem

A process engineer can measure temperature, pressure and composition. What the engineer needs are quantities no instrument reports directly: molar density (line sizing and inventory), enthalpy (duty), entropy (compressor and turbine efficiency), and the fugacity of every component in every phase (phase equilibrium, and hence the existence of the separation at all). Thermodynamics converts the second set into the first, but only up to a missing function. Statistical mechanics of an isolated molecule, informed by spectroscopy, gives the ideal-gas heat capacity $C_P^{ig}(T)$ and hence $H^{ig}(T)$ to high accuracy, accounting for translation, rotation, vibration and electronic excitation of molecules that do not see one another. Everything that remains, the

entire energetic and entropic consequence of intermolecular forces, is contained in the difference between the real fluid and the ideal gas at the same T and P. That difference is a residual, or departure, property, and it is computable from the PVT relation alone.

Key idea: the equation of state as closure

Thermodynamics supplies exact relations among properties; spectroscopy supplies the ideal-gas contribution. Neither supplies the effect of intermolecular forces. An equation of state $P = P(T, V, \mathbf{x})$, equivalently $Z = Z(T, P, \mathbf{x})$, supplies exactly that, and from it every residual property, every fugacity coefficient and hence every phase-equilibrium calculation follows by differentiation and integration.

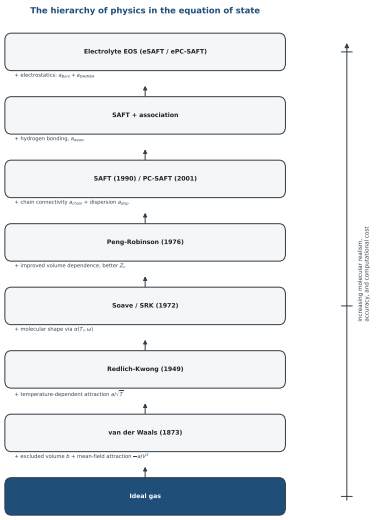

Figure 1.2: The hierarchy developed in these notes, read from the bottom upward. Each rung names the physics added and the equation of state that introduced it.

1.3 Mathematical development: the departure-function chain

Define the compressibility factor $Z = PV/RT$, with V the molar volume, and work at constant temperature and composition. For any fluid $\mathrm{d}G = V\,\mathrm{d}P$, and for the ideal gas at the same T and P, $\mathrm{d}G^{ig} = (RT/P)\,\mathrm{d}P$. Subtracting,

$$\mathrm{d}\left(G - G^{ig}\right)_T = \left(V - \frac{RT}{P}\right)\mathrm{d}P = RT\,(Z-1)\,\frac{\mathrm{d}P}{P}. \tag{1.1}$$

Real fluid and ideal gas share the same limit as $P \to 0$, so the residual Gibbs energy vanishes there and the integration constant is zero:

$$\frac{G^{\mathrm{res}}(T,P)}{RT} = \int_0^P (Z-1)\,\frac{\mathrm{d}P}{P}. \tag{1.2}$$

Since $G^{\mathrm{res}} = RT\ln\varphi$ defines the fugacity coefficient,

$$\ln\varphi = \int_0^P (Z-1)\,\frac{\mathrm{d}P}{P} \qquad (T \text{ constant}). \tag{1.3}$$

Equation (1.3) is the most consequential result of the chapter: the quantity governing whether a component prefers vapor or liquid is a pure functional of the PVT surface, and nothing else enters. Enthalpy follows by a Gibbs–Helmholtz step. Applying $H = -T^2[\partial(G/T)/\partial T]_P$ to both real fluid and ideal gas gives $H^{\mathrm{res}}/RT = -T[\partial(G^{\mathrm{res}}/RT)/\partial T]_P$, so differentiating Equation (1.2) under the integral sign,

$$H^{\mathrm{res}} = H - H^{ig} = -RT^2\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{\mathrm{d}P}{P}, \qquad S^{\mathrm{res}} = \frac{H^{\mathrm{res}} - G^{\mathrm{res}}}{T}. \tag{1.4}$$

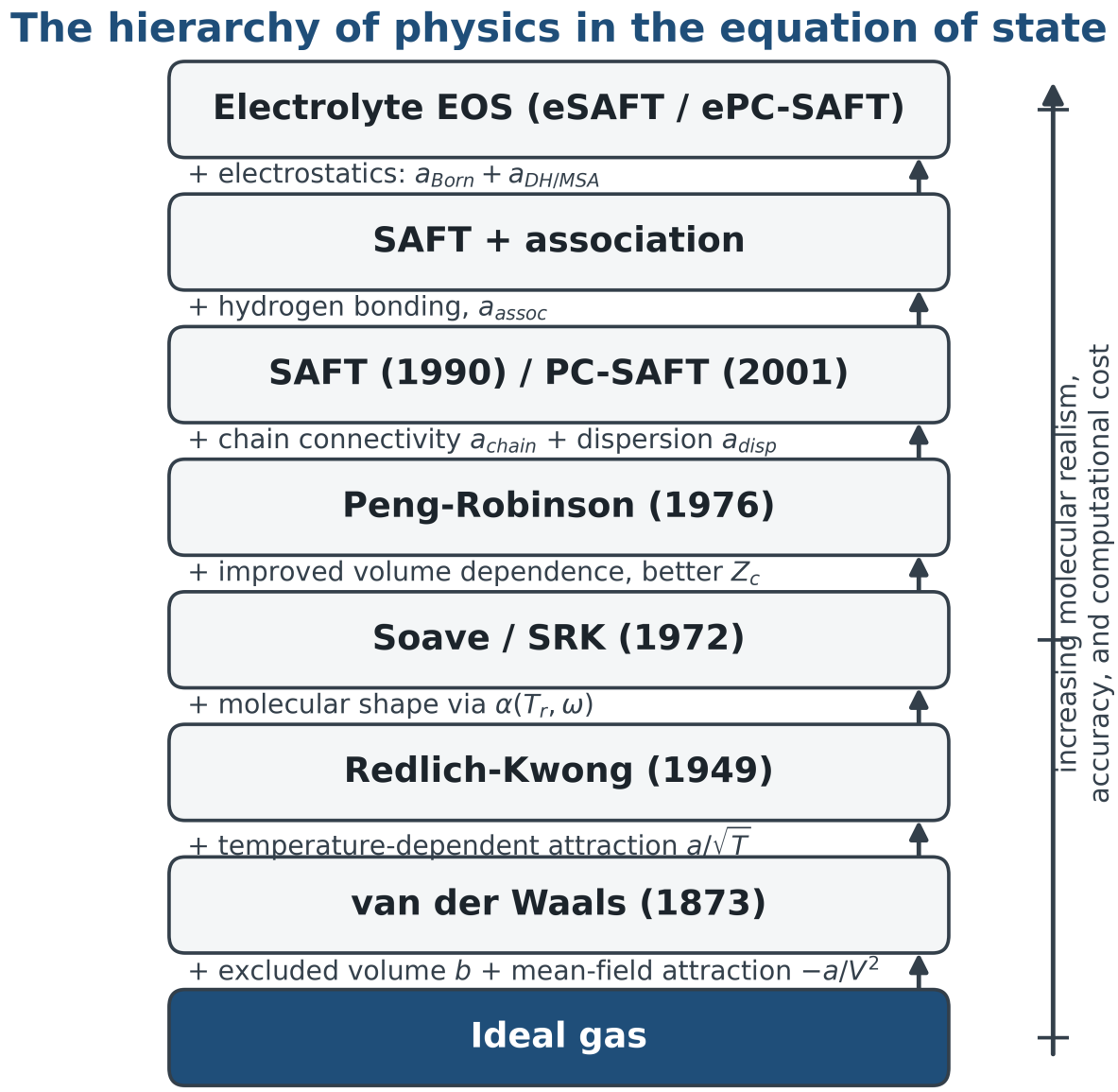

Figure 1.2 (enlarged). The hierarchy of physics contained in an equation of state.

Two approximations are involved, and only two. First, the lower limit is the zero-pressure ideal-gas state, so the isotherm must be known continuously from $P = 0$ upward; a model valid only in a narrow pressure band cannot deliver a departure function at all. Second, the derivative in Equation (1.4) is at constant pressure, so the model must be differentiable in temperature; an equation fitted to a single isotherm cannot deliver an enthalpy. For a mixture the same chain runs with partial molar quantities, giving $\hat{\varphi}_i$ and hence

$$K_i = \frac{y_i}{x_i} = \frac{\hat{\varphi}_i^{L}}{\hat{\varphi}_i^{V}}. \tag{1.5}$$

When one equation of state is used for both phases, vapor–liquid equilibrium becomes a consequence of the volumetric model rather than an independent model.

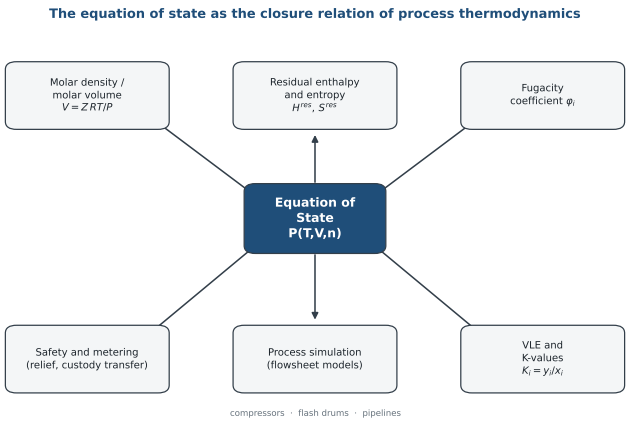

Figure 1.3: The equation of state as the central closure: measurable T, P and composition on one side; molar density, residual enthalpy and entropy, fugacity coefficients, K-values and the resulting process, safety and metering calculations on the other.

1.4 Engineering interpretation

In a steady-state simulator the equation of state is called more often than any other model: every unit operation evaluates it at least once per iteration, every flash twice per outer loop, every column on every stage of every inner loop. Errors therefore do not stay local. Take methane at 300 K and 100 bar, a routine gas-transmission condition. The Peng–Robinson equation gives $Z = 0.8339$, so the molar volume is $208.0\,\mathrm{cm^3\,mol^{-1}}$ against the ideal-gas value $249.4\,\mathrm{cm^3\,mol^{-1}}$. A vessel sized on the ideal gas law is oversized by 19.9 %, and the inventory in a fixed volume is underestimated by 16.6 %; in custody transfer that same figure is a direct financial error. The residual enthalpy at this state is $H - H^{ig} = -1.759\,\mathrm{kJ\,mol^{-1}}$, so for a modest $100\,\mathrm{kmol\,h^{-1}}$ stream, omitting it misplaces the compressor duty by 48.9 kW. In relief-valve sizing the discharge mass flux scales with the square root of the density at the relieving condition, so a density error enters the required orifice area directly.

Key idea: error propagation

Volumetric error propagates into compressor and turbine duty through H^{res}, into vessel and pipe sizing through ρ, into relief-valve area through the discharge mass flux, into custody metering through the volume correction factor, and into every separation specification through K_i. These are the places where an equation-of-state error becomes money or safety.

1.5 Limitations of the framework

Limitations

- The departure chain is exact but inherits every error of the PVT model, and amplifies some: H^{res} depends on $(\partial Z/\partial T)_P$, so a model with good densities and the wrong temperature slope gives poor enthalpies.
- The integrals require the isotherm from $P = 0$ upward, which excludes narrow-range correlations.
- No purely thermodynamic argument selects among candidate equations of state; the choice is physical, and is the subject of the remaining twelve chapters.
- An equation of state says nothing about transport properties, kinetics or interfacial phenomena.

1.6 Transition to Chapter 2

The framework is complete but empty until a specific $Z(T,P)$ is supplied. The simplest possible choice is $Z = 1$ everywhere, which asserts that molecules occupy no volume and exert no forces. Chapter 2 develops that model, establishes where it is accurate to 1 %, and identifies the two distinct ways it fails. The full sequence of repairs that follows is previewed in Figure 13.3.

Student handout: Chapter 1

Summary

- Thermodynamics gives exact relations but no substance-specific information; the equation of state is the closure that supplies it.
- Ideal-gas heat capacities cover isolated-molecule behavior; everything arising from intermolecular forces sits in the residual properties, functionals of the PVT surface alone.
- The chain runs $Z \to G^{\mathrm{res}} \to \varphi \to K_i$, and separately $Z \to H^{\mathrm{res}}, S^{\mathrm{res}}$, so phase equilibrium is a consequence of the volumetric model when one equation of state serves both phases.
- In a simulator the equation of state is the most frequently evaluated model; its errors reach duty, sizing, relief and metering. Residual enthalpy depends on $(\partial Z/\partial T)_P$ and is a more demanding test of a model than density.

Key equations

$$Z = \frac{PV}{RT}, \qquad \ln\varphi = \int_0^P (Z-1)\,\frac{\mathrm{d}P}{P} \tag{1.6}$$

$$H - H^{ig} = -RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{\mathrm{d}P}{P} \tag{1.7}$$

$$S^{\mathrm{res}} = \frac{H^{\mathrm{res}} - G^{\mathrm{res}}}{T}, \qquad K_i = \frac{\hat{\varphi}_i^{L}}{\hat{\varphi}_i^{V}} \tag{1.8}$$

Concept map

measurable $T, P, \mathbf{x}$ but unknown density and fugacity $\to$ a volumetric closure $Z(T,P,\mathbf{x}) \to$ departure integrals for G^{res}, H^{res}, S^{res}, $\varphi \to$ accuracy limited entirely by the PVT model chosen

Practice questions

1. State, without algebra, why residual enthalpy tests an equation of state more searchingly than residual Gibbs energy.
2. Show that Equation (1.3) requires $\varphi \to 1$ as $P \to 0$ for any model with a finite second virial coefficient.
3. Using the Peng–Robinson equation and the constants of §8 of the design specification, compute Z, φ and H^{res} for carbon dioxide at 320 K and 80 bar; compare $|H^{\mathrm{res}}|$ with the methane value in the text.
4. Compute the error in the inventory of a 500 m^3 vessel holding methane at 300 K and 100 bar if the ideal gas law is used.
5. Explain why an equation of state fitted only to a 300 K isotherm cannot give a compressor duty, even if it reproduces that isotherm exactly.

Recommended references

- J. M. Smith, H. C. Van Ness, M. M. Abbott and M. T. Swihart, *Introduction to Chemical Engineering Thermodynamics*, 9th ed., McGraw-Hill, 2022, Chapters 3 and 6.
- J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, 1999, Chapters 2 and 3.
- S. I. Sandler, *Chemical, Biochemical, and Engineering Thermodynamics*, 5th ed., Wiley, 2017, Chapter 6.

Chapter 2

The ideal gas law

2.1 Historical background

The ideal gas law was not discovered; it was assembled over some one hundred and seventy years from independent empirical regularities. Robert Boyle reported in 1662, in the second edition of *New Experiments Physico-Mechanicall, Touching the Spring of the Air*, that the volume of a fixed quantity of air at fixed temperature varies inversely with the applied pressure; Edme Mariotte published the same relation independently in 1679 and added the essential proviso that temperature be held constant. The thermal behavior came much later: Jacques Charles obtained results on the thermal expansion of gases in the 1780s but did not publish them, and Gay-Lussac published in 1802 the quantitative result that all sufficiently dilute gases expand by very nearly the same fractional amount per degree. Avogadro proposed in 1811 that equal volumes of gases at the same temperature and pressure contain equal numbers of particles, supplying the proportionality to amount of substance, and Clapeyron combined these strands in 1834 into a single statement equivalent to $PV = nRT$.

The molecular explanation developed more slowly. Daniel Bernoulli had argued in *Hydrodynamica* (1738) that gas pressure arises from the impacts of moving particles on the container wall, but the argument was not taken up. It was revived by Krönig in 1856 and placed on a proper footing by Clausius in 1857 and by Maxwell in 1860, whose velocity distribution converted the kinetic picture into a quantitative theory.

2.2 Physical motivation and the assumptions made

An ideal gas is defined by three statements about the molecules, and precision about each is worthwhile because Chapters 3 onward consist of removing them one at a time.

Physics assumed absent

1. **Point particles.** Molecules occupy no volume, so the volume available for translation is the full container volume.
2. **No interaction energy.** The pair potential $u(r)$ is zero at all separations, so the internal energy is purely kinetic and depends on temperature alone.
3. **Elastic collisions.** Collisions among molecules and with the wall conserve kinetic energy; none is stored in the collision.

Every subsequent equation of state in these notes is generated by relaxing assumption 1 (excluded volume), assumption 2 (attraction, dispersion, association, electrostatics), or both.

Assumptions 1 and 2 are not independent statements about geometry and about force; they are the two limits of a single pair potential. A real $u(r)$ has a steeply repulsive core at short separation, which makes a molecule occupy volume, and a weakly attractive tail at larger separation, which makes molecules cohere. Setting $u(r) \equiv 0$ discards both at once.

2.3 Mathematical development: the kinetic-theory route

Consider N identical molecules of mass m in a cubic container of side L and volume $V_{\mathrm{tot}} = L^3$, and take one molecule with velocity component v_x normal to a wall. Because the collision is elastic and the wall rigid, the molecule rebounds with $-v_x$ and transfers momentum $\Delta p_x = 2mv_x$; it must traverse the box and return before striking that wall again, a round trip of length $2L$, so $\Delta t = 2L/v_x$ and the time-averaged force

from this one molecule is

$$F_x = \frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}. \tag{2.1}$$

Replacing a train of impulses by a steady force is the first approximation: it is valid only as a time average over many collisions, and it requires free flight between impacts, which is assumption 2. Summing over all N molecules and dividing by the wall area L^2,

$$P = \frac{1}{L^2}\sum_{i=1}^{N}\frac{mv_{x,i}^2}{L} = \frac{Nm\langle v_x^2\rangle}{V_{\mathrm{tot}}}. \tag{2.2}$$

Isotropy requires $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle$, and since $\langle v^2\rangle$ is their sum, $\langle v_x^2\rangle = \langle v^2\rangle/3$. Hence

$$PV_{\mathrm{tot}} = \tfrac{1}{3}Nm\langle v^2\rangle = \tfrac{2}{3}N\langle \varepsilon_{\mathrm{tr}}\rangle, \qquad \langle \varepsilon_{\mathrm{tr}}\rangle = \tfrac{1}{2}m\langle v^2\rangle. \tag{2.3}$$

Equation (2.3) is mechanical; no thermodynamics has entered. Temperature enters at the next step, and that is the second approximation: the Maxwell–Boltzmann distribution, or equivalently equipartition over the three translational degrees of freedom, gives $\langle \varepsilon_{\mathrm{tr}}\rangle = \tfrac{3}{2}kT$. Substituting,

$$PV_{\mathrm{tot}} = NkT, \qquad \text{and per mole} \qquad PV = RT, \quad R = N_A k = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}. \tag{2.4}$$

Note what the derivation did *not* require: nothing was assumed about internal molecular structure. Rotation and vibration contribute to the heat capacity but not to the pressure, because they carry no net momentum to the wall, which is why the ideal gas law has the same form for argon and for octane while their heat capacities differ several-fold. In the notation of Chapter 1, Equation (2.4) is simply $Z = 1$ at every state.

Key idea

The ideal gas law states that the only mechanism producing pressure is the momentum flux of freely translating molecules. It contains no molecular parameter whatsoever, which is simultaneously its universality and its defect: a model with no adjustable molecular content cannot distinguish one substance from another.

2.4 Engineering interpretation: where it is accurate to one percent

The useful question is not whether the ideal gas law is exact but where its error falls below the tolerance of the calculation at hand. Taking 1 % in Z as the criterion and the Peng–Robinson equation as reference, the boundary is computed directly: for methane at 300 K, Z falls to 0.99 at 4.63 bar; for carbon dioxide the limit is 1.86 bar, and for propane only 0.62 bar. In reduced coordinates the pattern is systematic: for a simple fluid the pressure at which $|Z-1|$ reaches 1 % is $P_{\mathrm{r}} = 0.026$ at $T_{\mathrm{r}} = 1.0$, 0.043 at $T_{\mathrm{r}} = 1.2$, 0.085 at $T_{\mathrm{r}} = 1.5$ and 0.243 at $T_{\mathrm{r}} = 2.0$. The working rule is therefore that the ideal gas law is safe below roughly $P_{\mathrm{r}} = 0.05$ at ordinary reduced temperatures, the envelope widening rapidly only above $T_{\mathrm{r}} \approx 2$.

2.5 Limitations: the two distinct failure modes

Limitations

The ideal gas law fails in two ways that are physically different and must not be conflated.

- **High density.** As ρ rises, the volume occupied by the molecules ceases to be negligible and the attractive tail of $u(r)$ becomes significant. At 300 K and 100 bar methane has $Z = 0.8339$; at 600 bar, $Z = 1.221$, so the error changes sign as well as magnitude.
- **Proximity to saturation.** This occurs at modest *absolute* pressure and is not captured by any pressure criterion. Propane at 300 K saturates at only 9.99 bar, yet the saturated vapor there has $Z = 0.8149$, an error of 18.5 %; *n*-butane at 350 K saturates at 9.47 bar with $Z = 0.8078$. Ten bar is unremarkable; the proximity to condensation is not.
- **No liquid phase.** $Z = 1$ admits one volume root at every (T, P), so the model cannot represent condensa-

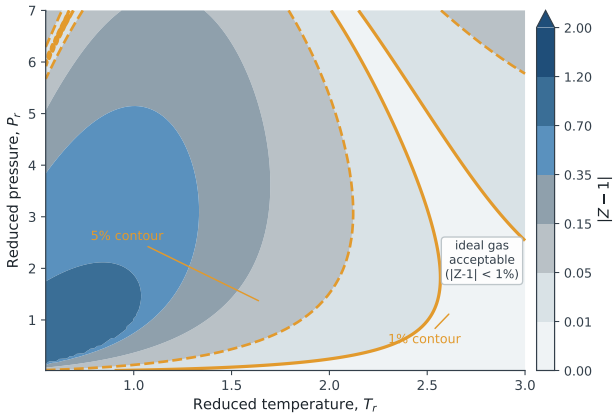

Figure 2.1: Contours of $|Z-1|$ in the reduced (T_r, P_r) plane for a simple fluid. The shaded region is where the ideal gas law meets the highlighted tolerance; the envelope narrows sharply near the saturation boundary.

tion, produce a saturation pressure, or support any vapor–liquid equilibrium calculation.

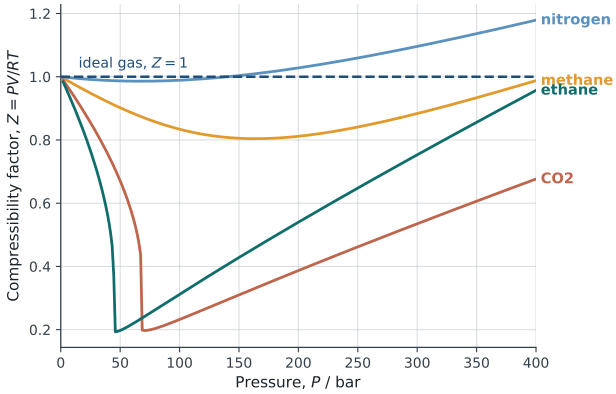

Figure 2.2: Compressibility factor against pressure at 300 K for methane, carbon dioxide, ethane and nitrogen, computed with the Peng–Robinson equation. The dashed horizontal line at $Z = 1$ is the ideal gas law.

2.6 Transition to Chapter 3

These failures are quantitative symptoms of the two qualitative omissions listed in the physics box. So: what physics is missing? The answer, given in 1873 and still the foundation of every cubic equation of state in industrial use, is twofold. Molecules occupy volume, so the space available for translation is smaller than the container, and molecules attract one another, so the pressure on the wall is smaller than the momentum flux alone would suggest. Chapter 3 turns both statements into algebra.

Student handout: Chapter 2

Summary

- Assembled from Boyle (1662), Charles and Gay-Lussac (1780s–1802), Avogadro (1811) and Clapeyron (1834); given a kinetic derivation by Clausius and Maxwell in 1857–1860. Its three assumptions are point particles, zero interaction energy and elastic collisions; the first two are the two limits of a single vanishing pair potential.
- The kinetic route gives $PV_{\mathrm{tot}} = \tfrac{2}{3} N \langle \varepsilon_{\mathrm{tr}} \rangle$ mechanically; temperature enters only when $\langle \varepsilon_{\mathrm{tr}} \rangle = \tfrac{3}{2} kT$ is imposed. The law contains no molecular parameter, so it cannot distinguish substances, and internal degrees of freedom do not affect the pressure.
- It is accurate to 1 % below roughly $P_r = 0.05$ at ordinary reduced temperatures, and fails separately at high density and near saturation; it admits no liquid root.

Key equations

$$P = \frac{Nm\langle v_x^2\rangle}{V_{\text{tot}}}, \qquad \langle v_x^2\rangle = \tfrac{1}{3}\langle v^2\rangle \tag{2.5}$$

$$PV_{\text{tot}} = \tfrac{2}{3}N\langle \varepsilon_{\text{tr}}\rangle = NkT \tag{2.6}$$

$$PV = RT, \qquad Z = \frac{PV}{RT} = 1, \qquad R = N_A k = 83.14\,\text{cm}^3\,\text{bar}\,\text{mol}^{-1}\,\text{K}^{-1} \tag{2.7}$$

Concept map

need a first closure for $Z \to$ molecules as non-interacting point masses, pressure from momentum flux $\to$ $PV = RT$, that is $Z = 1 \to$ no molecular parameters, no liquid root, failure at high ρ and near saturation

Practice questions

1. Explain why molecular rotation and vibration do not appear in the kinetic derivation of the pressure although they do appear in C_V.
2. Identify which step of the derivation fails first as density increases, and justify it.
3. Using the constants of §8 of the design specification, compute with the Peng–Robinson equation the pressure at which Z falls to 0.99 for ethane at 300 K, and compare with the methane value of 4.63 bar.
4. Carbon dioxide at 300 K and 50 bar has $Z = 0.6708$. Compute the error in the mass held in a 10 m^3 vessel if the ideal gas law is used, and comment on the safety implication.
5. Construct a state for propane below 15 bar at which the ideal gas error exceeds 15 %, and name the failure mode responsible.

Recommended references

- J. M. Smith, H. C. Van Ness, M. M. Abbott and M. T. Swihart, *Introduction to Chemical Engineering Thermodynamics*, 9th ed., McGraw-Hill, 2022, Chapter 3.
- J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, 1999, Chapter 4.
- B. E. Poling, J. M. Prausnitz and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, 2001, Chapter 4.

Chapter 3

The van der Waals equation of state

3.1 Historical background

The provocation was experimental. Thomas Andrews presented to the Royal Society in 1869 a study of carbon dioxide under pressure entitled *On the continuity of the gaseous and liquid states of matter*. Compressing carbon dioxide along a sequence of isotherms, he observed that below about 31 °C the fluid separated into two phases with a visible meniscus, while above that temperature no meniscus formed however great the pressure. He named the temperature at which the distinction disappears the critical point and drew the conclusion that gave his paper its title: the gaseous and liquid states are not two substances but two regions of one continuous surface.

In June 1873 Johannes Diderik van der Waals defended his doctoral thesis *Over de continuïteit van den gas- en vloeistoftoestand* at the University of Leiden. He took Andrews' conclusion literally and asked what modification of the ideal gas law would produce a single equation covering both phases. His answer introduced two molecular parameters, one for the volume the molecules occupy and one for the attraction between them, and produced the critical point as a mathematical consequence rather than as an input. Maxwell reviewed the thesis in *Nature* in 1874; van der Waals received the Nobel Prize in Physics in 1910.

3.2 Physical motivation

Both omissions identified in Chapter 2 follow from the shape of the pair potential $u(r)$, strongly repulsive at short range and weakly attractive at longer range. Van der Waals treated the two regions with different mathematics: the repulsive core geometrically, as a reduction in the volume available for translation, and the attractive tail energetically, as a uniform background field. This separation into a hard reference plus a perturbing attraction is the same decomposition that underlies modern perturbation theories such as SAFT in Chapter 11.

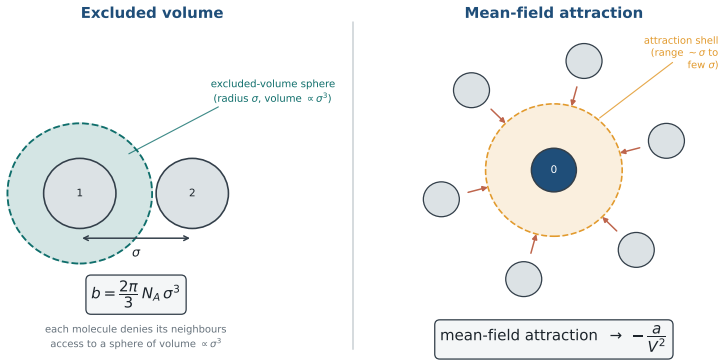

Figure 3.1: The two pieces of physics introduced by van der Waals. Left: the repulsive core excludes a sphere of radius σ around each molecule, giving $b = 2\pi N_A \sigma^3/3$. Right: the attractive tail acts as a mean field, giving a pressure reduction proportional to ρ^2.

3.3 Mathematical development

The co-volume from excluded volume

Model the repulsive core as a hard sphere of diameter σ: two molecules may not approach closer than a center-to-center separation σ. Fix one molecule and ask what region is forbidden to the center of a second.

It is the sphere of *radius* σ centered on the first, of volume $\frac{4}{3}\pi\sigma^3$. The radius is σ, not $\sigma/2$, because the constraint is on the distance between centers and both spheres have diameter σ; this is the commonest source of error in the derivation.

That volume is excluded by a *pair*, and assigning it in full to each participant would count it twice. Assigning half to each,

$$v_{\mathrm{excl}}^{\mathrm{molecule}} = \tfrac{1}{2}\cdot\tfrac{4}{3}\pi\sigma^3 = \tfrac{2}{3}\pi\sigma^3, \qquad \text{so} \qquad b = N_A\,\tfrac{2}{3}\pi\sigma^3 = \frac{2\pi N_A\sigma^3}{3}. \tag{3.1}$$

The volume accessible for translation is $V-b$ rather than V, and the repulsive contribution to the pressure is $RT/(V-b)$. The approximation introduced here is that excluded volumes of different pairs never overlap, which holds only in the dilute limit; b is thus a low-density result applied at all densities.

The attraction as a mean field

Now restore the attractive tail and let the local number density of neighbors be uniform and equal to the bulk value ρN_A everywhere outside the core. This is the mean-field approximation: positional correlations among neighbors are ignored and each molecule sees a smooth background. The potential energy of one molecule in that background is $\bar{u} = \rho N_A \int_\sigma^\infty u_{\mathrm{att}}(r)\,4\pi r^2\,\mathrm{d}r$, a negative quantity. Summing over the N_A molecules of a mole and dividing by two to avoid double counting pairs,

$$A_{\mathrm{att}} = \tfrac{1}{2}N_A\bar{u} = 2\pi N_A^2\rho\int_\sigma^\infty u_{\mathrm{att}}(r)\,r^2\,\mathrm{d}r \equiv -a\rho = -\frac{a}{V}, \qquad a \equiv -2\pi N_A^2\int_\sigma^\infty u_{\mathrm{att}}(r)\,r^2\,\mathrm{d}r > 0. \tag{3.2}$$

Pressure follows from $P = -(\partial A/\partial V)_T$, so $P_{\mathrm{att}} = -a/V^2 = -a\rho^2$. The quadratic density dependence is the signature of a pairwise interaction treated in mean field: the number of interacting pairs per unit volume is proportional to ρ^2. Adding the two contributions,

$$P = \frac{RT}{V-b} - \frac{a}{V^2}. \tag{3.3}$$

Physics introduced by van der Waals

Excluded volume: molecules are not points, so the accessible volume is $V-b$ and the pressure diverges as $V\to b$ rather than as $V\to 0$.
Mean-field attraction: molecules attract, so the measured pressure is lower than the momentum flux by $a\rho^2$. Together these give the first equation of state that predicts a liquid phase, a critical point and a saturation pressure without any of the three being supplied as input.

The critical point as a mathematical consequence

On a P–V diagram the critical point is where the flat two-phase segment shrinks to zero length, so the critical isotherm has a horizontal inflection: $(\partial P/\partial V)_{T_c} = (\partial^2 P/\partial V^2)_{T_c} = 0$. Differentiating Equation (3.3) twice,

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}, \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}. \tag{3.4}$$

Setting both to zero at (T_c, V_c) gives $RT_c/(V_c-b)^2 = 2a/V_c^3$ and $RT_c/(V_c-b)^3 = 3a/V_c^4$. Dividing the first by the second eliminates a, R and T_c simultaneously and yields $V_c - b = 2V_c/3$, hence $V_c = 3b$. Substituting back into the first condition, $RT_c/(2b)^2 = 2a/(27b^3)$, so

$$T_c = \frac{8a}{27Rb}, \qquad P_c = \frac{RT_c}{2b} - \frac{a}{9b^2} = \frac{4a}{27b^2} - \frac{3a}{27b^2} = \frac{a}{27b^2}. \tag{3.5}$$

These two relations invert. Forming $T_c/P_c = 8b/R$ gives b, and substituting back gives a:

$$a = \frac{27R^2T_c^2}{64P_c}, \qquad b = \frac{RT_c}{8P_c}, \qquad Z_c = \frac{P_cV_c}{RT_c} = \frac{a}{27b^2}\cdot 3b\cdot\frac{27b}{8a} = \frac{3}{8} = 0.375. \tag{3.6}$$

Key idea: parameters from critical constants

Equation (3.6) is the template followed by every cubic equation of state in these notes: two molecular parameters are fixed not by fitting density data but by forcing the model to reproduce the measured T_c and P_c. For carbon dioxide this gives $a = 0.3655\,\mathrm{Pa\,m^6\,mol^{-2}}$ and $b = 42.82\,\mathrm{cm^3\,mol^{-1}}$, which through Equation (3.1) corresponds to an effective molecular diameter $\sigma = 3.24\,\text{Å}$, a physically reasonable value.

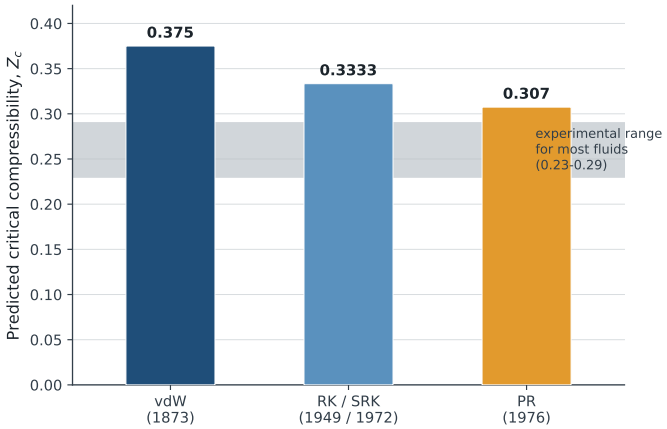

Figure 3.2: Critical compressibility factor predicted by the classical cubic equations against the band of measured values. The van der Waals value of 0.375 lies far outside the experimental range.

The subcritical loop and the Maxwell construction

Equation (3.3) is cubic in V, and below T_c it gives three real roots over a range of pressures, producing the loop of Figure 3.3. On the central branch $(\partial P/\partial V)_T > 0$, which violates mechanical stability: a region that expands when compressed cannot exist, because any density fluctuation grows without bound. The outer branches, extended beyond the saturation pressure, are metastable (superheated liquid and subcooled vapor). The physical isotherm replaces the loop by a horizontal tie line whose pressure follows from equality of chemical potentials. At constant T, $\mathrm{d}G = V\,\mathrm{d}P$, so equality of the molar Gibbs energy of the saturated phases requires $\int_L^V V\,\mathrm{d}P = 0$; integrating by parts along the isotherm,

$$0 = \big[PV\big]_L^V - \int_{V_L}^{V_V} P\,\mathrm{d}V \qquad \Longrightarrow \qquad \int_{V_L}^{V_V} P\,\mathrm{d}V = P^{\mathrm{sat}}\,(V_V - V_L)\,. \tag{3.7}$$

The tie line must therefore cut the loop so that the two enclosed areas are equal. This is Maxwell's equal-area construction; it is not an extra postulate but thermodynamic equilibrium expressed in the coordinates of the diagram.

3.4 Engineering interpretation

The van der Waals equation is no longer used for design, but three of its features survive in the equations that replaced it. The cubic form guarantees at most three real volume roots, the largest vapor and the smallest liquid, so one model returns both phases and root selection becomes a routine, automatable step. The parameters come from T_c and P_c, tabulated for tens of thousands of compounds, so the model is predictive for substances on which it was never fitted. And because a and b enter only through T_c and P_c, the equation obeys two-parameter corresponding states exactly, a prediction examined in Chapter 6.

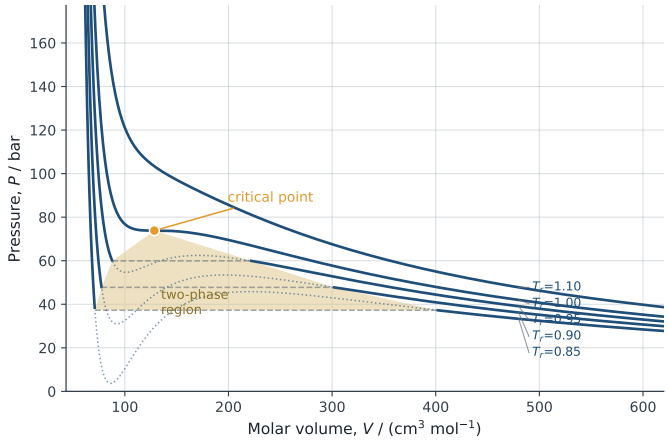

Figure 3.3: Van der Waals isotherms for carbon dioxide at several reduced temperatures, with the two-phase dome from the equal-area construction shaded and the critical point marked.

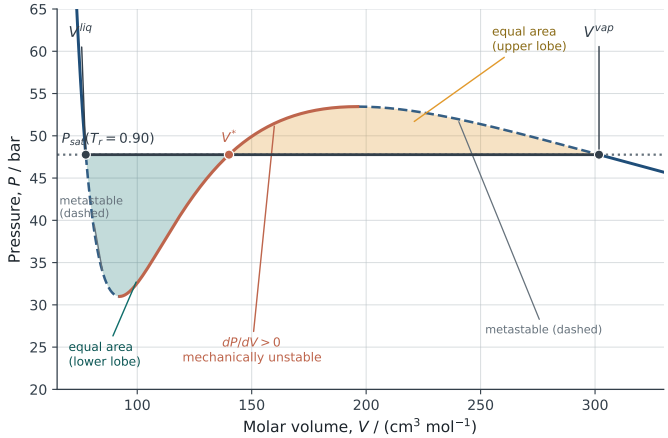

Figure 3.4: Enlargement of a subcritical loop. The mechanically unstable branch, where $(\partial P/\partial V)_T > 0$, is shown in rust; metastable extensions are dashed; the two shaded areas are equal at the saturation pressure.

3.5 Limitations

Limitations

- **The critical compressibility factor is wrong, and universally so.** Equation (3.6) gives $Z_c = 0.375$ for every substance, against measured values between about 0.23 and 0.29. This is the first quantitative indictment: the error is large, cannot be tuned away, and makes the predicted critical volume too large by roughly a third.
- **Liquid densities are poor** and **saturation pressures badly predicted.** Since $V_c = 3b$, the whole liquid branch is displaced. The equal-area construction applied to Equation (3.3) gives $P_r^{sat} = 0.647$ at $T_r = 0.9$ for every substance, against 0.479 for carbon dioxide and 0.498 for propane from the modern reference model. At $T_r = 0.7$ it gives $P_r^{sat} = 0.2005$, corresponding to an acentric factor of -0.302, whereas real simple fluids have $\omega \approx 0$.
- **The attraction parameter is temperature-independent**, so a single a cannot reproduce both the low- and the high-temperature behavior of the attractive term, and **mean field fails near the critical point**, where density fluctuations are long-ranged.

3.6 Transition to Chapter 4

Van der Waals introduced two adjustable parameters and immediately generated a falsifiable prediction, $Z_c = 3/8$, which experiment rejects. Before the model can be repaired, the deviation from ideality must

be described systematically rather than substance by substance. Chapter 4 introduces the compressibility factor as the bookkeeping device for exactly that, and shows that its behavior separates cleanly into attraction-dominated and repulsion-dominated regimes.

Student handout: Chapter 3

Summary

- Andrews' 1869 carbon dioxide experiments established the continuity of the gas and liquid states; van der Waals' 1873 Leiden thesis produced the first equation covering both.
- The repulsive core is treated geometrically as a co-volume $b = 2\pi N_A \sigma^3/3$; the factor of two arises because a pair excludes a sphere of radius σ and the exclusion is shared between the two molecules.
- The attractive tail is treated as a uniform mean field, giving a pressure reduction proportional to ρ^2, that is $-a/V^2$.
- Imposing a horizontal inflection at the critical point determines a and b from T_c and P_c alone and forces $Z_c = 3/8$.
- The subcritical loop contains a mechanically unstable branch; Maxwell's equal-area construction, which is equality of chemical potential in disguise, recovers the physical isotherm.
- $Z_c = 0.375$ against a measured range of 0.23 to 0.29 is the first quantitative failure; a temperature-independent a is the second.

Key equations

$$P = \frac{RT}{V-b} - \frac{a}{V^2}, \qquad b = \frac{2\pi N_A \sigma^3}{3} \tag{3.8}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \implies a = \frac{27R^2T_c^2}{64P_c}, \quad b = \frac{RT_c}{8P_c} \tag{3.9}$$

$$Z_c = \frac{3}{8} = 0.375, \qquad \int_{V_L}^{V_V} P\,\mathrm{d}V = P^{\mathrm{sat}}(V_V - V_L) \tag{3.10}$$

Concept map

ideal gas has no liquid and fails at high ρ $\rightarrow$ excluded volume plus mean-field attraction $\rightarrow$ $P = RT/(V-b) - a/V^2$, cubic in V with a critical point $\rightarrow$ $Z_c = 0.375$, poor liquid density, temperature-independent a

Practice questions

1. Explain why the excluded sphere has radius σ rather than $\sigma/2$, and why the result is then halved.
2. Show that the mean-field argument necessarily produces a ρ^2 dependence for any pairwise attraction, whatever the form of $u_{\mathrm{att}}(r)$.
3. Using the constants of §8 of the design specification, compute a and b for methane and for water, compare the implied molecular diameters from Equation (3.1), and comment on whether the comparison is physically sensible for a hydrogen-bonding fluid.
4. Derive $Z_c = 3/8$ from Equation (3.3) without consulting the text, and state which experimental quantity the result contradicts.
5. Verify by numerical integration that the equal-area construction applied to the van der Waals equation for carbon dioxide at $T_r = 0.9$ gives $P_r^{\mathrm{sat}} = 0.647$, and explain why this value is independent of the substance.

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Chapter 4

The compressibility factor

4.1 Historical background

By the middle of the nineteenth century it was clear that real gases deviate from $PV = nRT$, but there was no agreed way of reporting the deviation. Henri Victor Regnault's precision measurements, made in Paris from the 1840s, established the deviations quantitatively at moderate pressure. Emile Amagat then extended the measurements to very high pressure during the 1870s and 1880s, reaching of the order of three thousand atmospheres, and plotted his results as PV against P along isotherms. The resulting curves, still known as Amagat curves, revealed what no low-pressure experiment could show: along many isotherms PV first falls with increasing pressure, passes through a minimum, and then rises without limit. A single fluid can therefore be both more and less compressible than an ideal gas.

Kamerlingh Onnes, working at Leiden from 1901, formalized the description by writing the deviation as a power series (Chapter 5) and by making systematic use of reduced coordinates. The ratio $Z = PV/RT$ acquired its modern name and role in the engineering literature of the following decades, and generalized charts of Z against reduced pressure, of which the set published by Nelson and Obert in the 1950s is the most widely reproduced, became a standard design tool in the era before computers.

4.2 Physical motivation

The compressibility factor is defined as

$$Z = \frac{PV}{RT} = \left.\frac{V}{V^{ig}}\right|_{T,P}, \tag{4.1}$$

the ratio of the actual molar volume to the volume the same material would occupy as an ideal gas at the same T and P. It introduces no physics and makes no assumption. Its value is that it converts every equation of state into a single dimensionless surface that can be compared, plotted and integrated, and Chapter 1 showed that all residual properties are integrals over that surface. The interpretation of its magnitude follows from the two competing mechanisms of Chapter 3: attraction pulls molecules toward one another, reducing the momentum delivered to the wall and hence the pressure at fixed volume, while repulsion, through the excluded volume, does the opposite.

Physics made explicit by Z

$Z < 1$: the attractive part of the pair potential dominates; the fluid is more compressible than an ideal gas and its molar volume is smaller than RT/P.
$Z > 1$: the repulsive core dominates; the fluid is less compressible than an ideal gas and its molar volume is larger than RT/P.
$Z = 1$: the two contributions cancel exactly. This is a balance, not an absence of intermolecular forces, and it is the essential point of the chapter.

The last statement deserves emphasis. A fluid with $Z = 1$ is not behaving ideally in any molecular sense; its molecules attract and repel vigorously and the two effects merely cancel in their contribution to the pressure. Every other residual property may be far from zero there.

4.3 Mathematical development

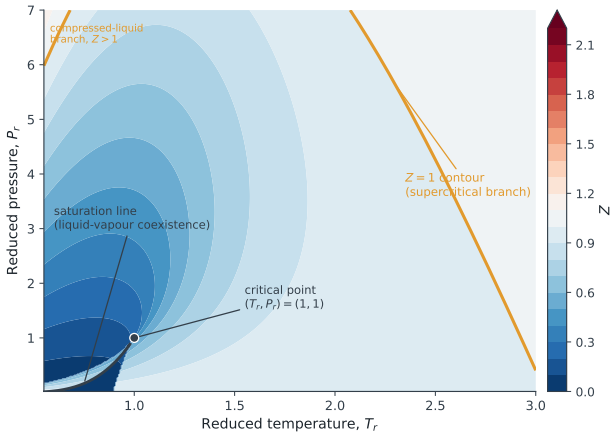

Figure 4.1: The compressibility surface in the reduced $(T_\mathrm{r}, P_\mathrm{r})$ plane. The highlighted contour is $Z = 1$, where attraction and repulsion cancel; the saturation line is also shown.

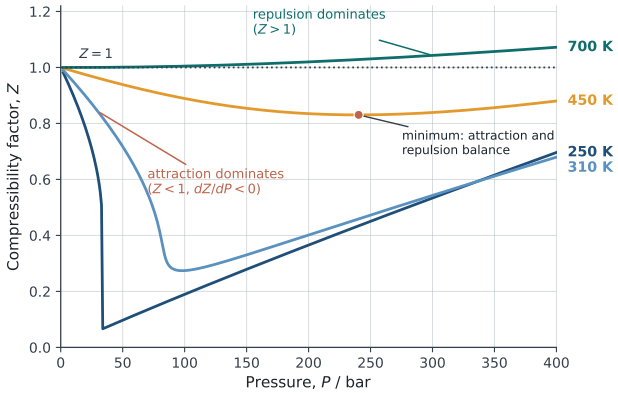

Figure 4.2: Compressibility factor of carbon dioxide against pressure along several isotherms. The initial negative slope and the minimum mark the attraction-dominated region; the crossover to $Z > 1$ marks the repulsion-dominated region.

The initial slope and the Boyle temperature

Expand any equation of state about the zero-density limit, $Z(T,\rho) = 1 + B_2(T)\rho + O(\rho^2)$ with $\rho = 1/V$. The coefficient of ρ is the second virial coefficient of Chapter 5, and its sign determines whether the isotherm leaves $Z = 1$ from above or below. Taking the van der Waals equation, dividing Equation (3.3) by RT/V and expanding $(1 - b\rho)^{-1} = 1 + b\rho + b^2\rho^2 + \dots$ for $b\rho \ll 1$,

$$Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT} = 1 + \left(b - \frac{a}{RT}\right)\rho + b^2\rho^2 + \dots \qquad \Longrightarrow \qquad B_2(T) = b - \frac{a}{RT}. \tag{4.2}$$

The structure of Equation (4.2) is the whole story in one line. The repulsive contribution b is positive and temperature-independent; the attractive contribution $-a/RT$ is negative and decays as temperature rises, because faster molecules spend less time within range of the attractive well. At low temperature attraction wins and $B_2 < 0$; at high temperature repulsion wins and $B_2 > 0$. The temperature at which they balance, so that $B_2 = 0$ and the isotherm departs from $Z = 1$ with zero initial slope, is the Boyle temperature T_B. For the van der Waals equation,

$$b = \frac{a}{RT_B} \qquad \Longrightarrow \qquad T_B = \frac{a}{bR} = \frac{27T_\mathrm{c}}{8} = 3.375\,T_\mathrm{c}. \tag{4.3}$$

The prediction that T_B/T_c is universal is again a consequence of two-parameter corresponding states, and real fluids do not obey it: with the Peng–Robinson equation as reference, $T_B/T_\mathrm{c} = 2.99$ for methane, 2.87 for nitrogen, 2.49 for propane and 2.33 for carbon dioxide, that is $T_B = 570$, 363, 922 and 708 K. Below T_B the isotherm dips; above it, it rises immediately from the origin.

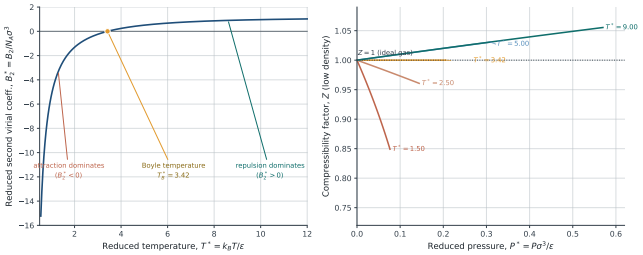

Figure 4.3: Second virial coefficient of a Lennard-Jones fluid against reduced temperature with the Boyle temperature marked, and the accompanying change in sign of the initial slope of Z against P.

The minimum in Z along an isotherm

For $T < T_B$ the two terms of Equation (4.2) act in opposite directions and their relative importance shifts with density. The attractive term is linear in ρ; the repulsive term contains all higher powers. Attraction therefore dominates at low density and repulsion must eventually dominate at high density, so the isotherm has a minimum between. Setting $(\partial Z/\partial \rho)_T = 0$ in the truncated expansion,

$$\rho_{\min} \simeq \frac{1}{2b^2}\left(\frac{a}{RT} - b\right), \tag{4.4}$$

which is positive precisely when $T < T_B$ and moves to higher density as T rises toward T_B, where the minimum disappears.

Computed with the Peng–Robinson equation, methane at 300 K has $Z_{\min} = 0.804$ at 163.9 bar ($P_r = 3.56$) and recovers to $Z = 1.221$ by 600 bar. Nitrogen at the same temperature, much closer to its Boyle temperature, has a shallow minimum of 0.986 at 67.2 bar, while carbon dioxide at 320 K, far below its Boyle temperature, has a deep minimum of 0.343 at 122.1 bar.

Key idea: Z as a bookkeeping device

Z does not model anything. It records, in one dimensionless number, the net balance of attraction and repulsion at a given state, and through the departure integrals of Chapter 1 it carries that record into every thermodynamic property. Its initial slope is the second virial coefficient, its sign change with temperature defines the Boyle temperature, and its minimum along an isotherm marks the density at which repulsion overtakes attraction.

4.4 Engineering interpretation: the generalized chart

If the equation of state contains only T_c and P_c as substance-specific inputs, as the van der Waals equation does, then Z as a function of T_r and P_r is the *same function for every substance*. That is the principle of corresponding states, and its engineering artefact is the generalized compressibility chart: one set of curves of Z against P_r at constant T_r, from which the density of any fluid can be read once its critical constants are known.

Computed with a modern reference model at zero acentric factor, the chart gives $Z = 0.954$, 0.882, 0.759 and 0.550 at $T_r = 1.2$ for $P_r = 0.2$, 0.5, 1.0 and 2.0; along $T_r = 2.0$ the same pressures give 0.992, 0.980, 0.964 and 0.940. The deviation is an order of magnitude smaller on the higher isotherm, which is the quantitative form of the statement that gases become more nearly ideal away from their critical temperature. Before computers the chart was the calculation; today it survives as a sanity check, since an engineer who obtains $Z = 0.62$ at $T_r = 1.8$ and $P_r = 0.4$ has almost certainly made an input error. The basis of the collapse, and the reason it fails for polar and elongated molecules, is developed in Chapter 6.

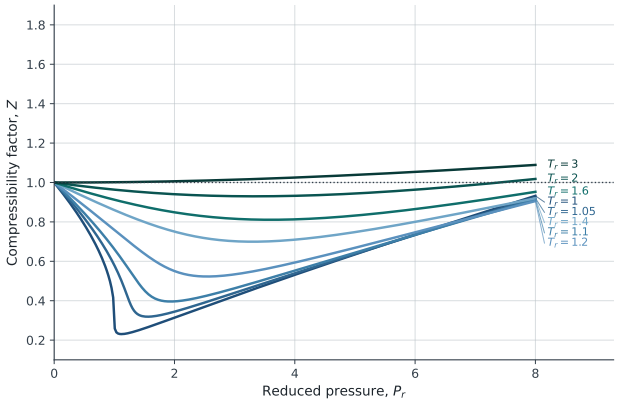

Figure 4.4: Generalized compressibility chart: Z against reduced pressure along reduced isotherms, computed at zero acentric factor so that the curves depend on T_r and P_r alone.

4.5 Limitations

Limitations

- Z is a description, not a model: it reports the deviation but does not predict it, so an equation of state must still be supplied.
- The contour $Z = 1$ is not the ideal-gas locus in any molecular sense: along it H^{res}, S^{res} and $\ln\varphi$ are all non-zero, so treating such a state as ideal is a serious error in any energy balance.
- A single value of Z says nothing about $(\partial Z/\partial T)_P$ and therefore nothing about residual enthalpy; two models can agree on density and disagree substantially on duty.
- The generalized chart rests on two-parameter corresponding states. Strongly polar, elongated or hydrogen-bonding fluids do not collapse onto it, and the departure is systematic rather than random. Reading such a chart to three figures is in any case not possible.

4.6 Transition to Chapter 5

Equation (4.2) was obtained by expanding a particular empirical equation of state, so its coefficients inherit whatever is wrong with that equation. The density expansion of Z can instead be constructed from first principles, with coefficients that are exact functions of the intermolecular potential. Chapter 5 develops the virial equation of state, in which $B_2(T)$ is given exactly by an integral over the pair potential, and examines the price paid for that rigor.

Student handout: Chapter 4

Summary

- $Z = PV/RT$ is the ratio of the actual molar volume to the ideal-gas volume at the same T and P; it introduces no physics and makes no approximation.
- $Z < 1$ indicates attraction-dominated behavior, $Z > 1$ repulsion-dominated behavior, and $Z = 1$ an exact cancellation of the two, not their absence. The initial slope of Z against density is the second virial coefficient; for van der Waals, $B_2 = b - a/RT$.
- The Boyle temperature is where $B_2 = 0$; van der Waals predicts the universal value $T_B = 3.375\,T_\mathrm{c}$, while real fluids give ratios between roughly 2.3 and 3.0.
- Below T_B every isotherm has a minimum in Z, marking the density at which repulsion overtakes attraction; the minimum deepens as temperature falls. The generalized chart embodies two-parameter corresponding states and is useful today mainly as a check on computed results.

Key equations

$$Z = \frac{PV}{RT} = \left.\frac{V}{V^{ig}}\right|_{T,P}, \qquad Z = 1 + B_2(T)\rho + O(\rho^2) \tag{4.5}$$

$$B_2^{\mathrm{vdW}}(T) = b - \frac{a}{RT}, \qquad B_2(T_B) = 0 \implies T_B^{\mathrm{vdW}} = \frac{a}{bR} = \frac{27T_{\mathrm{c}}}{8} \tag{4.6}$$

$$Z = Z(T_{\mathrm{r}}, P_{\mathrm{r}}) \quad \text{(two-parameter corresponding states)} \tag{4.7}$$

Concept map

deviations from ideality reported inconsistently, substance by substance → one dimensionless ratio recording the attraction/repulsion balance → $Z(T_{\mathrm{r}}, P_{\mathrm{r}})$ with its initial slope B_2, its Boyle temperature and its minimum → Z describes but does not predict, and the universal chart fails for polar and elongated molecules

Practice questions

1. A fluid has $Z = 1.000$ at a particular state. Is its residual enthalpy zero? Justify the answer using Equation (1.4).
2. Derive Equation (4.2) from the van der Waals equation, stating the condition under which the geometric expansion is valid.
3. Using §8 of the design specification, compute the van der Waals Boyle temperature of nitrogen and of carbon dioxide from Equation (4.3) and compare with the Peng–Robinson values of 363 K and 708 K.
4. Compute Z for methane at 300 K and at 100, 200, 400 and 600 bar with the Peng–Robinson equation, locate the minimum, and compare with 0.804 at 163.9 bar.
5. Explain why nitrogen at 300 K has a much shallower minimum in Z than carbon dioxide at 320 K, referring to the Boyle temperatures.

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Chapter 5

The virial equation of state

5.1 Historical background

Heike Kamerlingh Onnes, director of the cryogenic laboratory at Leiden, proposed in 1901 that the deviation of a real gas from ideality be represented not by a closed algebraic form but by a power series in density, $Z = 1 + B/V + C/V^2 + \dots$. He named the coefficients *virial coefficients*, borrowing the word from Clausius, who had introduced the virial theorem of mechanics in 1870. The proposal was at first purely empirical: a flexible way of correlating the high-precision isotherms the Leiden laboratory was producing, with no claim about where the coefficients came from.

Its status changed with the cluster expansion in statistical mechanics. Ursell in 1927 and, decisively, Joseph Mayer in 1937 showed that the configuration integral of a classical fluid can be expanded systematically in powers of density, and that the resulting coefficients are integrals over the intermolecular potential of successively larger clusters of molecules. The second virial coefficient became an exact two-body integral, the third an exact three-body integral, and so on. The virial equation is therefore unique among the equations of state in this course: it is not a model of a fluid but a theorem about one.

5.2 Physical motivation

Chapter 4 obtained $B_2 = b - a/RT$ by expanding the van der Waals equation, so that result inherits both the assumption that excluded volumes never overlap and the assumption that attraction acts as a uniform mean field. The virial route reverses the logic: instead of writing down a plausible equation and expanding it, one expands the exact partition function in density and asks what each order requires. The first correction to ideality then involves exactly two molecules at a time, the second exactly three, and so on. Nothing is assumed about the shape of the potential and nothing is averaged.

5.3 Mathematical development

The two expansions and the relation between them

The density (Leiden) form and the pressure form are

$$Z = 1 + B_2(T)\rho + B_3(T)\rho^2 + \dots \quad (\rho = 1/V), \qquad Z = 1 + B'(T)P + C'(T)P^2 + \dots \tag{5.1}$$

They are not independent. Substituting $\rho = P/(ZRT)$ into the first and using $Z^{-1} = 1 - B'P + O(P^2)$ from the second,

$$Z = 1 + \frac{B_2}{RT}P\left(1 - B'P\right) + \frac{B_3}{(RT)^2}P^2 + O(P^3). \tag{5.2}$$

Matching powers of P gives at first order $B' = B_2/RT$, and at second order, after substituting that result, $C' = (B_3 - B_2^2)/(RT)^2$. The simple proportionality therefore holds only for the leading coefficient; confusing B' with B_2 beyond first order is a common error, and the two have different units.

The second virial coefficient from the pair potential

The statistical-mechanical result, obtained from the Mayer cluster expansion of the configuration integral for a classical fluid of spherically symmetric molecules, is

$$B_2(T) = -2\pi N_A \int_0^\infty \left[\mathrm{e}^{-u(r)/kT} - 1\right] r^2 \,\mathrm{d}r. \tag{5.3}$$

The bracket is the Mayer f-function, $f(r) = \mathrm{e}^{-u(r)/kT} - 1$, and its behavior is the whole content of the result. Where $u(r) \gg kT$, inside the repulsive core, $\mathrm{e}^{-u/kT} \to 0$ and $f \to -1$; the integrand is then $-r^2$, and because of the leading minus sign this region contributes *positively* to B_2. Where $u(r) < 0$, in the attractive well, $\mathrm{e}^{-u/kT} > 1$ and $f > 0$, so this region contributes *negatively*. Where $u(r) \approx 0$ at large separation, $f \to 0$ and there is no contribution; the integral converges provided $u(r)$ decays faster than r^{-3}, which dispersion forces (r^{-6}) satisfy and unscreened Coulomb interactions do not. That last point is why Chapter 12 requires a different treatment for electrolytes. The f-function is thus a switch that turns on only where molecules are close enough to influence one another, which is why the two-body integral is finite even when the integral of u itself is not.

Physics introduced: an exact bridge to the intermolecular potential

Equation (5.3) is not a correlation. It states that the first correction to the ideal gas law is determined completely and exactly by the interaction of two isolated molecules. For the first time in this course a macroscopic thermodynamic quantity is expressed as an integral over a microscopic potential, with no adjustable parameter and no averaging approximation. Every later molecular equation of state, including SAFT in Chapter 11, rests on the same bridge.

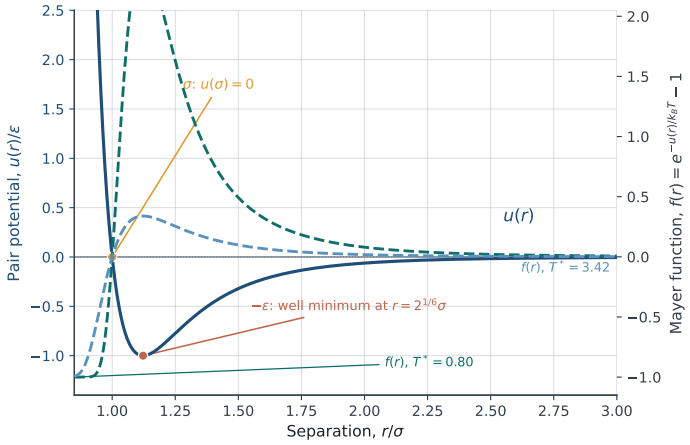

Figure 5.1: The Lennard-Jones pair potential and the corresponding Mayer function at two temperatures, with σ and ε marked. The f-function is -1 inside the core, positive in the attractive well, and zero at large separation.

Two limiting checks

First, take hard spheres of diameter σ: $u = \infty$ for $r < \sigma$ and zero otherwise, so $f = -1$ on $[0, \sigma]$ and zero beyond, giving

$$B_2 = -2\pi N_A \int_0^{\sigma} (-1)\, r^2 \, \mathrm{d}r = \frac{2\pi N_A \sigma^3}{3} = b. \tag{5.4}$$

The exact theory reproduces the van der Waals co-volume of Equation (3.1) exactly, confirming that the excluded-volume argument of Chapter 3 was correct at leading order in density.

Second, add a weak attractive tail with $|u| \ll kT$ for $r > \sigma$, so that $\mathrm{e}^{-u/kT} - 1 \approx -u/kT$. The tail then contributes

$$-2\pi N_A \int_{\sigma}^{\infty} \left(-\frac{u(r)}{kT}\right) r^2 \, \mathrm{d}r = \frac{2\pi N_A}{kT} \int_{\sigma}^{\infty} u(r)\, r^2 \, \mathrm{d}r = -\frac{a}{RT}, \tag{5.5}$$

with a exactly as defined in Equation (3.2), since $R = N_A k$. Hence $B_2 \to b - a/RT$: the van der Waals form is recovered as the high-temperature limit of the exact expression, and its two parameters acquire rigorous meanings.

The Lennard-Jones case and the Boyle temperature

For a realistic potential the integral must be evaluated numerically. Taking the Lennard-Jones form $u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$, Equation (5.3) depends on temperature only through $T^{*} = kT/\varepsilon$ and on σ only through the scale $b_0 = 2\pi N_A \sigma^3/3$. Writing $B_2^{*} = B_2/b_0$, numerical integration gives $B_2^{*} = -2.538$ at $T^{*} = 1$, -0.628 at $T^{*} = 2$, -0.115 at $T^{*} = 3$ and $+0.115$ at $T^{*} = 4$. The sign change, the Boyle temperature of the Lennard-Jones fluid, occurs at

$$T_B^{*} = \frac{kT_B}{\varepsilon} = 3.418 \approx 3.42. \tag{5.6}$$

This single number is why the Boyle temperature is a genuinely molecular quantity: it fixes the ratio of thermal energy to well depth at which attraction and repulsion exactly cancel, and it is the same for every fluid whose pair potential has the Lennard-Jones shape. At higher temperature B_2^{*} passes through a shallow maximum of about 0.53 near $T^{*} = 25$ and then declines slowly, because the repulsive core is soft and its effective diameter shrinks as molecules collide harder.

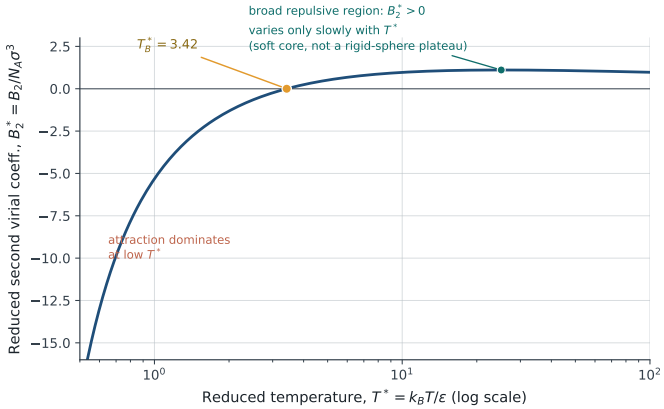

Figure 5.2: Second virial coefficient of the Lennard-Jones fluid in reduced form, obtained by numerical integration of Equation (5.3), showing the steep negative low-temperature branch and the flat repulsive plateau at high temperature.

5.4 Engineering interpretation

Truncated after the second term, the pressure series becomes $Z = 1 + B_2 P/RT$, an explicit and trivially invertible expression that is the standard tool for vapor-phase corrections at moderate pressure: gas metering, vapor-phase fugacity coefficients in low-pressure vapor–liquid equilibrium, and Poynting-corrected activity coefficient models. For mixtures the composition dependence is exact and quadratic, $B_{2,\mathrm{mix}} = \sum_i \sum_j y_i y_j B_{2,ij}$, a far stronger statement than any empirical mixing rule. The practical question is where truncation is acceptable. For methane at 300 K, using a modern cubic equation as reference, $B_2 = -54.26\,\mathrm{cm^3\,mol^{-1}}$ and $B' = -2.18 \times 10^{-3}\,\mathrm{bar^{-1}}$, and comparison against the reference isotherm gives:

ρ/ρ_c	reference Z	two-term error	three-term error
0.10	0.9531	−0.45 %	+0.02 %
0.25	0.8971	−2.80 %	+0.33 %
0.50	0.8355	−10.97 %	+2.50 %
0.75	0.8071	−23.70 %	+7.68 %
1.00	0.8082	−39.65 %	+16.07 %

The two-term truncation holds to a few percent only up to about a quarter of the critical density; the three-term truncation extends that to roughly half. Beyond half the critical density the neglected terms are no longer corrections.

Key idea: exactness and uselessness are the same property

The virial equation is the only equation of state in this course that is exact in principle: each coefficient is a defined integral over the potential, and the series is derived rather than postulated. It is precisely for that reason that it is useless in the liquid phase. A liquid is a state in which every molecule interacts simultaneously with a dozen neighbors, so the physically relevant terms are of order B_{12}; an expansion ordered by the number of interacting bodies is the worst possible ordering for a dense phase. Approximate equations of state succeed in the liquid because they resum, rather than truncate, that infinite series.

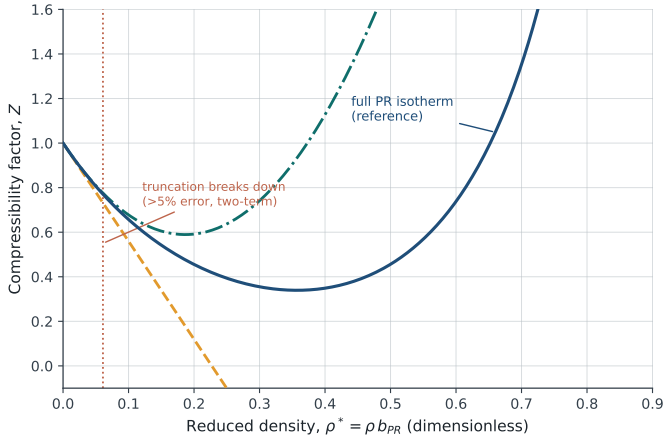

Figure 5.3: Compressibility factor against reduced density for the two-term and three-term virial truncations compared with a reference isotherm, showing where truncation ceases to be a correction.

5.5 Limitations

Limitations

- **Restricted to roughly half the critical density.** The three-term truncation errs by 2.5 % at $\rho = 0.5\rho_c$ and by 16 % at ρ_c; the two-term form is limited to about a quarter of the critical density.
- **No liquid root and no phase transition.** Any finite truncation is a polynomial in ρ and is analytic everywhere, so it cannot reproduce the non-analytic behavior at a first-order transition, and the series itself has a finite radius of convergence that does not reach liquid densities.
- **The higher coefficients are intractable.** B_3 requires a three-body configuration integral and, for real molecules, genuine three-body forces; B_4 and beyond are computed only for the simplest model potentials. Exactness in principle is not availability in practice.
- **A pair potential must be known.** For non-spherical, polar or hydrogen-bonding molecules $u(r)$ depends on orientation and Equation (5.3) acquires an angular average that is itself a modeling problem. The integral also fails to converge for unscreened Coulomb interactions, so the virial route cannot be applied directly to electrolytes.

5.6 Transition to Chapter 6

Two routes have now been exhausted. Van der Waals produced an equation valid over the whole density range but quantitatively wrong, most conspicuously in Z_c; the virial expansion produced coefficients that are exact but that cannot be carried to liquid densities. What both share, and what Chapter 4 exhibited in the generalized chart, is the observation that in reduced coordinates the behavior of different fluids very nearly coincides. Chapter 6 examines that observation, establishes the molecular assumptions required for it to hold exactly, and identifies the classes of molecule for which it demonstrably fails.

Student handout: Chapter 5

Summary

- Kamerlingh Onnes proposed the virial expansion empirically in 1901; the cluster expansion of Ursell (1927) and Mayer (1937) made its coefficients exact integrals over the intermolecular potential.
- The density and pressure series are related by $B' = B_2/RT$ at leading order but not term by term thereafter: $C' = (B_3 - B_2^2)/(RT)^2$.
- $B_2(T)$ is an exact two-body integral of the Mayer function; the repulsive core contributes positively and the attractive well negatively.
- The hard-sphere limit returns $B_2 = 2\pi N_A \sigma^3/3 = b$ exactly and the high-temperature limit returns $b - a/RT$, so the van der Waals parameters acquire rigorous definitions.
- For the Lennard-Jones fluid the Boyle temperature is $T_B^* = 3.42$, a universal number for that potential shape.
- The equation is exact in principle and therefore useless in the liquid phase: an expansion ordered by the number of interacting bodies converges poorly where every molecule interacts with many neighbors.

Key equations

$$Z = 1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots = 1 + B'P + C'P^2 + \dots \tag{5.7}$$

$$B' = \frac{B_2}{RT}, \qquad C' = \frac{B_3 - B_2^2}{(RT)^2} \tag{5.8}$$

$$B_2(T) = -2\pi N_A \int_0^\infty \left[\mathrm{e}^{-u(r)/kT} - 1 \right] r^2 \,\mathrm{d}r, \qquad B_2^{\mathrm{HS}} = \frac{2\pi N_A \sigma^3}{3} = b \tag{5.9}$$

$$B_{2,\mathrm{mix}} = \sum_i \sum_j y_i y_j B_{2,ij} \tag{5.10}$$

Concept map

empirical equations give coefficients of unknown validity $\rightarrow$ an exact density expansion of the partition function, ordered by the number of interacting molecules $\rightarrow Z = 1 + B_2\rho + B_3\rho^2 + \dots$ with B_2 an exact integral over $u(r)$
$\rightarrow$ truncation limits the equation to about half the critical density and forbids a liquid phase

Practice questions

1. Explain, in terms of the Mayer function, why the repulsive core contributes a positive term to B_2 despite the leading minus sign in Equation (5.3).
2. Derive $C' = (B_3 - B_2^2)/(RT)^2$ from Equation (5.1), showing every substitution.
3. Using the constants of §8 of the design specification and a cubic equation of state as reference, compute B_2 for carbon dioxide and for propane at 300 K. Verify the quoted values of -133.7 and $-401.9\,\mathrm{cm^3\,mol^{-1}}$ and explain the ordering in terms of the well depth.
4. For methane at 300 K with $B_2 = -54.26\,\mathrm{cm^3\,mol^{-1}}$, compute Z from the two-term pressure series at 10, 30 and 60 bar, and estimate the pressure at which the truncation error reaches 2 %.
5. State the sense in which the virial equation is exact and the sense in which it is useless, and explain why the two statements are consequences of the same property.

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Chapter 6

The principle of corresponding states

6.1 Historical background

The last chapter of van der Waals' 1873 thesis already contains the observation that his equation, written in units of the critical constants, loses every reference to the substance. He developed the consequence into a general statement, the law of corresponding states, in work published in 1880: fluids at the same reduced temperature and reduced pressure are in corresponding states and have the same reduced volume. The claim was made about a particular model, but it was immediately tested as though it were a law of nature, and to a remarkable degree it survived. Kamerlingh Onnes used it at Leiden to estimate the critical constants of the permanent gases and to plan the liquefaction of hydrogen and, in 1908, of helium. Its theoretical basis was supplied much later. Guggenheim, in *The principle of corresponding states* (*J. Chem. Phys.* **7** (1939) 583), showed that the collapse follows from the form of the intermolecular potential rather than from any equation of state, and demonstrated it quantitatively for argon, krypton, xenon, nitrogen, oxygen, carbon monoxide and methane. Those seven substances have been called simple fluids ever since. In the engineering literature the principle became the generalized compressibility chart.

6.2 Physical motivation

An equation of state carries substance-specific information as molecular parameters: a size, an energy, and in general a shape. If a fluid is characterized by only two of them, one length and one energy, both can be absorbed into the units in which volume and temperature are measured, and what remains must be the same for every fluid in the class. The critical point supplies exactly two measurable quantities to fix those units, and the principle of corresponding states is the statement that nothing else is needed. The argument is dimensional analysis constrained by molecular physics, and it fails in exactly one way: if a molecule requires a third parameter, no choice of units can remove it.

6.3 Mathematical development

The reduced van der Waals equation

Inverting the critical relations of Chapter 3 gives $b = V_c/3$, $a = 3P_cV_c^2$ and $RT_c = 8P_cV_c/3$. Inserting these into Equation (3.3) together with $P = P_rP_c$, $T = T_rT_c$ and $V = V_rV_c$,

$$P_rP_c = \frac{(8P_cV_c/3)\,T_r}{V_cV_r - V_c/3} - \frac{3P_cV_c^2}{V_c^2V_r^2} = \frac{8P_cT_r}{3\,(V_r - 1/3)} - \frac{3P_c}{V_r^2}. \tag{6.1}$$

Every occurrence of V_c has cancelled, and dividing through by P_c removes the last substance-specific quantity:

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}. \tag{6.2}$$

Equation (6.2) contains no a, no b, no R and no reference to any substance. It is a single surface on which, if the van der Waals equation were correct, every fluid in the universe would lie. Setting $T_r = V_r = 1$ returns $P_r = 8/2 - 3 = 1$, confirming that the critical point is a fixed point of the reduced equation.

Key idea: the units carry the chemistry

The two molecular parameters of a two-parameter equation of state can always be eliminated by measuring T, P and V in units of their critical values. Any such equation is therefore *obliged* to obey two-parameter corresponding states, and any prediction it makes for a reduced quantity, such as Z_c or $P_r^{\mathrm{sat}}(T_r)$, is necessarily

the same number for every substance. Corresponding states is thus not evidence in favour of the van der Waals equation; it is a constraint the equation cannot avoid.

The statistical-mechanical basis: conformal fluids

Equation (6.2) inherits every defect of its parent. The deeper question is under what molecular conditions the collapse holds independently of any model. Consider a classical fluid of molecules interacting through a pairwise additive, spherically symmetric potential that can be written as

$$u(r) = \varepsilon F\left(\frac{r}{\sigma}\right), \tag{6.3}$$

where ε is an energy scale, σ a length scale, and F a dimensionless *shape function* common to all members of the class. Such fluids are called conformal; the Lennard-Jones family of Chapter 5, all of whose members share $F(x) = 4(x^{-12} - x^{-6})$, is the standard example. Measuring all lengths in the configuration integral $Q_N = \int \exp[-\sum_{i<j} u(r_{ij})/kT]\,\mathrm{d}\mathbf{r}^N$ in units of σ and all energies in units of ε converts it into a function of $T^* = kT/\varepsilon$ and $\rho^* = \rho N_A \sigma^3$ alone, so $Z = Z(T^*, \rho^*)$ with a universal functional form. The critical point of that function occurs at fixed T_c^* and ρ_c^*, so $kT_c \propto \varepsilon$ and $V_c \propto N_A\sigma^3$ with universal constants of proportionality, and eliminating ε and σ in favour of T_c and V_c gives

$$Z = Z(T_r, V_r) \quad \text{or equivalently} \quad Z = Z(T_r, P_r), \qquad Z_c = \text{universal constant}. \tag{6.4}$$

Physics behind the collapse

Two-parameter corresponding states holds exactly for fluids whose molecules satisfy four conditions: the interaction is (i) pairwise additive, (ii) spherically symmetric, (iii) conformal, that is of the single shape $u = \varepsilon F(r/\sigma)$, and (iv) classical, so that the de Broglie wavelength is small compared with σ. Under these conditions the partition function itself is universal in reduced variables, and the collapse is a theorem rather than a correlation.

Which molecules obey it

The four conditions identify the obedient substances directly. Argon, krypton and xenon are monatomic and closed-shell, so their potentials are spherical and very nearly conformal, and they collapse essentially perfectly. Methane is tetrahedral and its interaction is spherical after orientational averaging to an excellent approximation; nitrogen and oxygen are slightly elongated and carry small quadrupole moments, and collapse to within a few percent. These are the simple fluids. The failures are equally systematic:

- **Elongated molecules** (propane, *n*-octane, higher paraffins): the potential depends on the relative orientation of two chains and the anisotropy grows with chain length, so condition (ii) fails.
- **Quadrupolar and dipolar molecules** (carbon dioxide, benzene, ammonia): the leading electrostatic terms are orientation-dependent and their thermal averages carry their own temperature dependence, which no rescaling removes.
- **Hydrogen-bonding fluids** (water, alcohols, hydrogen fluoride): association is short-ranged, directional and comparable with the dispersion energy. It is not a perturbation of F but a different mechanism, treated separately in Chapter 11.
- **Quantum fluids** (helium, hydrogen, neon at low temperature) violate condition (iv).

The falsifiable consequence: a universal Z_c

Equation (6.4) forces Z_c to be one number for all substances. The van der Waals equation puts that number at $3/8 = 0.375$; measured values lie between roughly 0.23 and 0.29, as Figure 3.2 showed. Two distinct failures are contained in that comparison and must not be confused. The first is that 0.375 is the wrong value, a defect of the van der Waals equation, repaired in Chapters 8 to 10 by changing the

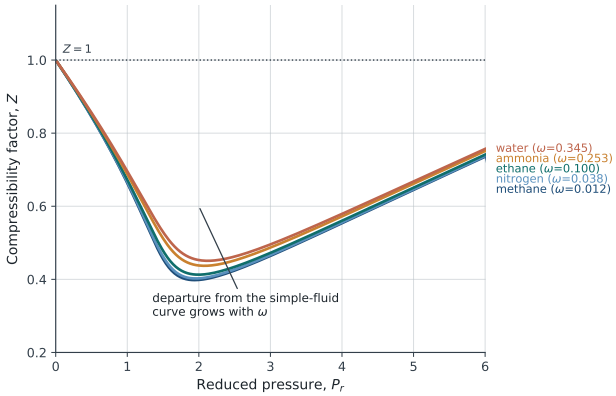

Figure 6.1: Compressibility factor against reduced pressure at $T_r = 1.10$ for five fluids, all computed with the same reference equation of state so that the comparison is like-for-like. Under strict two-parameter corresponding states the five curves would coincide; the spread grows monotonically with the acentric factor of Chapter 7.

volume dependence. The second is that the measured values are *not all equal*, a defect of two-parameter corresponding states itself, which no two-parameter equation whatever can repair. The same conclusion follows from the saturation curve: the equal-area construction of Chapter 3 applied to the van der Waals equation gives $P_r^{sat} = 0.2005$ at $T_r = 0.7$ and 0.6470 at $T_r = 0.9$, identical for methane, propane, carbon dioxide and water alike, whereas real fluids disagree with each other at $T_r = 0.7$ by more than an order of magnitude. It is that disagreement that Chapter 7 turns into a quantitative third parameter.

6.4 Engineering interpretation: the generalized chart

The engineering embodiment of Equation (6.4) is the generalized compressibility chart of Figure 4.4: one family of curves of Z against P_r at constant T_r, valid for every substance whose critical constants are known. Critical constants were tabulated for thousands of compounds; volumetric data were not. The chart converted two tabulated numbers into a complete PVT surface, and through the residual-property integrals of Chapter 1 into enthalpy and entropy departures. The size of its residual error is easily quantified. Computed like-for-like at $T_r = 1.10$ and $P_r = 2.0$, real fluids give 0.399 for methane, 0.403 for nitrogen, 0.413 for ethane, 0.433 for carbon dioxide, 0.438 for ammonia and 0.453 for water. The three simple fluids agree to within 3.6 %; water lies 13.6 % above methane. That spread measures the failure of two-parameter corresponding states, and is a lower bound, since the reference model contains no description of hydrogen bonding. The surface itself appears in reduced coordinates in Figure 4.1.

6.5 Limitations

Limitations

- **A single universal Z_c is predicted and is false.** Measured critical compressibility factors range from about 0.23 to 0.29 in a way that correlates with molecular shape and polarity. No two-parameter equation of state can reproduce that variation.
- **Accuracy is restricted to simple fluids.** Argon, krypton, xenon, methane and nitrogen collapse to within a few percent. Departures grow systematically with chain length, quadrupole moment, dipole moment and hydrogen bonding, and are worst near the saturation line and near the critical point, where most process equipment operates.
- **Quantum fluids are excluded.** Helium, hydrogen and neon at low reduced temperature violate the classical assumption behind Equation (6.3); using effective critical constants for them is a patch, not a correction.
- **The principle predicts nothing about mixtures**, since extension requires pseudo-critical constants and hence combining rules with no basis in Equation (6.3).

6.6 Transition to Chapter 7

The diagnosis is now precise. The two conditions that fail for industrially important fluids are spherical symmetry and conformality, and both failures have the same origin: the intermolecular field of a real molecule is not centrally symmetric. What is required is a third parameter that measures that departure, that can be obtained from a routine measurement, and that enters as a small correction so that the two-parameter framework is retained rather than discarded. Chapter 7 shows that the slope of the reduced vapour-pressure curve supplies exactly such a parameter, and that a single measurement at $T_\mathrm{r} = 0.7$ determines it.

Student handout: Chapter 6

Summary

- Substituting $b = V_\mathrm{c}/3$, $a = 3P_\mathrm{c}V_\mathrm{c}^2$ and $RT_\mathrm{c} = 8P_\mathrm{c}V_\mathrm{c}/3$ into the van der Waals equation gives $P_\mathrm{r} = 8T_\mathrm{r}/(3V_\mathrm{r} - 1) - 3/V_\mathrm{r}^2$, which contains no substance-specific constant.
- Any two-parameter equation of state is forced to obey corresponding states, so the collapse is a constraint on such equations rather than evidence for any one of them.
- The molecular basis is conformality: for pairwise additive, spherically symmetric, classical potentials of the single form $u = \varepsilon F(r/\sigma)$ the configuration integral is universal in $T^* = kT/\varepsilon$ and $\rho^* = \rho N_A \sigma^3$, hence $Z = Z(T_\mathrm{r}, P_\mathrm{r})$. Argon, krypton, xenon, methane and nitrogen obey the principle closely; elongated, quadrupolar, dipolar, hydrogen-bonding and quantum fluids do not.
- Two-parameter corresponding states forces one universal Z_c; measured values run from about 0.23 to 0.29, which falsifies the principle independently of the value $3/8$. The generalized chart inherits exactly these limitations.

Key equations

$$P_\mathrm{r} = \frac{8T_\mathrm{r}}{3V_\mathrm{r} - 1} - \frac{3}{V_\mathrm{r}^2} \qquad \text{(no substance-specific constants)} \tag{6.5}$$

$$u(r) = \varepsilon F(r/\sigma) \quad \Longrightarrow \quad Z = Z(T^*, \rho^*), \qquad T^* = \frac{kT}{\varepsilon}, \;\; \rho^* = \rho N_A \sigma^3 \tag{6.6}$$

$$Z = Z(T_\mathrm{r}, P_\mathrm{r}), \qquad Z_\mathrm{c} = \text{universal} \tag{6.7}$$

Concept map

volumetric data exist for few substances but critical constants for many → two molecular scales, one energy and one length, absorbed into the units → $P_\mathrm{r} = 8T_\mathrm{r}/(3V_\mathrm{r} - 1) - 3/V_\mathrm{r}^2$ and $Z = Z(T_\mathrm{r}, P_\mathrm{r})$ for conformal fluids → a single universal Z_c is forced and is contradicted by experiment for every non-spherical molecule

Practice questions

1. Derive Equation (6.2) from Equation (3.3) without consulting the text, and state which step removes the last substance-specific quantity.
2. Explain why the collapse of many fluids onto one chart is not evidence that the van der Waals equation is correct.
3. State the four molecular conditions under which two-parameter corresponding states is exact, and identify which is violated by (a) *n*-octane, (b) carbon dioxide, (c) water, (d) helium at 10 K.
4. Using §8 of the design specification and a cubic equation of state, compute Z at $T_\mathrm{r} = 1.10$ and $P_\mathrm{r} = 2.0$ for methane, ethane and water. Verify the values 0.399, 0.413 and 0.453 and quantify the failure of the principle.
5. Show that any equation of state whose parameters depend only on T_c and P_c predicts a single value of $P_\mathrm{r}^\mathrm{sat}$ at $T_\mathrm{r} = 0.7$, and verify numerically that the van der Waals value is 0.2005 for both methane and water.

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Chapter 7

The Pitzer acentric factor

7.1 Historical background

Kenneth Pitzer and his co-workers at Berkeley published in 1955 a pair of papers in the *Journal of the American Chemical Society* (**77** (1955) 3427 and 3433) that resolved the difficulty left by Chapter 6 in the most economical way available. Rather than abandon corresponding states they added one parameter to it, and that parameter was not measured on a molecule but extracted from the vapour-pressure curve, available accurately for hundreds of compounds. The choice of observable was deliberate: the vapour pressure is the most sensitive routinely available probe of the intermolecular field, being governed by the free-energy difference between a dense phase and a dilute one. Pitzer called the result the *acentric factor*, the name recording its meaning: a measure of the departure of the molecular force field from central, that is spherical, symmetry. The accompanying tables of Z were recast in analytic form by Lee and Kesler in 1975, and that implementation is what modern software calls the Pitzer correlation.

7.2 Physical motivation

A two-parameter equation of state predicts one universal reduced vapour-pressure curve, as Chapter 6 established. Real fluids produce a family of curves sharing the point $(T_\mathrm{r}, P_\mathrm{r}^{\mathrm{sat}}) = (1, 1)$, which is the definition of the critical constants, but separating below it, and the separation is ordered rather than random: at fixed subcritical T_r, spherical molecules have the highest reduced vapour pressure and elongated, polar or hydrogen-bonding molecules progressively lower ones.

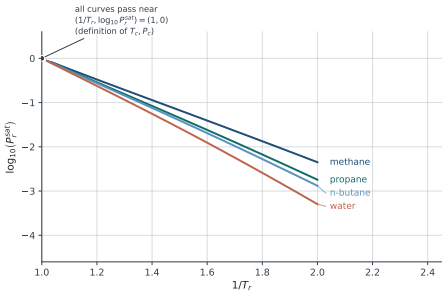

Figure 7.1: Reduced vapour-pressure curves plotted as $\log_{10} P_\mathrm{r}^{\mathrm{sat}}$ against $1/T_\mathrm{r}$ for four fluids, computed with a common reference equation of state. The curves are close to straight, and all pass through $(1, 0)$ because that point defines T_c and P_c; their slopes differ systematically.

7.3 Mathematical development

Why the reduced vapour-pressure curve is nearly straight

The Clausius–Clapeyron equation for a vapour that is nearly ideal and much less dense than the liquid gives $\mathrm{d}\ln P^{\mathrm{sat}}/\mathrm{d}(1/T) = -\Delta H^{\mathrm{vap}}/R$. Where ΔH^{vap} varies slowly the curve is therefore straight to a good approximation, and dividing P^{sat} by P_c and T by T_c changes only the intercept, so

$$\log_{10} P_\mathrm{r}^{\mathrm{sat}} \simeq S\left(\frac{1}{T_\mathrm{r}} - 1\right), \tag{7.1}$$

the intercept being fixed by the requirement that the line pass through $P_\mathrm{r}^{\mathrm{sat}} = 1$ at $T_\mathrm{r} = 1$. This is the crux of the argument: because the critical point is common to all fluids in reduced coordinates, only the slope S is unknown, and one measurement anywhere on the curve determines the whole line.

The definition

Choose $T_\mathrm{r} = 0.7$, so that $1/T_\mathrm{r} - 1 = 3/7$ and Equation (7.1) gives $S = (7/3)\log_{10} P_\mathrm{r}^\mathrm{sat}|_{T_\mathrm{r}=0.7}$. Pitzer observed that the simple fluids of Chapter 6 all have $\log_{10} P_\mathrm{r}^\mathrm{sat} \approx -1.0$ there; measuring every other fluid against that reference, with the sign reversed so that the parameter increases with departure from sphericity, gives

$$\boxed{\omega \equiv -1 - \log_{10} P_\mathrm{r}^\mathrm{sat}\Big|_{T_\mathrm{r}=0.7}} \tag{7.2}$$

Simple fluids therefore have $\omega \approx 0$ by construction, and the slope of the reduced vapour-pressure line becomes

$$S = -\tfrac{7}{3}(1+\omega), \qquad \text{so} \qquad \log_{10} P_\mathrm{r}^\mathrm{sat} \simeq -\tfrac{7}{3}(1+\omega)\left(\frac{1}{T_\mathrm{r}} - 1\right). \tag{7.3}$$

The acentric factor is thus a slope in disguise, obtained from a single point.

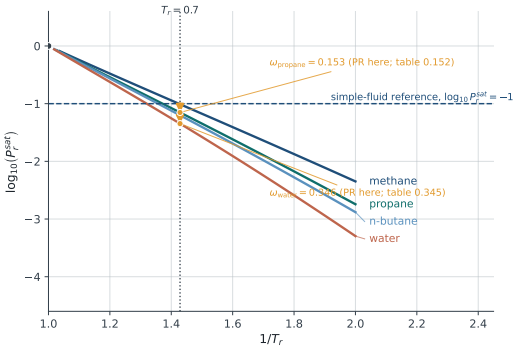

Figure 7.2: The Pitzer construction. The vertical line marks $T_\mathrm{r} = 0.7$ and the horizontal line the simple-fluid reference $\log_{10} P_\mathrm{r}^\mathrm{sat} = -1$. The acentric factor of a fluid is the vertical gap between the reference line and that fluid's curve at $T_\mathrm{r} = 0.7$.

Why $T_\mathrm{r} = 0.7$

Three requirements constrain the choice. First, the reference state must be experimentally accessible: with the reference equation of state used throughout these notes the reduced normal boiling point $T_\mathrm{b}/T_\mathrm{c}$ is 0.586 for methane, 0.624 for propane, 0.641 for *n*-butane, 0.592 for ammonia and 0.579 for water, so $T_\mathrm{r} = 0.7$ lies just above the normal boiling point of most fluids, where the vapour pressure is a few bar. Second, the state must be comfortably subcritical, so that the phases are clearly distinguished and Equation (7.1) is at its most accurate: at $T_\mathrm{r} = 0.9$ the vapour is dense and the linearization degrades, at $T_\mathrm{r} = 0.5$ many compounds have solidified. Third, near $T_\mathrm{r} = 1$ all curves converge to within experimental error, whereas at $T_\mathrm{r} = 0.7$ the family has separated by an order of magnitude.

Physics introduced: departure from central symmetry

The acentric factor measures how far the intermolecular field departs from spherical symmetry, through its effect on the free-energy difference between the saturated liquid and the saturated vapour. It therefore increases with anything that makes the field anisotropic or adds a directional interaction: chain length, quadrupole moment, dipole moment and hydrogen bonding. Representative values are 0.000 for argon, 0.012 for methane, 0.100 for ethane, 0.152 for propane, 0.200 for *n*-butane, 0.395 for *n*-octane, 0.224 for carbon dioxide, 0.253 for ammonia, 0.345 for water and 0.556 for methanol; the rise through the *n*-alkane series is the clearest signal that ω reports shape.

Three-parameter corresponding states

The natural correlation is then a first-order expansion of the reduced compressibility surface about the simple-fluid surface:

$$Z(T_\mathrm{r}, P_\mathrm{r}, \omega) = Z^{(0)}(T_\mathrm{r}, P_\mathrm{r}) + \omega Z^{(1)}(T_\mathrm{r}, P_\mathrm{r}). \tag{7.4}$$

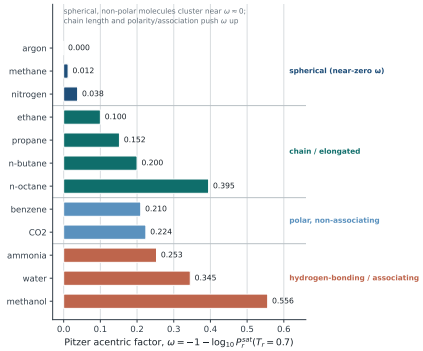

Figure 7.3: Acentric factors grouped by molecular family. Spherical non-polar molecules cluster near zero; chain length, polarity and hydrogen bonding each raise ω.

Here $Z^{(0)}$ is the compressibility factor of a simple fluid, so Equation (7.4) reduces to two-parameter corresponding states when $\omega = 0$, and $Z^{(1)}$ is the derivative of Z with respect to ω at fixed reduced conditions. Pitzer tabulated both from experimental data; Lee and Kesler later generated them from two modified Benedict–Webb–Rubin reference fluids, a simple fluid and *n*-octane, and that implementation is what appears in process simulators. The same linear structure carries over to $\log_{10} P_r^{\text{sat}}$ and to the residual enthalpy and entropy. The linearity is an approximation, but a good one: computed with the reference cubic equation of these notes, Z departs from a straight line in ω over $0 \le \omega \le 0.4$ by at most 0.0019 at $(T_r, P_r) = (1.2, 1.0)$ and 0.0058 at $(1.2, 2.0)$.

Key idea: ω is a correlating parameter, not a molecular property

The acentric factor is not measured on a molecule; it is not a dipole moment, a polarizability or an aspect ratio. Equation (7.2) defines it as a point on a vapour-pressure curve, so it inherits whatever mixture of effects that curve contains: *n*-octane and ammonia depart from sphericity for quite different reasons, yet have similar ω and are predicted to behave alike, which they do not.

7.4 Engineering interpretation

Three consequences account for the durability of the acentric factor. The first is coverage: ω needs only one vapour-pressure datum, so it is tabulated for essentially every industrial compound alongside T_c and P_c. The second is compatibility: Equation (7.4) corrects the existing framework rather than replacing it. The third and most important is that ω is the input through which molecular shape enters every modern cubic equation of state, through the correlations $m(\omega)$ and $\kappa(\omega)$ of Chapters 9 and 10; applied to such a model's own saturation curve, Equation (7.2) recovers 0.153 against a tabulated 0.152 for propane.

7.5 Limitations

Limitations

- **The vapour-pressure curve is not exactly linear in $1/T_r$, and the curvature grows with ω.** Measured as the departure of the point at $T_r = 0.7$ from the chord joining $T_r = 0.6$ and $T_r = 0.8$, the curvature in $\log_{10} P_r^{\text{sat}}$ is 0.0001 for methane, 0.0050 for propane, 0.0091 for ammonia and 0.0133 for water, so the residual of a one-point definition grows for exactly the fluids that motivated it.
- **Extrapolation to low reduced temperature fails for associating fluids.** Equation (7.3) at $T_r = 0.55$ overestimates the reference P_r^{sat} by 3.5 % for methane and 6.1 % for propane, but underestimates it by 21.3 % for water.
- **One parameter cannot separate distinct mechanisms, and there is no rule for mixtures.** Elongation, quadrupole moment, dipole moment and association are collapsed onto one axis, so any two fluids with equal ω are predicted to have identical reduced properties; and extension to mixtures demands a mixing rule for ω that does not follow from the definition.

7.6 Transition to Chapter 8

Chapters 6 and 7 have supplied a diagnosis and a parameter but no new equation of state. The van der Waals equation remains the only closed form available and is quantitatively poor: $Z_c = 0.375$, liquid volumes far too large, and Equation (7.2) applied to its own universal saturation curve returns $\omega = -0.302$ for every substance. The first repair attempted was not the introduction of ω, which came later, but a correction of the temperature and volume dependence of the attraction: the Redlich–Kwong equation of 1949, the subject of Chapter 8.

Student handout: Chapter 7

Summary

- Clausius–Clapeyron with a slowly varying ΔH^{vap} makes $\log_{10} P_r^{\mathrm{sat}}$ nearly linear in $1/T_r$, and all fluids pass through $(1/T_r, \log_{10} P_r^{\mathrm{sat}}) = (1, 0)$, so one further point fixes the line.
- Simple fluids have $\log_{10} P_r^{\mathrm{sat}} = -1.0$ at $T_r = 0.7$, so $\omega = -1 - \log_{10} P_r^{\mathrm{sat}}|_{T_r=0.7}$ vanishes for them by construction. That temperature lies just above the reduced normal boiling point of most fluids (0.58–0.64) and is comfortably subcritical.
- ω rises with chain length, quadrupole moment, dipole moment and hydrogen bonding. Three-parameter corresponding states writes $Z = Z^{(0)} + \omega Z^{(1)}$, tabulated by Pitzer and implemented analytically by Lee and Kesler; for the reference model this linearity holds to better than 0.006 in Z over $0 \le \omega \le 0.4$.
- But ω is a correlating parameter extracted from a vapour pressure, not a molecular property, and it fails for associating fluids.

Key equations

$$\log_{10} P_r^{\mathrm{sat}} \simeq S\left(\frac{1}{T_r} - 1\right), \qquad \omega = -1 - \log_{10} P_r^{\mathrm{sat}}\Big|_{T_r=0.7} \tag{7.5}$$

$$S = -\tfrac{7}{3}(1+\omega) \quad \Longrightarrow \quad \log_{10} P_r^{\mathrm{sat}} \simeq -\tfrac{7}{3}(1+\omega)\left(\frac{1}{T_r} - 1\right) \tag{7.6}$$

$$Z(T_r, P_r, \omega) = Z^{(0)}(T_r, P_r) + \omega Z^{(1)}(T_r, P_r) \tag{7.7}$$

Concept map

two-parameter corresponding states fails for non-spherical molecules → departure from central symmetry, read from the slope of the reduced vapour-pressure curve → $\omega = -1 - \log_{10} P_r^{\mathrm{sat}}(T_r = 0.7)$ and $Z = Z^{(0)} + \omega Z^{(1)}$ → one parameter cannot separate elongation, polarity and association

Practice questions

1. Derive Equation (7.3) from Equation (7.1) and explain why no second measurement is required.
2. Give three reasons for the choice $T_r = 0.7$, and state what goes wrong at $T_r = 0.95$ and at $T_r = 0.5$.
3. Using §8 of the design specification, compute P^{sat} of propane at $T_r = 0.8$ from Equation (7.3); verify 9.040 bar against 8.978 bar from the isofugacity condition.
4. Repeat for water at $T_r = 0.55$ and verify the discrepancy of 21.3 %.
5. Ammonia ($\omega = 0.253$) and *n*-butane ($\omega = 0.200$) have similar acentric factors and very different molecular physics. State what three-parameter corresponding states predicts about them, and why it should be distrusted.

Recommended references

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Chapter 8

The Redlich–Kwong equation of state

8.1 Historical background

Otto Redlich and Joseph Neng Shun Kwong published their equation in 1949 in *Chemical Reviews* (**44** (1949) 233), as one of a series of papers on the thermodynamics of solutions. Redlich was then in industrial research at the Shell Development Company, and the motivating problem was the calculation of fugacities in gaseous mixtures at the elevated pressures of hydrocarbon processing. The van der Waals equation was seventy-six years old, qualitatively right and quantitatively unsatisfactory, and a great deal of high-pressure volumetric data had accumulated since. The authors were explicit that their modification was empirical: they claimed no new molecular argument, only a functional form that reproduced the available compressibility and fugacity data far better at comparable cost. The equation dominated vapour-phase calculations for two decades and is the parent of both modern industrial cubics.

8.2 Physical motivation

Two defects of the van der Waals attraction term were visible in the data. The first is its temperature dependence, or rather its absence: a is a constant, so the attractive pressure $-a/V^2$ is the same at 200 K as at 800 K at equal density. The mean-field derivation of Chapter 3 makes clear why this cannot be right. The quantity a is a thermal average of the attractive energy of a molecule in the field of its neighbours, and that average depends on how long a molecule remains within range of the attractive well; as the temperature rises molecules traverse the well faster and the equilibrium distribution shifts weight toward larger separations, so the averaged attractive energy falls. An effective attraction parameter must therefore *decrease* with temperature.

The second defect is the volume dependence. The term $-a/V^2$ grows without limit as V falls, which makes the van der Waals liquid branch too soft and its critical volume $V_c = 3b$ too large. Replacing V^2 by $V(V+b)$ leaves the dilute limit unchanged but weakens the attraction where V is of the order of b.

Physics introduced by Redlich and Kwong

A temperature-dependent effective attraction. The attraction parameter takes the form $a/\sqrt{T}$, so the attractive pressure falls as the thermal energy rises and the attractive contribution to B_2 decays as $T^{-3/2}$ rather than T^{-1}.
A softened volume dependence. The denominator V^2 becomes $V(V+b)$, unchanged in the dilute limit but weaker at liquid-like densities, moving Z_c from 0.375 to $1/3$.
Neither change carries new molecular content of the kind introduced in Chapter 3; both are corrections to the form of the mean field, justified by data.

8.3 Mathematical development

The equation

The Redlich–Kwong equation is

$$P = \frac{RT}{V-b} - \frac{a}{\sqrt{T}\,V(V+b)}. \tag{8.1}$$

It differs from Equation (3.3) in exactly two independent respects: the factor $T^{-1/2}$ changes the temperature dependence of the attraction, and the denominator $V(V+b)$ in place of V^2 changes its volume dependence. Separating them makes the subsequent history intelligible: Soave (Chapter 9) revises the first, Peng and Robinson (Chapter 10) the second.

Parameters from the critical conditions

The route is the template of Equation (3.6), but it is more convenient to impose the critical conditions on the dimensionless cubic than on the derivatives of the equation itself. Introducing $A = aP/(R^2T^{2.5})$ and $B = bP/(RT)$, substituting $V = ZRT/P$ into Equation (8.1) and clearing denominators gives

$$Z^3 - Z^2 + \left(A - B - B^2\right) Z - AB = 0. \tag{8.2}$$

At the critical point the horizontal inflection of Chapter 3 forces the three roots of Equation (8.2) to coincide, so the cubic must be identical to $(Z - Z_c)^3 = Z^3 - 3Z_cZ^2 + 3Z_c^2Z - Z_c^3 = 0$. Matching coefficients gives

$$3Z_c = 1, \qquad 3Z_c^2 = A - B - B^2, \qquad Z_c^3 = AB. \tag{8.3}$$

The first requires no algebra at all and gives $Z_c = 1/3 = 0.3333$. The remaining two determine A and B at the critical point, where they take the universal values Ω_a and Ω_b; eliminating A between them gives a single cubic in Ω_b,

$$\Omega_b^3 + \Omega_b^2 + \tfrac{1}{3}\Omega_b - \tfrac{1}{27} = 0, \tag{8.4}$$

whose only positive root is $\Omega_b = (2^{1/3} - 1)/3 = 0.086640$, and then $\Omega_a = Z_c^3/\Omega_b = 1/\left[9(2^{1/3} - 1)\right] = 0.427480$. Restoring dimensions,

$$a = 0.42748\,\frac{R^2T_c^{2.5}}{P_c}, \qquad b = 0.08664\,\frac{RT_c}{P_c}, \qquad Z_c = \frac{1}{3}, \qquad V_c = \frac{b}{2^{1/3} - 1} = 3.8473\,b. \tag{8.5}$$

Key idea: Z_c is set by the volume dependence alone

The critical compressibility factor of a cubic equation of state depends only on the denominator of the attractive term, never on its temperature dependence, because the critical conditions are derivatives at constant temperature. Van der Waals' V^2 gives 0.375, Redlich and Kwong's $V(V + b)$ gives $1/3$, and the Peng–Robinson denominator of Chapter 10 gives 0.3074. This is why $T^{-1/2}$ improves the vapour phase without improving the liquid, and why Chapter 9, which changes only the temperature dependence, leaves Z_c at $1/3$.

The alpha function in retrospect

Writing $a_c = 0.42748\,R^2T_c^2/P_c$ for the attraction parameter at the critical temperature, Equation (8.1) can be recast in the form used from Chapter 9 onward,

$$P = \frac{RT}{V - b} - \frac{a_c\,\alpha(T_r)}{V(V + b)}, \qquad \alpha^{\mathrm{RK}}(T_r) = T_r^{-1/2}. \tag{8.6}$$

Van der Waals has $\alpha = 1$ and Redlich–Kwong $\alpha = T_r^{-1/2}$, giving 1.1952 at $T_r = 0.7$ and 0.7071 at $T_r = 2.0$; both satisfy $\alpha(1) = 1$, so the critical constraint of Equation (8.5) is preserved. It is a fixed power law with no adjustable content and, decisively, no dependence on the substance.

8.4 Engineering interpretation

The improvement in the vapour phase was the reason for the equation's adoption. For propane at $T_r = 1.2$, measured against a modern reference model, the van der Waals compressibility factor is in error by $-8.8\,\%$ at $P_r = 2.0$ and $7.0\,\%$ at $P_r = 3.0$, whereas the Redlich–Kwong values are in error by $-1.9\,\%$ and $1.2\,\%$. At low reduced pressure both are adequate; the advantage appears where the gas is dense, the regime of compressor discharge and gas transmission.

The liquid phase is not improved to a comparable degree. At $T_r = 0.7$ the saturated liquid molar volume of propane from Equation (8.1) is $87.5\,\mathrm{cm^3\,mol^{-1}}$, against $126.8\,\mathrm{cm^3\,mol^{-1}}$ from van der Waals and $75.7\,\mathrm{cm^3\,mol^{-1}}$ from the modern reference: most of the van der Waals error has gone, but the Redlich–Kwong volume remains some 16 % too large, a direct consequence of $Z_c = 1/3$.

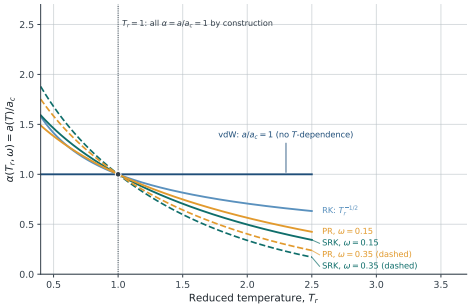

Figure 8.1: Attraction parameter normalized by its critical value against reduced temperature. Van der Waals is constant; Redlich–Kwong is the fixed power law $T_\mathrm{r}^{-1/2}$; the Soave and Peng–Robinson functions of Chapters 9 and 10 depend in addition on the acentric factor.

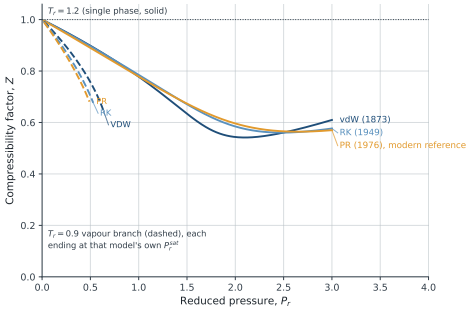

Figure 8.2: Compressibility factor of propane against reduced pressure computed with the van der Waals, Redlich–Kwong and Peng–Robinson equations on a supercritical and a subcritical isotherm, with Peng–Robinson labelled as the modern reference.

The vapour pressure is worse still, for a structural reason. Equation (8.1) contains only T_c and P_c, so by the argument of Chapter 6 it predicts one universal saturation curve. Applying Equation (7.2) to that curve gives

$$P_\mathrm{r}^\mathrm{sat}\big|_{T_\mathrm{r}=0.7} = 0.08744 \qquad \Longrightarrow \qquad \omega^\mathrm{RK} = 0.0583 \quad \text{for every substance.} \tag{8.7}$$

This is an enormous improvement on the van der Waals value of -0.302 and is close to the tabulated acentric factors of the simple fluids, 0.000 for argon, 0.012 for methane and 0.038 for nitrogen. It is useless for anything else: propane has $\omega = 0.152$, carbon dioxide 0.224 and water 0.345. For propane the Redlich–Kwong saturation pressure exceeds that of the three-parameter reference of Chapter 9 by 32.6 % at $T_\mathrm{r} = 0.6$, 24.1 % at $T_\mathrm{r} = 0.7$, 15.1 % at $T_\mathrm{r} = 0.8$ and 7.0 % at $T_\mathrm{r} = 0.9$, the error growing as the phases become less alike.

8.5 Limitations

Limitations

- **No molecular-shape parameter.** Equation (8.1) contains only T_c and P_c and is therefore locked to two-parameter corresponding states, predicting a single acentric factor of 0.0583 for every fluid in existence.
- **Vapour–liquid equilibrium is quantitatively unusable, and liquid densities remain poor.** Errors of 24 % in P^sat at $T_\mathrm{r} = 0.7$ for a fluid as ordinary as propane propagate directly into K-values through Equation (1.5); and $Z_\mathrm{c} = 1/3$ is still well above the measured range of roughly 0.23 to 0.29, leaving the saturated liquid volume of propane about 16 % too large.
- **The temperature dependence is a guess.** $T^{-1/2}$ was selected empirically; no argument makes this exponent correct and no mechanism lets it differ between substances. Polar and associating fluids lie outside the scope of the equation, and near-critical behaviour remains mean-field.

8.6 Transition to Chapter 9

Redlich and Kwong showed that making the attraction parameter temperature-dependent improves the equation substantially, using a dependence chosen by inspection that contains no information about the substance. Chapter 7 had meanwhile supplied exactly the missing information in the form of ω, defined through the vapour pressure, the property Equation (8.1) predicts worst. The remaining step was not taken for twenty-three years: stop guessing $\alpha(T)$ and determine it by requiring the equation to reproduce the measured vapour pressure, with ω distinguishing one substance from another. That is the content of Soave's 1972 paper.

Student handout: Chapter 8

Summary

- Redlich and Kwong (1949) made two independent empirical changes to the van der Waals attraction: the temperature factor $T^{-1/2}$ and the volume dependence $V(V+b)$ in place of V^2. An effective attraction must weaken with temperature because a is a thermal average: at higher kinetic energy molecules spend less time within range of the attractive well.
- Imposing a triple root on the dimensionless cubic gives $Z_\mathrm{c} = 1/3$ immediately from the Z^2 coefficient, and then $\Omega_b = (2^{1/3}-1)/3 = 0.08664$ and $\Omega_a = 1/[9(2^{1/3}-1)] = 0.42748$.
- Z_c is fixed by the volume dependence of the attraction alone and is untouched by its temperature dependence.
- Vapour-phase compressibility factors improve markedly: for propane at $T_\mathrm{r} = 1.2$ and $P_\mathrm{r} = 2.0$ the error falls from $-8.8\,\%$ to $-1.9\,\%$. But with no shape parameter the equation predicts $\omega = 0.0583$ for every fluid, overpredicts the vapour pressure of propane by $24\,\%$ at $T_\mathrm{r} = 0.7$, and leaves the saturated liquid volume about $16\,\%$ too large.

Key equations

$$P = \frac{RT}{V-b} - \frac{a}{\sqrt{T}\,V(V+b)} = \frac{RT}{V-b} - \frac{a_\mathrm{c}\,T_\mathrm{r}^{-1/2}}{V(V+b)} \tag{8.8}$$

$$Z^3 - Z^2 + \left(A - B - B^2\right)Z - AB = 0, \qquad A = \frac{aP}{R^2T^{2.5}}, \quad B = \frac{bP}{RT} \tag{8.9}$$

$$a = 0.42748\,\frac{R^2T_\mathrm{c}^{2.5}}{P_\mathrm{c}}, \qquad b = 0.08664\,\frac{RT_\mathrm{c}}{P_\mathrm{c}}, \qquad Z_\mathrm{c} = \tfrac{1}{3} \tag{8.10}$$

Concept map

van der Waals attraction is too strong at high temperature and at liquid densities $\rightarrow$ a thermally averaged attraction that weakens with T, plus a softer volume dependence $\rightarrow P = RT/(V-b) - a/[\sqrt{T}V(V+b)]$ with $Z_\mathrm{c} = 1/3 \rightarrow$ good vapour-phase Z, but no shape parameter, so one universal $\omega = 0.058$ and unusable vapour pressures

Practice questions

1. Name the two changes made by Redlich and Kwong and state which determines Z_c, justifying the answer from the form of the critical conditions.
2. Derive Equation (8.2) from Equation (8.1), then obtain $Z_\mathrm{c} = 1/3$, Ω_b and Ω_a by matching it to $(Z - Z_\mathrm{c})^3 = 0$.
3. Explain, in terms of the thermal average of Equation (3.2), why an effective attraction parameter must decrease with increasing temperature.
4. Using §8 of the design specification, compute a and b for propane and evaluate Z for the vapour at $T_\mathrm{r} = 1.2$ and $P_\mathrm{r} = 2.0$; compare with the van der Waals and Peng–Robinson values of 0.5435 and 0.5961.
5. Show that Equation (8.1) predicts one universal reduced saturation curve, verify $P_\mathrm{r}^\mathrm{sat} = 0.08744$ at $T_\mathrm{r} = 0.7$, and state which real fluids it describes acceptably.

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- O. Redlich and J. N. S. Kwong, "On the thermodynamics of solutions. V.", *Chem. Rev.* **44** (1949) 233.
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Chapter 9

Soave–Redlich–Kwong

9.1 Historical background

Giorgio Soave published *Equilibrium constants from a modified Redlich–Kwong equation of state* in *Chemical Engineering Science* (**27** (1972) 1197). The paper is short and its argument is single. Redlich and Kwong had shown that the attraction parameter must depend on temperature and had chosen the dependence by inspection; Soave observed that the choice need not be made at all. It can be *determined*, by requiring the equation to reproduce the one experimental quantity available for almost every compound and most sensitive to the attractive term, namely the vapour pressure.

The timing is significant. By 1972 the acentric factor had been available for seventeen years, digital computers were entering process engineering departments, and the hydrocarbon industries needed equilibrium ratios for multicomponent mixtures at high pressure, where activity-coefficient methods based on a separate liquid model do not apply. The modern process simulator, in which one equation of state generates densities, enthalpies, entropies and K-values for a whole flowsheet, dates from this paper and from the Peng–Robinson paper four years later.

9.2 Physical motivation

The Redlich–Kwong exponent of $-1/2$ has no theoretical justification, and it is the same for every substance, which contradicts everything established in Chapters 6 and 7: the rate at which the effective attraction is averaged away by thermal motion must depend on the shape of the molecular force field. A spherical molecule and an extended chain do not lose their attraction at the same rate as the temperature rises, because in the chain the attraction is distributed over segments whose relative orientations are themselves temperature-sensitive. The temperature dependence should therefore be flexible rather than fixed, and it should carry a substance-specific parameter. The acentric factor is the natural candidate, because it is available for every industrial compound and because it was itself defined from the vapour-pressure curve, which is the property being targeted.

Physics introduced by Soave

The temperature dependence of the effective attraction is no longer postulated. It is *measured*, indirectly, by demanding that the equation reproduce the experimental saturation pressure along the whole coexistence curve, and made substance-specific by letting the acentric factor set its steepness. The physical content added relative to Chapter 8 is exactly the content of ω: departure of the molecular force field from central symmetry, now expressed as a rate of thermal weakening of the attraction.

9.3 Mathematical development

The alpha function

Soave kept the Redlich–Kwong volume dependence and wrote

$$P = \frac{RT}{V-b} - \frac{a_c\,\alpha(T_r,\omega)}{V(V+b)}, \qquad a_c = 0.42748\,\frac{R^2T_c^2}{P_c}, \qquad b = 0.08664\,\frac{RT_c}{P_c}, \tag{9.1}$$

with the constants unchanged from Equation (8.5) because the critical conditions are unchanged. The function α must satisfy $\alpha(1)=1$, or the equation would no longer reproduce T_c and P_c; this is a constraint, not a fitted result. Soave's form is

$$\alpha(T_r,\omega) = \left[1 + m\left(1-\sqrt{T_r}\right)\right]^2, \qquad m = 0.480 + 1.574\,\omega - 0.176\,\omega^2. \tag{9.2}$$

Three properties deserve comment. First, $\alpha(1)=1$ identically, for every m. Second, $\sqrt{\alpha}=(1+m)-m\sqrt{T_\mathrm{r}}$ is linear in $\sqrt{T_\mathrm{r}}$, which is the empirical regularity Soave found in the data and the reason for the squared form. Third, differentiating at the critical point gives $(\mathrm{d}\alpha/\mathrm{d}T_\mathrm{r})|_{T_\mathrm{r}=1}=-m$, so m, and therefore ω, controls the rate at which the attraction strengthens as the fluid is cooled below its critical temperature. For the species of §8 of the design specification, $m=0.4989$ for methane, 0.7152 for propane, 0.8237 for carbon dioxide and 1.0021 for water.

How the function was obtained

The procedure is worth stating explicitly, because every subsequent alpha function has been generated by it.

1. Select pure compounds with accurate vapour pressures. Soave used hydrocarbons, from methane through the higher paraffins, with a few light gases.
2. For one compound and one subcritical temperature, treat α as an unknown: solve Equation (9.1) for its liquid and vapour roots at the measured P^sat and adjust α until the isofugacity condition $\varphi^\mathrm{L}=\varphi^\mathrm{V}$, equivalent to the equal-area construction of Equation (3.7), holds exactly. This returns one value of α at one T_r, with no functional form assumed.
3. Repeat along the saturation curve and plot $\sqrt{\alpha}$ against $\sqrt{T_\mathrm{r}}$. The result is very nearly a straight line passing through $(1,1)$, which fixes the form of Equation (9.2) and identifies its slope as $-m$.
4. Repeat for every compound in the set and regress the resulting values of m against the tabulated acentric factors. The quadratic $m=0.480+1.574\omega-0.176\omega^2$ is that regression.

The acentric factor therefore enters the equation of state through the same property from which it was defined. The construction is self-consistent: applying Equation (7.2) to the saturation curve predicted by Equation (9.1) returns $\omega=0.0121$ for methane against a tabulated 0.012, 0.1521 for propane against 0.152, 0.2242 for carbon dioxide against 0.224 and 0.3453 for water against 0.345. Agreement to within 0.0003 is not a test of the physics; it confirms that $m(\omega)$ does what it was built to do.

Key idea: fitting a function rather than a constant

Van der Waals fitted two constants to the critical point; Redlich and Kwong did the same and guessed a temperature dependence; Soave did the same and then determined the entire temperature dependence from the saturation curve, compressing it into a single substance-specific number that was already tabulated. This is the step at which the cubic equation of state ceased to be a qualitative model of a fluid and became a quantitative correlating engine for vapour–liquid equilibrium.

Compressibility factor and fugacity coefficient

In dimensionless form, with $A=a_\mathrm{c}\alpha P/(R^2T^2)$ and $B=bP/(RT)$, the Soave–Redlich–Kwong equation gives the same cubic as Equation (8.2),

$$Z^3-Z^2+\left(A-B-B^2\right)Z-AB=0, \tag{9.3}$$

the only change being that A now carries $\alpha(T_\mathrm{r},\omega)$. The fugacity coefficient follows from Equation (1.3) by integrating $(Z-1)\,\mathrm{d}P/P$ along the isotherm, which for Equation (9.1) can be done analytically:

$$\ln\varphi=Z-1-\ln\left(Z-B\right)-\frac{A}{B}\ln\left(\frac{Z+B}{Z}\right). \tag{9.4}$$

Equation (9.4) is evaluated once with the largest root of Equation (9.3) for the vapour and once with the smallest root for the liquid. Equating the two fugacities defines the saturation pressure of a pure fluid; equating them component by component in a mixture gives the equilibrium ratios K_i of Equation (1.5). For propane at 300 K and 10 bar, Equation (9.3) gives $Z=0.82515$ and Equation (9.4) gives $\varphi=0.85120$, agreeing to eight decimal places with direct numerical integration of $(Z-1)/P$ from zero pressure.

9.4 Engineering interpretation

The practical gain is concentrated in the vapour pressure and therefore in phase equilibrium. Taking the Soave–Redlich–Kwong prediction for propane as the reference, the unmodified Redlich–Kwong equation is high by 32.6 % at $T_\mathrm{r} = 0.6$ and 24.1 % at $T_\mathrm{r} = 0.7$, whereas the Peng–Robinson equation of Chapter 10, which uses an alpha function of the same structure, agrees with it to within 2.2 % over $0.6 \le T_\mathrm{r} \le 0.9$. The two three-parameter equations agree because they are fitted to the same information; the two-parameter equation does not, because it does not have that information.

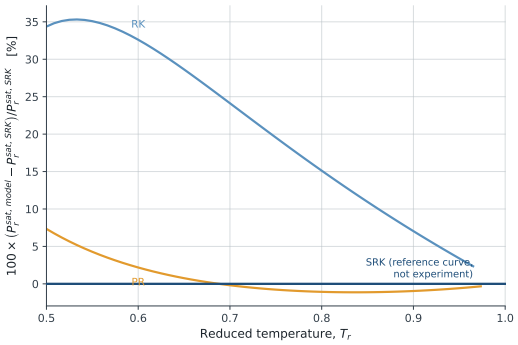

Figure 9.1: Predicted reduced vapour pressure of propane, plotted as relative deviation from the Soave–Redlich–Kwong result taken as the reference curve. The comparison is between models, not against experiment. The two-parameter Redlich–Kwong equation departs strongly at low reduced temperature; Peng–Robinson, which carries the acentric factor in the same way, tracks Soave closely.

Because $K_i = \varphi_i^\mathrm{L} / \varphi_i^\mathrm{V}$, an error of 24 % in the vapour pressure of a component translates into an error of comparable size in its equilibrium ratio, and hence into several theoretical stages in a distillation column or a wrong vapour fraction from a flash drum. Removing that error at no computational cost and with no parameter beyond the ω already available is why the Soave modification was adopted almost immediately across the hydrocarbon processing industry.

Figure 8.1 shows the family of alpha functions on one set of axes. The Soave curves fan out with ω, lying above the Redlich–Kwong power law below the critical temperature and below it above, which is the quantitative statement that a chain molecule loses its effective attraction faster on heating than a spherical one. At $T_\mathrm{r} = 2.0$ the Redlich–Kwong value is 0.7071 while Soave gives 0.4953 for propane and 0.3421 for water.

9.5 Limitations

Limitations

- **The volume dependence was not touched, so Z_c is still $1/3 = 0.3333$** against measured values between roughly 0.23 and 0.29. Liquid densities remain the weakest part of the model: at $T_\mathrm{r} = 0.7$ the saturated liquid molar volume of propane predicted by Equation (9.1) is 85.71 cm^3 mol^{-1}, 13.3 % larger than the 75.68 cm^3 mol^{-1} given by the Peng–Robinson equation, and comparison against measured saturated densities, documented in the standard compilations, shows errors of order ten to twenty percent for the heavier hydrocarbons.
- **The alpha function misbehaves at high reduced temperature.** Equation (9.2) is a parabola in $\sqrt{T_\mathrm{r}}$ and so has a minimum, at $T_\mathrm{r} = [(1+m)/m]^2$, where α reaches zero, after which it *increases*. For water ($m = 1.0021$) the zero lies at $T_\mathrm{r} = 3.99$; for a heavy compound with $\omega = 1.0$ ($m = 1.878$) it lies at $T_\mathrm{r} = 2.35$, and by $T_\mathrm{r} = 5$ the function has climbed back to 1.75, an attraction stronger than at the critical point. This matters for supercritical and combustion applications.
- **Fitted to hydrocarbons, and accurate for hydrocarbons.** Polar and hydrogen-bonding fluids are represented only through ω, which cannot distinguish association from elongation, and hydrogen, whose acentric factor is negative, lies outside the regression range. Near-critical behaviour is unchanged, since the equation remains mean-field, and the quadratic mixing rule with a binary interaction parameter k_{ij} is

an additional fitted layer, not a consequence of Equation (9.1).

9.6 Transition to Chapter 10

Soave repaired the temperature dependence of the attraction and left its volume dependence exactly as Redlich and Kwong had written it. The consequence is visible above: Z_c is unchanged at $1/3$, and the liquid density, which depends on where the liquid root of the cubic falls, is unchanged with it. For vapour–liquid equilibrium that is tolerable, because K-values are governed by fugacity ratios rather than absolute densities; for custody transfer, pump and compressor sizing and reservoir volumetrics it is not, because those are calculations of mass in a known volume. Chapter 10 examines the modification made by Peng and Robinson in 1976: a change to the denominator of the attractive term, chosen so that Z_c falls to 0.3074.

Student handout: Chapter 9

Summary

- Soave (1972) replaced the guessed $T^{-1/2}$ of Redlich and Kwong by a function determined from experiment: $a(T) = a_c\alpha(T_r,\omega)$ with $\alpha = [1+m(1-\sqrt{T_r})]^2$ and $m = 0.480 + 1.574\omega - 0.176\omega^2$. The condition $\alpha(1)=1$ is imposed, not fitted, so T_c and P_c are still reproduced and the constants 0.42748 and 0.08664 are unchanged.
- The fitting procedure is: extract α point by point by forcing the isofugacity condition to reproduce the measured P^{sat}, observe that $\sqrt{\alpha}$ is linear in $\sqrt{T_r}$, and regress the resulting slopes m against ω. The construction is self-consistent: the acentric factor recovered from the predicted saturation curve matches the tabulated value to within 0.0003 for every species in §8 of the design specification.
- This is the point at which cubic equations of state became quantitative for vapour–liquid equilibrium, and therefore the point at which single-model process simulation of hydrocarbon systems became possible.
- The volume dependence was untouched, so $Z_c = 0.3333$ and liquid densities remain poor; α passes through zero and rises again at high T_r; polar, associating and quantum fluids are poorly served.

Key equations

$$P = \frac{RT}{V-b} - \frac{a_c\alpha(T_r,\omega)}{V(V+b)}, \qquad a_c = 0.42748\frac{R^2T_c^2}{P_c}, \quad b = 0.08664\frac{RT_c}{P_c} \tag{9.5}$$

$$\alpha = \left[1+m\left(1-\sqrt{T_r}\right)\right]^2, \qquad m = 0.480 + 1.574\,\omega - 0.176\,\omega^2, \qquad \alpha(1)=1 \tag{9.6}$$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0, \qquad A = \frac{a_c\alpha P}{R^2T^2}, \quad B = \frac{bP}{RT} \tag{9.7}$$

$$\ln\varphi = Z - 1 - \ln(Z-B) - \frac{A}{B}\ln\left(\frac{Z+B}{Z}\right) \tag{9.8}$$

Concept map

Redlich–Kwong has one universal temperature dependence and therefore one universal vapour pressure → molecular shape, entering as the rate at which thermal motion averages away the attraction → $a_c[1+m(1-\sqrt{T_r})]^2$ with $m(\omega)$ regressed against saturation data → liquid density still poor, Z_c still $1/3$, α unphysical at high T_r

Practice questions

1. Show that $\alpha(1)=1$ for any m, and explain why the condition must be imposed rather than fitted.
2. Show that $\sqrt{\alpha}$ is linear in $\sqrt{T_r}$ and that $(\mathrm{d}\alpha/\mathrm{d}T_r)|_{T_r=1} = -m$, and interpret m physically.
3. Describe how α was extracted from vapour-pressure data, naming the equilibrium condition used at each temperature.
4. Using §8 of the design specification, compute m and α for propane at 300 K, then Z and φ for the vapour at 10 bar from Equations (9.3) and (9.4). Verify $Z = 0.82515$ and $\varphi = 0.85120$.
5. Locate the minimum of the Soave alpha function for water and for a compound with $\omega = 1.0$, and explain why the behaviour beyond that temperature is unphysical.

Recommended references

- G. Soave, “Equilibrium constants from a modified Redlich–Kwong equation of state”, *Chem. Eng. Sci.* **27** (1972) 1197.
- B. E. Poling, J. M. Prausnitz and J. P. O’Connell, *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, 2001, Chapters 4 and 8.
- G. M. Kontogeorgis and G. K. Folas, *Thermodynamic Models for Industrial Applications*, Wiley, 2010, Chapter 3.

Chapter 10

Peng–Robinson and the industrial standard

10.1 Historical background

Ding-Yu Peng and Donald B. Robinson published *A new two-constant equation of state* in *Industrial and Engineering Chemistry Fundamentals* (**15** (1976) 59). They were working at the University of Alberta on natural gas systems, at a time when the Canadian gas industry required accurate phase and volumetric predictions for sour gas, gas condensate and enhanced-recovery calculations. Unlike their predecessors they stated their design objectives in advance: the parameters were to be expressible in terms of T_{c}, P_{c} and ω alone; the equation was to be accurate near the critical point, and in particular for the critical compressibility factor and the liquid density; the mixture form was to use a single binary interaction parameter; and one equation was to serve for all the properties needed in natural gas processing. The last two objectives were already met by Soave. The novelty lies in the second: where Soave had modified the temperature dependence of the attraction and left its volume dependence alone, Peng and Robinson modified the volume dependence.

10.2 Physical motivation

Chapter 9 closed on a specific defect. The Soave–Redlich–Kwong equation predicts vapour pressures well and liquid densities badly, and the two failures are independent because they are controlled by different parts of the equation. The vapour pressure is governed by the temperature dependence of the attraction, which Soave fitted; the liquid density is governed by where the smallest root of the cubic falls, which is governed by the volume dependence, which Soave did not touch. Consequently Z_{c} remained at $1/3$ and, as Chapter 9 recorded, the saturated liquid molar volume of propane at $T_{\mathrm{r}} = 0.7$ came out 13.3 % larger than the value obtained from the equation of this chapter. Against measured saturated liquid densities, documented in the standard property compilations, errors of order five to twenty percent are typical for the Soave form across the light hydrocarbons.

An error of that size is unimportant for a distillation calculation, which depends on ratios of fugacities, and unacceptable for three calculations ubiquitous in the oil and gas industry: custody transfer, which converts a measured volume into a mass or an energy content and is a commercial transaction; pump and compressor sizing; and reservoir volumetrics, which converts a pore volume into a quantity of oil in place. In each the answer is proportional to the density.

Physics introduced by Peng and Robinson

The mean-field attraction is given a volume dependence that falls off faster at liquid-like densities than either $1/V^2$ or $1/[V(V+b)]$, while remaining identical to both in the dilute limit. Physically this expresses the fact that in a dense fluid the attractive field experienced by a molecule saturates: once the first coordination shell is full, further compression adds little attractive energy but a great deal of repulsion. The mathematical consequence is a smaller predicted critical volume, $V_{\mathrm{c}} = 3.9514\,b$ with $Z_{\mathrm{c}} = 0.3074$ instead of 0.3333, and hence a liquid branch of the isotherm displaced inward toward realistic densities.

10.3 Mathematical development

The equation and its constants

The Peng–Robinson equation is

$$P = \frac{RT}{V-b} - \frac{a_{\mathrm{c}}\,\alpha(T_{\mathrm{r}},\omega)}{V(V+b)+b(V-b)}. \tag{10.1}$$

The denominator expands to $V^2+2bV-b^2$, which factorizes as

$$V^2+2bV-b^2=(V+\delta_1 b)\,(V+\delta_2 b)\,,\qquad \delta_1=1+\sqrt{2}=2.41421,\qquad \delta_2=1-\sqrt{2}=-0.41421. \tag{10.2}$$

This places Equation (10.1) in the same family as the equations of Chapters 3, 8 and 9, which correspond to $(\delta_1,\delta_2)=(0,0)$ and $(1,0)$ respectively. The alpha function has the Soave structure with a re-regressed coefficient:

$$\alpha(T_\mathrm{r},\omega)=\left[1+\kappa\left(1-\sqrt{T_\mathrm{r}}\right)\right]^2,\qquad \kappa=0.37464+1.54226\,\omega-0.26992\,\omega^2. \tag{10.3}$$

The re-regression is necessary rather than cosmetic: κ must compensate for the changed volume dependence in order to reproduce the same vapour pressures. For the species of §8 of the design specification, $\kappa=0.3931$ for methane, 0.6028 for propane, 0.7066 for carbon dioxide and 0.8746 for water.

Substituting $V=ZRT/P$ into Equation (10.1) and writing $A=a_\mathrm{c}\alpha P/(R^2T^2)$ and $B=bP/(RT)$ gives the dimensionless cubic

$$Z^3-(1-B)\,Z^2+\left(A-2B-3B^2\right)Z-\left(AB-B^2-B^3\right)=0. \tag{10.4}$$

Imposing a triple root at the critical point, that is matching Equation (10.4) to $(Z-Z_\mathrm{c})^3=0$, gives three relations exactly as in Chapter 8. The Z^2 coefficient now yields $Z_\mathrm{c}=(1-\Omega_b)/3$ rather than $1/3$, and eliminating Ω_a between the remaining two leaves

$$64\,\Omega_b^3+6\,\Omega_b^2+12\,\Omega_b-1=0, \tag{10.5}$$

whose only real root is $\Omega_b=0.0777961$. The other two constants follow immediately:

$$a_\mathrm{c}=0.45724\,\frac{R^2T_\mathrm{c}^2}{P_\mathrm{c}},\qquad b=0.07780\,\frac{RT_\mathrm{c}}{P_\mathrm{c}},\qquad Z_\mathrm{c}=0.30740,\qquad V_\mathrm{c}=3.9514\,b. \tag{10.6}$$

The value 0.3074 is not correct, since measured critical compressibility factors lie between roughly 0.23 and 0.29, but it is closer than 0.3333 and far closer than 0.375, and the improvement propagates down the whole liquid branch.

Key idea: two knobs, two failures, two repairs

A cubic equation of state of the form $P=RT/(V-b)-a_\mathrm{c}\alpha(T)/[(V+\delta_1 b)(V+\delta_2 b)]$ has exactly two independent degrees of design freedom. The function $\alpha(T)$ controls the temperature dependence and therefore the vapour pressure; the pair (δ_1,δ_2) controls the volume dependence and therefore Z_c and the liquid density. Soave repaired the first and Peng and Robinson the second. Nothing further of that kind remains to be done, which is why the development of cubic equations of state essentially stopped in 1976 and why the next advance, in Chapter 11, had to come from a different construction altogether.

The fugacity coefficient

Integrating $(Z-1)\,\mathrm{d}P/P$ along an isotherm as in Equation (1.3), with the general denominator of Equation (10.2), gives

$$\ln\varphi=Z-1-\ln(Z-B)-\frac{A}{B\,(\delta_1-\delta_2)}\ln\!\left(\frac{Z+\delta_1 B}{Z+\delta_2 B}\right), \tag{10.7}$$

and since $\delta_1-\delta_2=2\sqrt{2}$ for Equation (10.1),

$$\ln\varphi=Z-1-\ln(Z-B)-\frac{A}{2\sqrt{2}\,B}\ln\!\left(\frac{Z+\left(1+\sqrt{2}\right)B}{Z+\left(1-\sqrt{2}\right)B}\right). \tag{10.8}$$

For propane at 300 K and 10 bar, Equation (10.6) gives $b=56.308\,\mathrm{cm^3\,mol^{-1}}$, hence $A=0.183718$ and $B=0.022576$; the largest root of Equation (10.4) is $Z=0.81468$ and Equation (10.8) gives $\varphi=0.84215$, against $Z=0.82515$ and $\varphi=0.85120$ from Soave–Redlich–Kwong. Both fugacity coefficients agree to eight decimal places with direct numerical integration of $(Z-1)/P$ from zero pressure, which is the check every implementation should be made to pass before it is trusted.

10.4 Engineering interpretation

The effect on the liquid

The saturated liquid molar volume of propane predicted by Equation (10.1) is smaller than the Soave–Redlich–Kwong value by 11.4 % at $T_\mathrm{r} = 0.6$, 11.7 % at $T_\mathrm{r} = 0.7$, 11.9 % at $T_\mathrm{r} = 0.8$ and 11.6 % at $T_\mathrm{r} = 0.9$. The displacement is nearly uniform along the saturation line, which is the signature of a change in Z_c rather than in the temperature dependence, and it moves the prediction toward the measured values throughout.

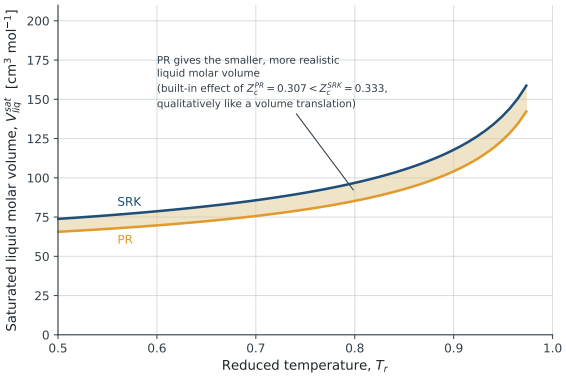

Figure 10.1: Saturated liquid molar volume of propane against reduced temperature from the Soave–Redlich–Kwong and Peng–Robinson equations. The Peng–Robinson branch lies below the Soave branch by close to twelve percent at every temperature, which is the direct consequence of $Z_\mathrm{c} = 0.3074$ against 0.3333.

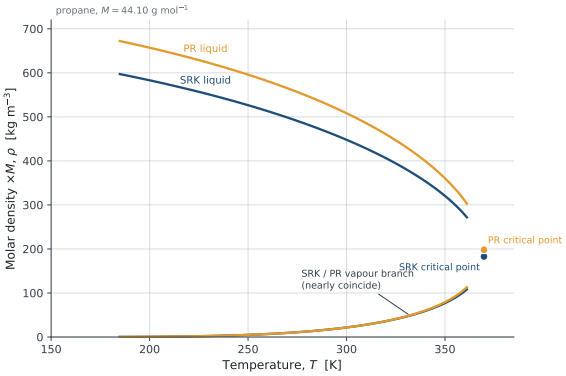

Figure 10.2: Density–temperature coexistence envelopes for propane from the two equations, with each model's own critical point marked. The vapour branches are almost indistinguishable; the liquid branches differ by roughly the ratio of the two critical compressibility factors.

The four equations compared

Model	Z_c	Vapour Z	Liquid density	Vapour pressure	Near-critical	Mixture capability	Computational cost
vdW (1873)	0.3750	poor	very poor	very poor	mean field	quadratic, no k_{ij}	one cubic
RK (1949)	0.3333	good	poor	poor	mean field	quadratic, no k_{ij}	one cubic
SRK (1972)	0.3333	good	poor	good	mean field	quadratic $+k_{ij}$	one cubic
PR (1976)	0.3074	good	fair	good	mean field	quadratic $+k_{ij}$	one cubic

The final column records that all four are cubics in Z, solved by the same closed-form or iterative procedure at the same cost, of the order of a microsecond per state point; no cubic equation of state has ever been rejected on grounds of expense. The comparison is displayed graphically in Figure 10.3, and its two constituent ingredients have already appeared: Figure 8.2 shows the vapour-phase improvement from van der Waals to Redlich–Kwong to Peng–Robinson, and Figure 8.1 shows the alpha functions that separate the

two-parameter from the three-parameter models. The entries for vapour pressure are quantitative rather than impressionistic: applying Equation (7.2) to each model's own saturation curve returns $\omega = -0.302$ for van der Waals and 0.058 for Redlich–Kwong, the same number for every substance, whereas Soave–Redlich–Kwong and Peng–Robinson return the tabulated acentric factor to within 0.0003 and 0.0025 respectively.

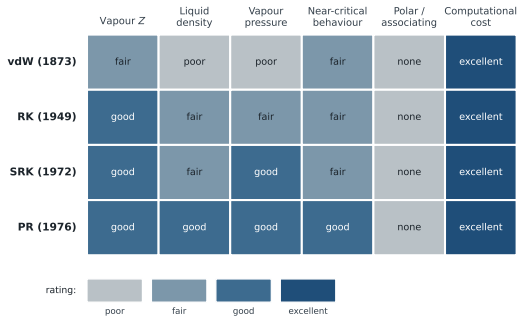

Figure 10.3: Qualitative comparison of the four classical cubic equations across the criteria that matter in process calculations. Shading runs from poor to good. The ratings are a pedagogical synthesis consistent with the quantitative comparisons computed elsewhere in this chapter, not a single numerical score.

Why Peng–Robinson became the industrial default

Four properties, taken together and not individually, account for the outcome.

Adequacy in both phases from one equation. Equation (10.1) is accurate enough for the vapour, adequate for the liquid, and consistent between them, so a single model supplies densities, enthalpies, entropies, fugacities and K-values for an entire flowsheet. Consistency matters more than accuracy here: a flash calculation using one model for the vapour and another for the liquid can violate the Gibbs phase rule outright.

Cost. A cubic has a closed-form solution and, more importantly, analytic derivatives: the Jacobian entries $(\partial \ln \varphi_i / \partial n_j)$ needed by every iterative equilibrium and energy balance follow in closed form from Equation (10.8), and a flowsheet may require millions of such evaluations.

Robust and well understood mixing rules. The van der Waals one-fluid rules, $a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - k_{ij})$ and $b = \sum_i x_i b_i$, require one binary parameter per pair, and large regressed banks of k_{ij} values exist for hydrocarbon, sour-gas and refrigerant systems. The behaviour of the model when a k_{ij} is set to zero is understood and usually tolerable for similar molecules.

Parameter availability. Equations (10.3) and (10.6) require only T_c, P_c and ω, which are tabulated for essentially every industrial compound and otherwise estimable by group contribution. No volumetric regression is needed to apply the model to a new substance, which is the decisive advantage over any model requiring compound-specific fitting.

The standard industrial patches

Two extensions are so widely implemented that they should be regarded as part of the working model rather than as refinements.

Volume translation (Peneloux, Rauzy and Freze, *Fluid Phase Equilib.* **8** (1982) 7) replaces the molar volume returned by the equation with $V^{\mathrm{corr}} = V - c$, where c is a constant fitted for each compound, usually to a single measured liquid density. Because the same constant shift is applied to both phases, it changes every fugacity by the same factor $\exp(cP/RT)$ and therefore leaves the saturation pressure and all K-values unchanged: it corrects the density without disturbing the phase equilibrium that the alpha function was fitted to reproduce.

Generalized alpha functions (Mathias and Copeman, *Fluid Phase Equilib.* **13** (1983) 91) replace the

single $\kappa(\omega)$ of Equation (10.3) by

$$\alpha = \left[1 + c_1\left(1 - \sqrt{T_\mathrm{r}}\right) + c_2\left(1 - \sqrt{T_\mathrm{r}}\right)^2 + c_3\left(1 - \sqrt{T_\mathrm{r}}\right)^3\right]^2, \tag{10.9}$$

with c_1, c_2 and c_3 regressed against the vapour-pressure curve of each compound individually (and $c_2 = c_3 = 0$ imposed above T_c to avoid the divergence of Chapter 9). This is the standard remedy for polar and associating fluids inside a cubic framework.

The cost of both patches is the same and should be stated plainly: each requires at least one additional parameter fitted to experimental data for each compound. The model is no longer predictive for a substance on which it has not been regressed, and the property that made the equation attractive in the first place, that three tabulated numbers suffice, has been given up.

10.5 Limitations

Limitations

- Z_c **is still wrong and still universal.** 0.3074 against a measured range of about 0.23 to 0.29. Liquid densities are improved but not solved, and volume translation repairs the symptom by fitting rather than the cause.
- **The equation contains no molecular structure, and therefore nothing is transferable.** The parameters a_c and b are properties of a substance, not of the groups composing it. Knowing the parameters of *n*-hexane tells one nothing about *n*-heptane that is not already contained in its critical constants, and there is no route from the molecular formula to the equation of state.
- **No chain connectivity.** A long chain molecule is represented by the same two constants as a small sphere. The physics of Chapter 6, that anisotropy grows with chain length, enters only through the single scalar ω inside $\alpha(T)$; the representation degrades steadily along a homologous series and fails for polymers, whose critical constants are not even measurable.
- **No hydrogen bonding and no electrostatics.** Association is short-ranged, strongly directional and saturable, and averaging it into a mean-field a/V^2-type term is qualitatively wrong; no alpha function can repair it. Water, alcohols, amines, acids and their mixtures are predicted poorly, and the errors are largest where they matter most, such as water content of natural gas and hydrate inhibition. Electrolytes lie outside the model entirely and require the treatment of Chapter 12.
- **Mean-field near the critical point, and mixtures resting on k_{ij}.** All cubic equations predict classical critical exponents and therefore the wrong shape of the coexistence curve close to T_c. The binary interaction parameters are fitted, are not transferable between models, and are often temperature-dependent, so predictions for systems with no regressed k_{ij} are extrapolations.

10.6 Transition to Chapter 11

The limitations above have a common structure. Every one is a consequence of the fact that a cubic equation of state describes a substance by two constants extracted from its critical point and therefore has no representation of what the molecule actually is. Chain length, branching, functional groups, directional bonding and charge are all invisible to Equation (10.1), and can be introduced only by adding fitted parameters, one substance at a time.

The alternative is to build the equation from the molecule outward: to start from a reference fluid of hard spheres whose thermodynamics is known accurately, bond those spheres into chains, add dispersion between segments as a perturbation, and add association as a separate, directional, saturable interaction. The resulting parameters are properties of segments rather than of substances, and are therefore transferable along homologous series and estimable for molecules never measured. Chapter 11 develops that construction, the statistical associating fluid theory, from Wertheim's thermodynamic perturbation theory of 1984 to 1986 through the original SAFT of 1990 and the PC-SAFT form of 2001.

Student handout: Chapter 10

Summary

- Soave repaired the temperature dependence of the attraction; Peng and Robinson (1976) repaired its volume dependence, replacing $V(V+b)$ by $V(V+b)+b(V-b)=(V+\delta_1 b)(V+\delta_2 b)$ with $\delta_1=1+\sqrt{2}$ and $\delta_2=1-\sqrt{2}$.
- Imposing a triple root gives $Z_\mathrm{c}=(1-\Omega_b)/3=0.30740$, with $\Omega_b=0.077796$ the real root of $64\Omega_b^3+6\Omega_b^2+12\Omega_b-1=0$, hence $a_\mathrm{c}=0.45724R^2T_\mathrm{c}^2/P_\mathrm{c}$ and $b=0.07780RT_\mathrm{c}/P_\mathrm{c}$; κ is re-regressed to $0.37464+1.54226\omega-0.26992\omega^2$.
- Saturated liquid volumes of propane fall roughly twelve percent below the Soave–Redlich–Kwong values at every reduced temperature, essentially the ratio of the two critical compressibility factors.
- Peng–Robinson became the industrial default because one cubic serves both phases adequately, costs almost nothing to evaluate, has robust one-fluid mixing rules with a single k_{ij}, and needs only T_c, P_c and ω, which are tabulated almost universally.
- Volume translation (Peneloux, 1982) corrects densities without changing K-values; Mathias–Copeman alpha functions (1983) extend the model to polar fluids. Both cost at least one fitted parameter per compound and sacrifice predictiveness.
- What remains is structural: no molecular architecture, hence no transferability, no chain connectivity, no hydrogen bonding, no electrostatics, and mean-field critical behaviour.

Key equations

$$P=\frac{RT}{V-b}-\frac{a_\mathrm{c}\alpha(T_\mathrm{r},\omega)}{V(V+b)+b(V-b)},\qquad \alpha=\left[1+\kappa\left(1-\sqrt{T_\mathrm{r}}\right)\right]^2 \tag{10.10}$$

$$a_\mathrm{c}=0.45724\frac{R^2T_\mathrm{c}^2}{P_\mathrm{c}},\quad b=0.07780\frac{RT_\mathrm{c}}{P_\mathrm{c}},\quad \kappa=0.37464+1.54226\omega-0.26992\omega^2 \tag{10.11}$$

$$Z^3-(1-B)Z^2+\left(A-2B-3B^2\right)Z-\left(AB-B^2-B^3\right)=0,\quad Z_\mathrm{c}=0.30740 \tag{10.12}$$

$$\ln\varphi=Z-1-\ln(Z-B)-\frac{A}{2\sqrt{2}B}\ln\left(\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right) \tag{10.13}$$

Concept map

Soave predicts vapour pressure well but liquid density badly, and density is money $\rightarrow$ an attractive field that saturates at liquid densities, encoded in the volume dependence $\rightarrow$ denominator $V(V+b)+b(V-b)$, $Z_\mathrm{c}=0.3074$, $\kappa(\omega)$ re-regressed $\rightarrow$ no molecular structure, hence no transferability, no chain connectivity and no association

Practice questions

1. Verify Equation (10.2) by expanding the product, and state the values of δ_1 and δ_2 for the van der Waals, Redlich–Kwong and Peng–Robinson equations.
2. Derive Equation (10.4) from Equation (10.1), then obtain $Z_\mathrm{c}=(1-\Omega_b)/3$ and the cubic satisfied by Ω_b by imposing a triple root.
3. Explain why $\kappa(\omega)$ had to be re-regressed rather than taken over from Soave, given that both alpha functions have identical algebraic form.
4. Using §8 of the design specification, compute A, B, Z and φ for propane vapour at 300 K and 10 bar. Verify $A=0.183718$, $B=0.022576$, $Z=0.81468$ and $\varphi=0.84215$, and check $\ln\varphi$ by numerical integration of $(Z-1)/P$.
5. Show that a Peneloux volume translation $V\rightarrow V-c$ applied to both phases leaves the predicted saturation pressure of a pure fluid unchanged, and state the practical price of the correction.

Recommended references

- D.-Y. Peng and D. B. Robinson, “A new two-constant equation of state”, *Ind. Eng. Chem. Fundam.* **15** (1976) 59.
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Chapter 11

SAFT: statistical associating fluid theory

11.1 Historical background

Between 1984 and 1986 Michael Wertheim published four papers in the *Journal of Statistical Physics* (**35** (1984) 19; **35** (1984) 35; **42** (1986) 459; **42** (1986) 477) on fluids with highly directional attractive forces. The problem he solved is one the cluster expansion of Chapter 5 handles very badly: if the attraction is short-ranged and confined to a small solid angle, so that a bonded site is sterically prevented from bonding again, the Mayer function is large over a tiny region of configuration space and small everywhere else, every virial coefficient is dominated by the same few graphs, and truncation is useless. Wertheim reorganized the expansion in terms of the fractions of molecules bonded at each site, showed that steric saturation eliminates whole classes of graphs, and resummed what remained. Truncating at the first order in which a site may take only one bond gives first-order thermodynamic perturbation theory, TPT1, from which two results follow directly: the free energy of an associating fluid, and, in the limit where association becomes a permanent bond, that of a chain of tangent spheres.

Wertheim's papers contain no engineering application. Walter Chapman, Keith Gubbins, George Jackson and Maciej Radosz supplied that in *New reference equation of state for associating liquids* (*Ind. Eng. Chem. Res.* **29** (1990) 1709), assembling the chain and association results with a hard-sphere reference and a dispersion term into one closed-form model with a small number of molecular parameters. The third step is due to Joachim Gross and Gabriele Sadowski (*Ind. Eng. Chem. Res.* **40** (2001) 1244). The original SAFT perturbs about a fluid of free hard spheres, which is the wrong reference for a chain molecule because the segments of a chain are not free; Gross and Sadowski perturbed about the hard-*chain* fluid instead, so that the dispersion term already knows the connectivity of the molecule it belongs to. This is perturbed-chain SAFT, PC-SAFT, the form most widely used in industry.

11.2 Physical motivation

Chapter 10 closed on a structural rather than a numerical objection: a cubic equation describes a substance by two constants extracted from its critical point and therefore contains no representation of what the molecule is. The remedy is a different starting point, not another algebraic patch.

That starting point is the observation that the residual Helmholtz energy is additive over physically distinct interactions in a way that pressure is not. Begin with a fluid of hard spheres, whose thermodynamics is known accurately; then bond the spheres into chains, switch on dispersion between segments, and switch on short-range directional bonding at specific sites. Each step changes the free energy by a computable amount, and the changes add, because free energy is a thermodynamic potential and each step is a perturbation about the previous result. Pressure inherits no such decomposition: one cannot write the pressure contribution of hydrogen bonding without first writing its free energy.

Key idea: the direction of the construction is reversed

Every equation of state in Chapters 3 to 10 is written as $P(V,T)$, and all other properties follow by integration. SAFT is written as $a^{\mathrm{res}}(T,\rho)$, and all others, including the pressure, follow by differentiation:

$$P = \rho^2 \left(\frac{\partial a^{\mathrm{res}}}{\partial \rho}\right)_T + \rho RT, \qquad Z = 1 + \rho \left(\frac{\partial \tilde{a}^{\mathrm{res}}}{\partial \rho}\right)_T, \qquad \tilde{a}^{\mathrm{res}} \equiv \frac{a^{\mathrm{res}}}{RT}, \tag{11.1}$$

with ρ the molar density. The second term is the ideal-gas contribution, since the ideal-gas molar Helmholtz energy contains $RT\ln\rho$. The model can therefore be assembled from separately derived physical pieces, and the result is not cubic and not solvable in closed form.

11.3 Mathematical development

The residual Helmholtz energy is a sum of four terms,

$$\tilde{a}^{\mathrm{res}} = \tilde{a}^{\mathrm{hs}} + \tilde{a}^{\mathrm{chain}} + \tilde{a}^{\mathrm{disp}} + \tilde{a}^{\mathrm{assoc}}, \tag{11.2}$$

the first two constituting the hard-chain reference $\tilde{a}^{\mathrm{hc}} = \tilde{a}^{\mathrm{hs}} + \tilde{a}^{\mathrm{chain}}$. The construction is shown stage by stage in Figure 11.1.

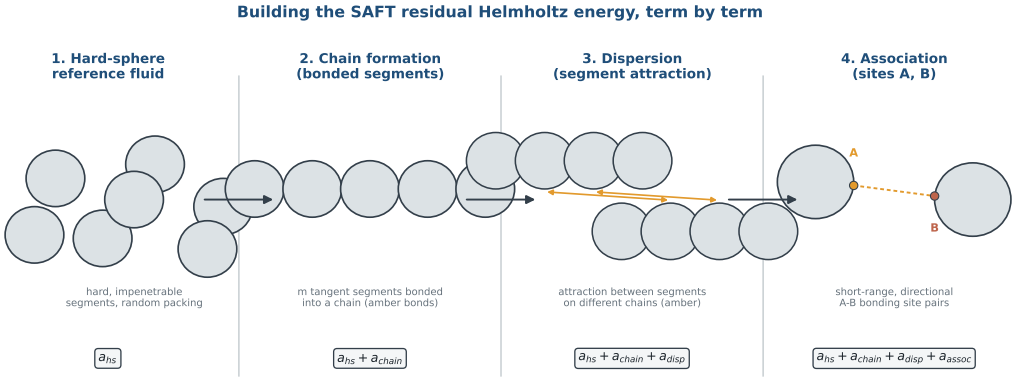

Figure 11.1: Schematic of the SAFT construction in four stages: a hard-sphere reference fluid, bonding of m tangent segments into a chain, dispersion between segments, and directional bonding at sites A and B. Amber marks the physics added at each stage. The diagram is schematic and carries no numerical content.

Hard spheres: excluded volume done correctly

The reference is a fluid of m hard spheres per molecule of effective diameter $d(T)$, at packing fraction η, with the Carnahan–Starling free energy:

$$\eta = \frac{\pi}{6}\rho_N m d^3, \quad d(T) = \sigma\left[1 - 0.12\,\mathrm{e}^{-3\varepsilon/kT}\right], \quad \tilde{a}^{\mathrm{hs}} = m\frac{4\eta - 3\eta^2}{(1-\eta)^2}, \quad Z^{\mathrm{hs}} = 1 + m\frac{4\eta - 2\eta^2}{(1-\eta)^3}, \tag{11.3}$$

where ρ_N is the number density of molecules. The diameter is temperature-dependent because a real repulsive wall is steep but not vertical, and a Barker–Henderson mapping onto an equivalent hard sphere gives a diameter that shrinks slightly on heating.

Two checks establish that this is the excluded volume of Chapter 3 done properly rather than guessed. Expanding at low density gives $\tilde{a}^{\mathrm{hs}}/m = 4\eta + 5\eta^2 + 6\eta^3 + \cdots$, and for a single sphere ($m = 1$) $Z^{\mathrm{hs}} = 1 + 4\eta + 10\eta^2 + 18\eta^3 + \cdots$, so the second and third hard-sphere virial coefficients are exact and the fourth, predicted as 18, is within about two percent of the value 18.365 obtained by numerical evaluation of the cluster integrals (Hansen and McDonald, *Theory of Simple Liquids*). Second, the leading term is $4\eta = \frac{2}{3}\pi\rho_N\sigma^3$ for $m = 1$ and $d = \sigma$, exactly $\rho_N b$ with the van der Waals co-volume of Equation (3.1). The term $RT/(V-b)$ is therefore the first term of Equation (11.3) and nothing more; it fails at liquid densities because it omits every subsequent term, and Equation (11.3) does not.

Chain: connectivity replaces the acentric factor

Wertheim's chain result, in the limit of complete bonding, is

$$\tilde{a}^{\mathrm{chain}} = (1-m)\ln g^{\mathrm{hs}}(d), \qquad g^{\mathrm{hs}}(d) = \frac{1 - \eta/2}{(1-\eta)^3}, \tag{11.4}$$

with $g^{\mathrm{hs}}(d)$ the hard-sphere radial distribution function at contact. Forming a bond removes a translational degree of freedom and raises the free energy, but the cost is reduced in proportion to the probability that

the two segments were already in contact, which is what $g^{\mathrm{hs}}(d)$ measures. Since $m > 1$ and $g^{\mathrm{hs}} > 1$ the term is negative and grows with chain length and density; at low density it contributes $Z^{\mathrm{chain}} \to \frac{5}{2}(1-m)\eta$, so a chain is more compressible than the same number of free spheres. This term carries the physics that Chapters 6 and 7 could only summarize in one scalar: the acentric factor measures a *consequence* of elongation, extracted from the vapour-pressure curve, whereas m is the elongation itself.

Dispersion: a perturbation series instead of $a\alpha(T)$

The attraction is a perturbation about the hard-chain reference, expanded in inverse temperature and truncated at second order:

$$\tilde{a}^{\mathrm{disp}} = -2\pi\rho_N I_1(\eta,m)\, m^2 \frac{\varepsilon}{kT}\sigma^3 - \pi\rho_N m C_1 I_2(\eta,m)\, m^2 \left(\frac{\varepsilon}{kT}\right)^2 \sigma^3, \quad C_1 = \left[1 + Z^{\mathrm{hc}} + \rho_N \frac{\partial Z^{\mathrm{hc}}}{\partial \rho_N}\right]^{-1}, \tag{11.5}$$

where I_1 and I_2 are power series in η whose coefficients depend on m through a set of universal constants, regressed once against pure-component data for the n-alkane series and used unchanged for every substance: they are properties of the perturbation theory, not of the fluid. In PC-SAFT the reference is the hard chain, so I_1 and I_2 carry m explicitly; in the SAFT of 1990 the reference is the hard-sphere fluid and the chain enters only through Equation (11.4), which is why PC-SAFT represents long-chain and polymeric fluids appreciably better. Contrast the cubic route, whose attractive term has a temperature dependence fitted to vapour pressures and a volume dependence chosen to place Z_{c} conveniently: in Equation (11.5) neither is fitted per substance.

Association: physics no cubic equation contains

Hydrogen bonding is short-ranged, strongly directional and saturable: a hydroxyl proton donates one bond and not two. Averaging such an interaction into a mean field is not an approximation but a category error, because the mean field has no mechanism for saturation. Wertheim's TPT1 result is

$$\tilde{a}^{\mathrm{assoc}} = \sum_A \left[\ln X^A - \frac{X^A}{2}\right] + \frac{M}{2}, \qquad X^A = \left[1 + \rho_N \sum_B X^B \Delta^{AB}\right]^{-1}, \tag{11.6}$$

where the sum runs over the M association sites and X^A is the fraction of sites of type A that are *not* bonded. The association strength is

$$\Delta^{AB} = g^{\mathrm{hs}}(d)\, \kappa^{AB} \left[\exp\left(\frac{\varepsilon^{AB}}{kT}\right) - 1\right], \tag{11.7}$$

whose three factors are the three physical ingredients: $g^{\mathrm{hs}}(d)$ is the probability that the molecules are in contact at all, κ^{AB} is the fraction of solid angle over which the sites can find each other, and the Boltzmann factor is the energetic reward, written so that it vanishes when the bond energy does. When κ^{AB} is a dimensionless association volume, Δ^{AB} carries an additional factor σ^3.

Equation (11.6) is implicit and must be solved iteratively at every state point, which is the principal reason a SAFT evaluation is expensive. For one donor site A and one acceptor site B per molecule with like-site bonding forbidden, symmetry gives $X^A = X^B = X$ and the system collapses to $\rho_N\Delta X^2 + X - 1 = 0$, with root

$$X = \frac{-1 + \sqrt{1 + 4\rho_N\Delta}}{2\rho_N\Delta}, \qquad \tilde{a}^{\mathrm{assoc}} = 2\ln X - X + 1. \tag{11.8}$$

Its behaviour is the behaviour required. As $\rho_N\Delta \to 0$, $X \to 1$ and $\tilde{a}^{\mathrm{assoc}} \to 0$: dilute or hot, nothing is bonded and the term disappears. As $\rho_N\Delta \to \infty$, $X \to (\rho_N\Delta)^{-1/2} \to 0$: dense and cold, everything is bonded, but X cannot fall below zero, so the free-energy reward saturates. No function of V and T multiplying $1/V^2$ can reproduce that.

Physics introduced by SAFT

Three pieces of molecular physics enter which no cubic equation contains. *Excluded volume as a function of density*, through the Carnahan–Starling term, in place of the constant b. *Chain connectivity*, through $(1-m)\ln g^{\mathrm{hs}}$, in place of the scalar ω inside an alpha function. *Directional, saturable association*, through the site balance of Equation (11.6), which has no counterpart at all in the cubic family. The price is that the model is a free energy and must be differentiated, and that the association balance must be solved iteratively at each state point.

The parameters and their transferability

A non-associating molecule requires three parameters, the segment number m, diameter σ and energy ε/k; an associating molecule requires ε^{AB}/k and κ^{AB} as well, together with an association scheme stating how many sites of each type the molecule carries and which pairs may bond. All are regressed against pure-component vapour pressures and saturated liquid densities.

The decisive property is the behaviour along a homologous series. For the n-alkanes, m grows almost linearly with carbon number while σ and ε/k remain nearly constant, which is what the construction predicts, because those two describe a methylene segment and the segment does not change when the chain is lengthened. As an order-of-magnitude illustration rather than a quoted regression result, a molecule such as n-decane is represented by a segment number of roughly four, fewer segments than it has carbon atoms, since a SAFT segment is a coarse-grained interaction centre and not an atom. The parameters can therefore be interpolated, extrapolated and estimated by group contribution. Polymers make the point sharply: a polymer has no measurable T_{c}, P_{c} or ω, because it decomposes long before reaching its critical point, so the cubic family is not merely inaccurate for polymers but inapplicable, whereas m, σ and ε/k follow by extrapolating the oligomer series with m proportional to molar mass.

11.4 Engineering interpretation

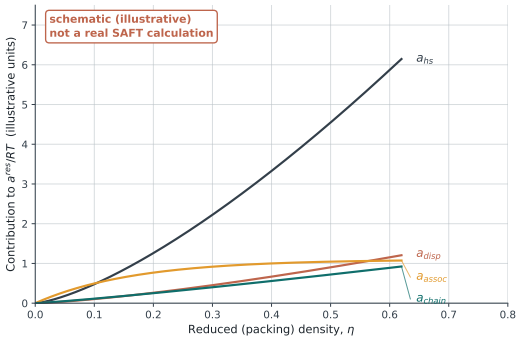

Figure 11.2: Schematic decomposition of the residual Helmholtz energy into its four contributions against packing fraction. The figure is explicitly labelled illustrative and is not the output of a SAFT implementation; it shows the qualitative ordering only.

Three features of Figure 11.2 follow from the equations rather than from the drawing. The hard-sphere term diverges as $\eta \to 1$, from the $(1-\eta)^{-2}$ factor in Equation (11.3); the chain term is negative and grows only logarithmically, so it never competes with the repulsion at high density; and the association term rises steeply at low density, because Δ^{AB} is exponential in ε^{AB}/kT and hydrogen-bond energies are an order of magnitude larger than kT, then flattens as the sites are used up.

Associating fluids. Water, alcohols, amines, glycols, acids and their mixtures with hydrocarbons are the systems on which cubic equations fail worst and on which the association term acts directly. The characteristic signatures, a saturated liquid density much higher than a non-associating fluid of the same molar mass, a much lower vapour pressure, and strongly non-ideal liquid–liquid behaviour with hydrocarbons, all follow from $\tilde{a}^{\mathrm{assoc}}$, so a single pair $(\varepsilon^{AB}/k, \kappa^{AB})$ corrects them together, as indicated schematically in Figure 11.3.

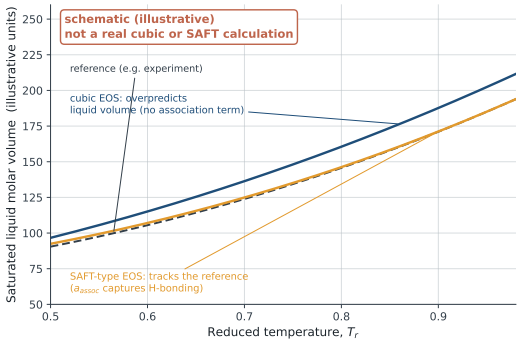

Figure 11.3: Schematic and explicitly illustrative comparison of the saturated liquid molar volume of an associating fluid. The cubic equation, having no association term, overpredicts the volume; a molecular equation carrying $\tilde{a}^{\text{assoc}}$ tracks the reference. The curves are not computed from either model.

Polymers and mixtures. Solvent solubility in polymers and polymer solution phase diagrams are calculations a cubic equation cannot attempt and which extrapolation of m makes routine. The mixture extension uses conventional combining rules, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}(1 - k_{ij})$, so a binary interaction parameter survives, generally smaller than the cubic k_{ij} for the same pair because more of the physics is already in the pure-component terms. Cross-association is handled by the same site balance, which is how a SAFT model predicts the mutual solubility of water and a hydrocarbon.

11.5 Limitations

Limitations

- **Five or more parameters per component, all regressed.** A cubic equation needs T_c, P_c and ω, tabulated for essentially every industrial compound. SAFT needs m, σ, ε/k and, for associating species, ε^{AB}/k, κ^{AB} and an assumed scheme, none of which is a measurable property. For a new compound with no vapour pressure or density data the model is not directly applicable.
- **Computational cost of roughly an order of magnitude.** There is no closed-form density: Equation (11.1) must be inverted numerically for ρ, and at every trial density the association balance must itself be solved iteratively, except in the few schemes reducing to Equation (11.8). Analytic derivatives exist but are long.
- **Non-uniqueness of the regressed parameters.** The objective function is flat along certain directions, notably m and ε/k (a longer chain of weaker segments resembles a shorter chain of stronger segments) and ε^{AB}/k and κ^{AB} (a deep narrow site resembles a shallow wide one), so different laboratories publish different sets that fit the same data equally well and extrapolate differently. Published parameters must be used with the mixing rules and scheme for which they were fitted.
- **The critical region is still mean-field.** The expansion is truncated at low order and contains no long-wavelength density fluctuations, so critical exponents are classical and the critical point is over-predicted, typically more severely than by a cubic equation, which is fitted to the critical point by construction.
- **No electrostatics.** A dissolved salt, an ionic liquid and a loaded aqueous amine all lie outside Equation (11.2): the Coulomb interaction is not short-ranged and cannot be absorbed into a dispersion or association term.

11.6 Transition to Chapter 12

One entry in that list is different in kind. The parameter count, the computational cost and the non-uniqueness are prices paid for physics that is present, and the mean-field critical region is a known deficiency of a truncated series; the absence of electrostatics is an omission of physics, of exactly the kind each preceding chapter identified in its predecessor. It cannot be repaired inside Equation (11.2), because of the range of the interaction. Dispersion falls off as r^{-6} and association is confined to contact, so both are local perturbations about a reference fluid, whereas the Coulomb interaction falls off as r^{-1}: at three molecular diameters, dispersion has fallen by a factor of $3^6 = 729$ while the Coulomb energy has

fallen only by a factor of three. An ion therefore interacts appreciably with hundreds of neighbours, and the pairwise expansion underlying Equation (11.5) does not converge. Chapter 12 develops the required treatment, which handles the long-range part collectively and accounts for the large free energy of placing a charge in a polar solvent.

Student handout: Chapter 11

Summary

- Wertheim (1984–1986) resummed the cluster expansion for short-range directional attraction; truncation at one bond per site gives TPT1, which yields both the association and the chain free energies. Chapman, Gubbins, Jackson and Radosz (1990) made it an engineering equation of state, and Gross and Sadowski (2001) perturbed about the hard chain rather than the hard sphere, giving PC-SAFT.
- The conceptual break is the direction of construction: a cubic writes $P(V,T)$ directly, whereas SAFT builds $a^{\mathrm{res}}(T,\rho)$ as a sum of separable contributions and obtains P by differentiation. Free energies add; pressures do not decompose.
- The four terms: hard sphere (Carnahan–Starling, excluded volume as a function of density rather than the constant b), chain ($(1-m)\ln g^{\mathrm{hs}}$, connectivity in place of ω), dispersion (a perturbation series in ε/kT in place of $a\alpha(T)$), and association (Wertheim site balance, directional saturable hydrogen bonding, absent from every cubic equation).
- The parameters m, σ, ε/k describe segments, not substances: along the n-alkanes m grows almost linearly with carbon number while σ and ε/k stay nearly constant, which is why SAFT extrapolates to polymers, for which T_{c}, P_{c} and ω do not exist and cubic equations are inapplicable rather than merely inaccurate.
- What remains: five or more regressed parameters per component, roughly an order of magnitude more computation, non-unique parameter sets, a mean-field and over-predicted critical point, and no electrostatics.

Key equations

$$\tilde{a}^{\mathrm{res}} = \tilde{a}^{\mathrm{hs}} + \tilde{a}^{\mathrm{chain}} + \tilde{a}^{\mathrm{disp}} + \tilde{a}^{\mathrm{assoc}}, \qquad Z = 1 + \rho\left(\frac{\partial \tilde{a}^{\mathrm{res}}}{\partial \rho}\right)_T \tag{11.9}$$

$$\tilde{a}^{\mathrm{hs}} = m\,\frac{4\eta - 3\eta^2}{(1-\eta)^2}, \quad \eta = \frac{\pi}{6}\rho_N m d^3, \quad \tilde{a}^{\mathrm{chain}} = (1-m)\ln g^{\mathrm{hs}}(d), \quad g^{\mathrm{hs}} = \frac{1-\eta/2}{(1-\eta)^3} \tag{11.10}$$

$$\tilde{a}^{\mathrm{assoc}} = \sum_A \left[\ln X^A - \frac{X^A}{2}\right] + \frac{M}{2}, \qquad X^A = \left[1 + \rho_N \sum_B X^B \Delta^{AB}\right]^{-1} \tag{11.11}$$

$$\Delta^{AB} = g^{\mathrm{hs}}(d)\,\kappa^{AB}\left[\exp\left(\varepsilon^{AB}/kT\right) - 1\right] \tag{11.12}$$

Concept map

A cubic knows nothing about the molecule, so nothing transfers and association is invisible → excluded volume at all densities, chain connectivity, segment dispersion, and directional saturable bonding → a^{res} built as a sum of perturbation terms with P obtained by differentiation → five regressed parameters, iterative solution, non-unique fits, mean-field critical point, no charge

Practice questions

1. Derive Equation (11.1) from $P = -(\partial A/\partial V)_{T,n}$, and explain why an additive decomposition is available for a^{res} but not for P.
2. Expand $\tilde{a}^{\mathrm{hs}}$ and Z^{hs} to third order in η for $m = 1$. Confirm the hard-sphere virial coefficients 4, 10 and 18, and show that the leading term reproduces the van der Waals co-volume of Equation (3.1).
3. Show that $\tilde{a}^{\mathrm{chain}}$ contributes $Z^{\mathrm{chain}} \to \frac{5}{2}(1-m)\eta$ at low density, and interpret the sign.
4. For the two-site scheme, derive Equation (11.8) from Equation (11.6), examine the limits $\rho_N\Delta \to 0$ and $\rho_N\Delta \to \infty$, and explain why a mean-field attraction cannot reproduce the second.
5. Explain why m, σ and ε/k transfer along a homologous series while a_{c} and b do not, and why this makes SAFT applicable to polymers.

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Chapter 12

Electrolyte equations of state

12.1 Historical background

The thermodynamics of ionic solutions developed for a century almost in isolation from the equation-of-state tradition of Chapters 3 to 11. Peter Debye and Erich Hückel published their theory of the ionic atmosphere in 1923, obtaining the limiting law that bears their names from a linearized Poisson–Boltzmann treatment of a charge surrounded by a diffuse cloud of counter-ions; Max Born had given, in 1920, the free energy of transferring a charged sphere from vacuum into a dielectric continuum. Kenneth Pitzer, in the 1970s, produced a virial-like expansion in molality with ion-specific coefficients which remains the standard for geochemical and brine calculations, and Chen and co-workers in the 1980s produced the electrolyte NRTL model. All of these are activity-coefficient models: they describe the liquid phase alone, at specified T and P, and say nothing about density, the vapour phase, or supercritical behaviour.

The merger came late. Once SAFT provided a framework in which the residual Helmholtz energy is assembled from separable contributions, adding electrostatics became a matter of adding summands to Equation (11.2) rather than of building a new model. The electrolyte variants of SAFT, of which ePC-SAFT (Held, Reschke, Mohammad, Luza and Sadowski, *Chem. Eng. Res. Des.* **92** (2014) 2884) and eSAFT-VR are the most widely used, date from the first decade of this century and are still developing.

12.2 Physical motivation

The industrial motivation is not narrow: carbon dioxide capture with amines, produced water, gas hydrates with inhibitors, hydrometallurgy, desalination, geothermal energy and lithium-ion battery electrolytes are all ionic systems, and in each case the engineering question requires phase equilibrium and density from the same model.

The physical difficulty is the range of the interaction, as anticipated at the end of Chapter 11. A convenient measure of that range is the Bjerrum length, the separation at which the Coulomb energy of two elementary charges equals kT,

$$\ell_{\mathrm{B}} = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 kT}, \tag{12.1}$$

which for water at 298.15 K with $\varepsilon_r = 78.4$ evaluates to 0.715 nm, two to three molecular diameters. Beyond that separation thermal motion dominates the interaction of any individual pair, but the interaction does not become negligible: it is merely shared among a large number of neighbours. A pairwise perturbation expansion of the kind used in Equation (11.5) therefore does not converge, and the long-range part must be handled collectively.

Physics introduced by electrolyte equations of state

Four contributions are added to the residual Helmholtz energy of Chapter 11. *Ion–ion electrostatics*, treated collectively through the screening of each charge by the ionic atmosphere around it (Debye–Hückel, or the mean spherical approximation for ions of finite size). *Ion–solvent solvation*, through the Born free energy of charging an ion in a dielectric medium. *Hydration*, through the composition dependence of the dielectric constant and the removal of solvent into bound coordination shells. *Ion pairing*, treated as chemical association by the site-balance machinery of Equation (11.6). The first is long-ranged, the second is enormous in magnitude, and the third and fourth are what make the model work above about one molal.

12.3 Mathematical development

The electrolyte equation of state extends Equation (11.2) by addition:

$$\tilde{a}^{\mathrm{res}} = \underbrace{\tilde{a}^{\mathrm{hs}} + \tilde{a}^{\mathrm{chain}} + \tilde{a}^{\mathrm{disp}} + \tilde{a}^{\mathrm{assoc}}}_{\text{Chapter 11}} + \underbrace{\tilde{a}^{\mathrm{DH/MSA}} + \tilde{a}^{\mathrm{Born}} + \tilde{a}^{\mathrm{hyd}}}_{\text{electrostatics}}, \tag{12.2}$$

the physical origin of each electrostatic term being shown in Figure 12.1.

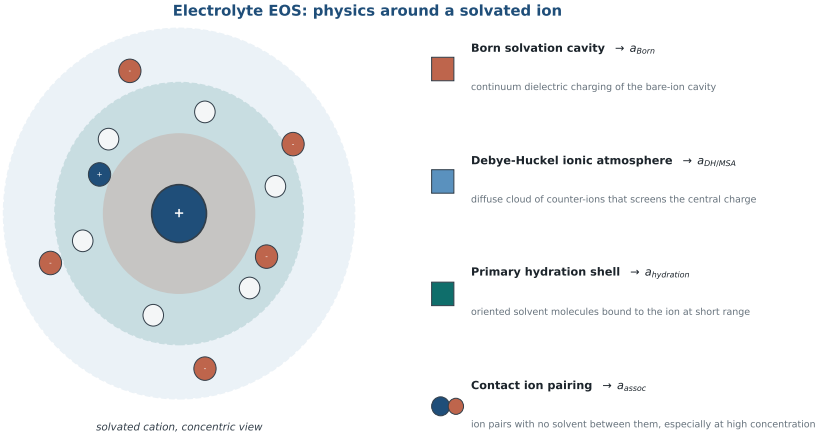

Figure 12.1: Schematic of the environment of a solvated cation: the Born solvation cavity, the diffuse Debye–Hückel ionic atmosphere, the primary hydration shell and a contact ion pair, each labelled with the Helmholtz contribution it generates. The diagram is schematic and carries no numerical content.

Long-range ion–ion electrostatics

Solving the linearized Poisson–Boltzmann equation for a point charge in a continuum of permittivity $\varepsilon_r\varepsilon_0$ gives a screened Coulomb potential $\propto r^{-1}\exp(-\kappa r)$, whose decay length is the Debye length:

$$\kappa^{-1} = \left(\frac{\varepsilon_r\varepsilon_0 kT}{e^2\sum_i \rho_i z_i^2}\right)^{1/2}, \qquad \log_{10}\gamma_\pm = -A\,|z_+z_-|\,\sqrt{I}, \qquad I = \tfrac{1}{2}\sum_i m_i z_i^2, \tag{12.3}$$

with ρ_i the number density of ion i and z_i its valence. Charging the ions reversibly in that atmosphere gives $\tilde{a}^{\mathrm{DH}}$, and differentiating with respect to ion number gives the limiting law shown on the right, with $A = 0.509$ in units of $(\mathrm{kg\,mol^{-1}})^{1/2}$ for water at 298.15 K (the corresponding constant on a natural-logarithm basis is $\ln(10)\times 0.509 = 1.172$).

The word *limiting* must be taken literally: the law is exact as $I \to 0$ and in no other circumstance, because its derivation assumes point ions, a linearized Boltzmann factor and a structureless solvent of fixed permittivity. Evaluating the Debye length for a 1:1 aqueous salt at 298.15 K shows how quickly those assumptions fail: $\kappa^{-1} = 9.61\,\mathrm{nm}$ at $1\,\mathrm{mmol\,L^{-1}}$, 3.04 nm at $10\,\mathrm{mmol\,L^{-1}}$, 0.96 nm at $0.1\,\mathrm{mol\,L^{-1}}$ and 0.30 nm at $1\,\mathrm{mol\,L^{-1}}$. At one molar the screening length has fallen below the diameter of a hydrated ion, so the atmosphere is no longer a diffuse cloud and the continuum picture has no domain of validity left. The standard repair is the mean spherical approximation, an analytic solution of the Ornstein–Zernike equation for charged hard spheres, which retains the collective screening but gives the ions a finite diameter; it reduces to Debye–Hückel as the diameters go to zero and is the form used in most electrolyte equations of state, because a diameter is already available from the SAFT segment parameters.

Ion–solvent solvation: the Born term

Debye–Hückel describes ions interacting with each other. It says nothing about the free energy of putting an ion into the solvent in the first place, which is the largest single number in the problem. Born's result for

charging a sphere of radius r_i in a dielectric continuum, relative to charging it in vacuum, is

$$A^{\mathrm{Born}} = -\frac{N_A e^2}{8\pi\varepsilon_0} \sum_i x_i z_i^2 \frac{1 - 1/\varepsilon_r}{r_i}. \tag{12.4}$$

Its magnitude is decisive. For a monovalent ion of radius 0.15 nm in water at 298.15 K with $\varepsilon_r = 78.4$, Equation (12.4) gives $-457\,\mathrm{kJ\,mol^{-1}}$ against $RT = 2.48\,\mathrm{kJ\,mol^{-1}}$, and it scales as z_i^2, so a divalent ion of the same radius is at $-1829\,\mathrm{kJ\,mol^{-1}}$. This is why salts dissolve in water and not in hexane, and why a model omitting the term cannot describe solvent partitioning at all.

Hydration, the dielectric constant, and ion pairing

Both the Debye length and Equation (12.4) contain ε_r, which they treat as a property of the pure solvent. It is not: adding salt lowers the dielectric constant of water substantially, because solvent molecules in the primary coordination shell of each ion are oriented by the ionic field and are no longer free to rotate in response to an applied one. Every electrolyte equation of state therefore requires a model $\varepsilon_r(T, \mathbf{x})$, and since ε_r appears inside a square root in one place and a difference in the other, errors propagate into every electrostatic term at once. The same physics has a second consequence: solvent bound in coordination shells is not available to solvate anything else. If each ion binds four to six solvent molecules, then at one molal a substantial minority of the water is already committed and by five molal very little free water remains, and the activity coefficient of the salt is governed by the free solvent, not the total.

Finally, when two oppositely charged ions approach to contact the interaction energy greatly exceeds kT and the pair persists long enough to be treated as a chemical species. This is exactly the situation Wertheim's theory was built for, so no new machinery is required: the ion pair is described by Equations (11.6) and (11.7), with cation and anion carrying complementary sites and ε^{AB}/k representing the depth of the contact minimum. In solvents of low permittivity, and at high concentration in any solvent, the pairs dominate.

Key idea: the shape of the activity coefficient curve

The mean ionic activity coefficient of a real salt falls at low ionic strength, passes through a minimum, and then rises steeply, in many cases above unity. The initial fall is electrostatic screening, given correctly by the limiting law in Equation (12.3). The upturn is not electrostatic at all, and no purely electrostatic model reproduces it: it comes from depletion of free solvent by hydration, which raises the effective salt concentration relative to the water available to solvate it, and from short-range repulsion between hydrated ions, which is excluded volume. An electrolyte equation of state captures the upturn because it already contains a hard-sphere term and an association term from Chapter 11, not because its electrostatics is better.

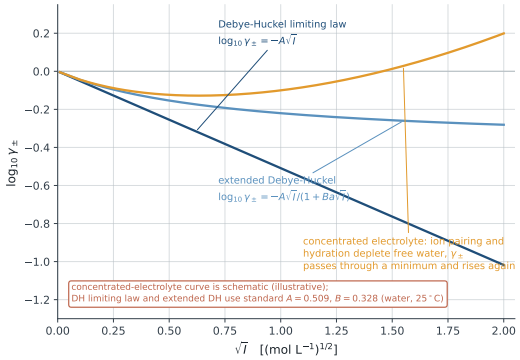

Figure 12.2: Mean ionic activity coefficient against the square root of ionic strength. The limiting law and the extended form use the standard aqueous constants $A = 0.509$ and $B = 0.328$ at 25 °C; the concentrated-electrolyte curve with the minimum and upturn is labelled illustrative on the figure and displays the mechanism, not a particular salt.

12.4 Engineering interpretation

On the activity-coefficient side stand Pitzer's ion-interaction model, a virial expansion in molality with coefficients fitted per ion pair and per triplet, and electrolyte NRTL, which superimposes a local-composition term on a Debye–Hückel term. Both are accurate, both are extensively parameterized, and both describe one liquid phase at specified T and P; anything volumetric, anything involving the vapour, and anything near the solvent critical point requires a second model, and the two must then be forced to agree.

On the equation-of-state side stand ePC-SAFT and eSAFT-VR, whose advantage is not primarily accuracy but scope and consistency: one $a^{\mathrm{res}}(T,\rho,\mathbf{x})$ delivers liquid activity coefficients, vapour fugacities, density, partial molar volumes, enthalpy of mixing and heat capacity from a single set of derivatives. A capture flowsheet needs acid-gas solubility in a loaded amine solution, the vapour composition above it, the density for column hydraulics and the heat of absorption for the reboiler duty; a battery cell model needs salt activity, solvent activity and electrolyte density at one composition. Computing these from one framework guarantees they satisfy the Gibbs–Duhem relation, which two separately fitted models do not.

Battery electrolytes

Lithium-ion electrolytes are the case in which the classical dilute-solution apparatus is least applicable, for four reasons.

Concentration. Working electrolytes are at one molar and above, where the Debye length is about 0.3 nm in water and less in the organic carbonates used in cells. The dilute limit in which Equation (12.3) is exact is not merely inaccurate here, it is meaningless: there is no separation of scales between the screening length and the ion size.

Solvation structure. Transport is governed by which species actually moves. Whether lithium travels as a solvent-separated ion, a contact ion pair or a larger aggregate sets the conductivity and the transference number, and the first solvation shell determines what decomposes at the electrode to form the solid electrolyte interphase, which controls cycle life. These are exactly the quantities the association term describes.

Solubility limits. A salt that precipitates in a cold cell disables it, and the saturation boundary requires the salt activity at high concentration and low temperature, the regime least well constrained by data.

Water-in-salt and localized high-concentration electrolytes. These are formulated so that nearly every solvent molecule is coordinated to a cation, which widens the electrochemical stability window because free solvent is what decomposes first. Solvent and solute have exchanged roles, the free-solvent fraction is the design variable, and a dilute-solution expansion has nothing to say.

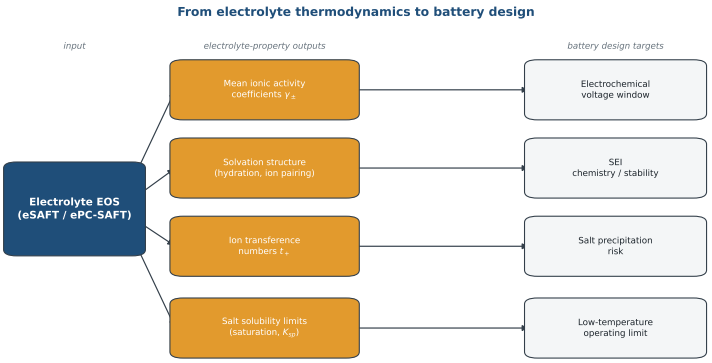

Figure 12.3: Concept map linking the outputs of an electrolyte equation of state, namely mean ionic activity coefficients, solvation structure, transference numbers and salt solubility limits, to the corresponding battery design targets. The diagram is schematic.

12.5 Limitations

Limitations

- **The dielectric constant model is a weak link.** $\varepsilon_r(T,\mathbf{x})$ is an empirical correlation appearing in both the screening and the solvation terms, and published correlations disagree appreciably at high salt content. Since it enters the Debye length under a square root and Equation (12.4) through $1-1/\varepsilon_r$, an error biases every electrostatic contribution at once and is partly absorbed into the fitted ion parameters, which conceals it.
- **Ion-specific parameters, and many of them.** Each ion requires at least a diameter and, in Equation (12.4), a Born radius, which is not the same quantity and is not independently measurable; ion pairing adds an association energy and volume per pair. The parameter count grows with the number of ion pairs rather than the number of components.
- **Data are scarce exactly where the model is needed.** Osmotic and activity coefficients are abundant for common aqueous salts at moderate molality near room temperature, and sparse for mixed solvents, multivalent and organic ions, high temperature and above a few molal; battery electrolytes are among the least well characterized thermodynamically.
- **Association and electrostatics are not cleanly separable.** A contact ion pair is held together by the Coulomb interaction, so representing it by an association term while also representing the Coulomb interaction by a screening term double-counts to an extent depending on the ion diameters and the association scheme. The split is a modelling convention, not a physical decomposition, so parameter sets are not transferable between codes that make it differently.
- **Everything inherited from Chapter 11 remains.** The critical region is still mean-field, the regression is still non-unique, and the cost is higher again, since the ion-pairing balance and the electrostatic terms must be evaluated at every trial density.

12.6 Transition to Chapter 13

The pattern of the preceding eleven chapters holds here too: physics was omitted, the omission produced an identifiable failure, and it was repaired at a specific cost. What is different is the character of the remaining limitations. They are no longer statements that a term is missing from the free energy; they are statements about a dielectric constant correlation, about the availability of data at high concentration, about the non-uniqueness of regressed parameters and about the arbitrariness of a boundary between two terms. The obstacle has moved from the physics to the parameterization and to the evidence. That change of character sets the agenda for the final chapter: if the limiting factor is data, molecular simulation can supply it where experiment cannot; if it is functional form, machine learning can propose one, provided physical constraints are imposed rather than hoped for; if it is non-uniqueness, uncertainty quantification must be part of the model; and if the application is electrochemical, activity, potential and transport must be described within one consistent framework.

Student handout: Chapter 12

Summary

- Ions interact through a $1/r$ potential whose range dwarfs that of dispersion, so the pairwise perturbation expansion of Chapter 11 does not converge and the long-range part must be treated collectively; the Bjerrum length in water at 25 °C is 0.715 nm.
- Four contributions are added: Debye–Hückel or MSA screening, the Born solvation term, hydration through the composition-dependent dielectric constant and the depletion of free solvent, and ion pairing treated as Wertheim association.
- The Debye–Hückel result is a limiting law, exact only as $I \to 0$: the Debye length for an aqueous 1:1 salt falls from 9.61 nm at 1 mmol L^{-1} to 0.30 nm at 1 mol L^{-1}, below the size of a hydrated ion. The Born term is the largest single number in the problem, about -457 kJ mol^{-1} for a monovalent ion of radius 0.15 nm in water, and proportional to z_i^2.
- The activity coefficient curve has a minimum and a steep upturn; the upturn is not electrostatic but comes from loss of free solvent to hydration and from short-range repulsion, captured through terms already present from Chapter 11.
- Model families: Pitzer and e-NRTL on the activity-coefficient side, ePC-SAFT and eSAFT-VR on the equation-of-state side; the advantage of the latter is scope and internal consistency, since one framework gives both phases and the

volumetric properties. Battery electrolytes are the extreme case, at one molar and above, where solvation structure controls transport and the interphase, precipitation sets the low-temperature limit, and in water-in-salt formulations essentially all solvent is coordinated.

Key equations

$$\tilde{a}^{\mathrm{res}} = \tilde{a}^{\mathrm{hs}} + \tilde{a}^{\mathrm{chain}} + \tilde{a}^{\mathrm{disp}} + \tilde{a}^{\mathrm{assoc}} + \tilde{a}^{\mathrm{DH/MSA}} + \tilde{a}^{\mathrm{Born}} + \tilde{a}^{\mathrm{hyd}} \tag{12.5}$$

$$\kappa^{-1} = \left(\frac{\varepsilon_r \varepsilon_0 kT}{e^2 \sum_i \rho_i z_i^2} \right)^{1/2}, \qquad \ell_{\mathrm{B}} = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 kT} \tag{12.6}$$

$$\log_{10}\gamma_{\pm} = -A\,|z_+ z_-|\,\sqrt{I}, \quad I = \tfrac{1}{2}\sum_i m_i z_i^2, \quad A = 0.509 \text{ (water, } 25\,^{\circ}\mathrm{C}) \tag{12.7}$$

$$A^{\mathrm{Born}} = -\frac{N_A e^2}{8\pi\varepsilon_0} \sum_i x_i z_i^2 \frac{1 - 1/\varepsilon_r}{r_i} \tag{12.8}$$

Concept map

Molecular equations of state contain no charge, yet capture, brines, hydrates and batteries are ionic $\rightarrow$ collective long-range screening, dielectric solvation, hydration and ion pairing $\rightarrow$ $\tilde{a}^{\mathrm{DH/MSA}} + \tilde{a}^{\mathrm{Born}} + \tilde{a}^{\mathrm{hyd}}$ added to the SAFT sum $\rightarrow$ dielectric-constant correlations, proliferating ion parameters, scarce concentrated data, and an arbitrary split between association and electrostatics

Practice questions

1. Using Equation (12.3), compute the Debye length of an aqueous 1:1 electrolyte at 298.15 K and $\varepsilon_r = 78.4$ for $0.001\,\mathrm{mol\,L^{-1}}$, $0.01\,\mathrm{mol\,L^{-1}}$, $0.1\,\mathrm{mol\,L^{-1}}$ and $1\,\mathrm{mol\,L^{-1}}$, verify the quoted values, and state where the continuum assumption becomes untenable and why.
2. Evaluate Equation (12.4) for monovalent and divalent ions of radius 0.10 nm, 0.15 nm and 0.30 nm in water, compare with RT, and explain why salts are insoluble in hydrocarbons.
3. Explain why the Debye–Hückel result is called a limiting law, listing the three assumptions in its derivation and where each first fails.
4. Identify the two mechanisms responsible for the upturn in $\gamma_{\pm}$ at high molality, and state which terms of Equation (12.2) contain them.
5. A battery electrolyte at $1.5\,\mathrm{mol\,L^{-1}}$ in a solvent with $\varepsilon_r = 20$ is to be modelled. State which terms of Equation (12.2) you expect to dominate, and which limitations of this chapter you expect to be controlling.

Recommended references

- C. Held, T. Reschke, S. Mohammad, A. Luza and G. Sadowski, “ePC-SAFT revised”, *Chem. Eng. Res. Des.* **92** (2014) 2884.
- G. M. Kontogeorgis and G. K. Folas, *Thermodynamic Models for Industrial Applications*, Wiley, 2010, Chapters 15 and 16.
- J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, 1999, Chapter 9.
- K. S. Pitzer, *Activity Coefficients in Electrolyte Solutions*, 2nd ed., CRC Press, 1991.

Chapter 13

Future directions

13.1 Historical background

The twelve preceding chapters cover three and a half centuries, and the pace of the argument is uneven in an instructive way. Between van der Waals in 1873 and Redlich and Kwong in 1949 lie seventy-six years with no change of substance; between Redlich and Kwong and Peng and Robinson lie twenty-seven years in which the cubic equation was brought to its final form. The timing is not accidental: Soave's method requires the vapour-pressure curve to be inverted numerically at many temperatures for many compounds, which was impractical before digital computation, SAFT required both Wertheim's statistical mechanics and the computing power to solve an implicit free-energy model at every state point, and electrolyte equations of state required SAFT. Each advance waited on two things, a piece of physics identified as missing and a tool capable of carrying it, and the four directions below are those in which both are now present.

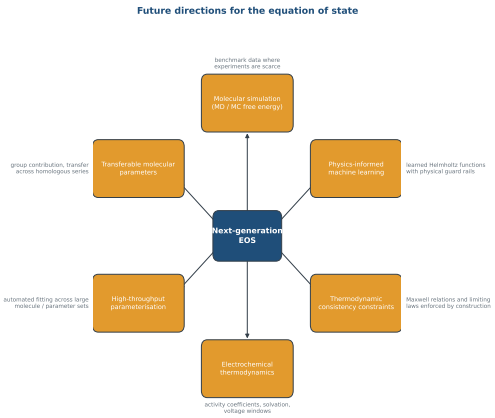

Figure 13.1: Concept map of the directions in which equation-of-state development is moving: molecular simulation, physics-informed machine learning, consistency constraints, electrochemical thermodynamics, transferable parameters and high-throughput parameterization. The diagram is schematic.

13.2 Physical motivation

Chapter 12 closed on an observation worth restating, because it is the premise of everything below. Through Chapter 11 the limitations of each model were statements that a term was missing from the free energy; by Chapter 12 they had become statements about correlations for auxiliary quantities, about the scarcity of data, about the non-uniqueness of regressed parameters and about the arbitrariness of the division between two terms. The binding constraint has moved from physics to evidence and to parameterization. That is a claim about where effort now returns the most, not that the physics is finished, and it explains the four threads below: one supplies evidence where experiment cannot, one supplies functional form where derivation cannot, one addresses the reliability of the result, and one addresses the application whose demands grow fastest.

Physics introduced by the next generation

What is added at this stage is not a term in the free energy but three ingredients around it. *Molecular-level evidence*, from simulation, in place of experiment that does not exist for the conditions or the species of interest.

A learned functional form for $a^{\mathrm{res}}(T,\rho,\mathbf{d})$, constrained so that thermodynamic structure holds by construction rather than by fitting. *Explicit uncertainty*, propagated from the parameter posterior, so that a prediction states how far it can be trusted. To these is added one genuinely new physical coupling, between chemical and electrical potentials and between equilibrium and transport, in the electrochemical thread.

13.3 Mathematical development

Thread 1: molecular simulation as the reference

Monte Carlo and molecular dynamics compute thermodynamic properties by sampling the configuration space of an assumed intermolecular potential. Their role is not to replace analytic models, which remain necessary because a flowsheet requires millions of evaluations, but to supply the reference data against which models are built and tested. Simulation reaches conditions experiment cannot, beyond the stability of any container and on species that are toxic, radioactive, short-lived or not yet synthesized, and it computes quantities experiment cannot isolate, most importantly the individual terms of Equation (11.2): a simulation of a hard-chain fluid tests $\tilde{a}^{\mathrm{hs}}+\tilde{a}^{\mathrm{chain}}$ directly, with no dispersion or association present to be disentangled. Free-energy methods matter more here than ordinary sampling, because the free energy is not a simple ensemble average of a mechanical variable; thermodynamic integration, free-energy perturbation and expanded-ensemble techniques construct it along a path between the system of interest and a reference of known free energy, and calculations of this kind established the hard-sphere virial coefficients quoted in Chapter 11. The limiting factor is not sampling but the force field: a simulation returns the exact thermodynamics of the potential it was given and no more, so if the potential is imperfect the result is precise and wrong, and the error is invisible from within the calculation.

Thread 2: machine-learned and physics-informed equations of state

The naive application of machine learning here is to regress P, or Z, against T, ρ and composition. It should be rejected, for a reason that follows from Chapter 1: pressure is a derivative of a potential, and separately regressed derivative properties are not guaranteed to come from any potential at all. Such a model violates the Maxwell relations, produces inconsistent enthalpies and entropies, and fails the isofugacity condition on which every phase-equilibrium calculation rests. The correct architecture is the one SAFT already uses, with the analytic terms replaced by a learned function: a network represents the residual Helmholtz energy $\tilde{a}^{\mathrm{res}}_{\theta}(T,\rho,\mathbf{d})$, where $\mathbf{d}$ is a vector of molecular descriptors, and every other property follows by automatic differentiation of the network itself:

$$Z = 1+\rho\left(\frac{\partial \tilde{a}^{\mathrm{res}}_{\theta}}{\partial \rho}\right)_{T}, \qquad \frac{H^{\mathrm{res}}}{RT} = -T\left(\frac{\partial \tilde{a}^{\mathrm{res}}_{\theta}}{\partial T}\right)_{\rho}+Z-1, \qquad \ln\varphi_i = \left(\frac{\partial\, n\tilde{a}^{\mathrm{res}}_{\theta}}{\partial n_i}\right)_{T,V,n_{j\neq i}} - \ln Z. \quad (13.1)$$

Consistency is then structural rather than fitted: the Maxwell relations hold because mixed partial derivatives of a single differentiable function commute, whatever the parameters θ happen to be.

Structural consistency is necessary but not sufficient, and the remaining physics is imposed as hard constraints rather than learned, as indicated in Figure 13.2. Four are essential: the ideal-gas limit, $\tilde{a}^{\mathrm{res}}_{\theta}\to 0$ as $\rho\to 0$, enforced by construction, for example by multiplying the network output by ρ; the Maxwell equal-area condition of Equation (3.7), equivalently equality of fugacities across the coexistence curve; positivity of the isochoric heat capacity, $-T(\partial^2 A/\partial T^2)_V > 0$, which is a stability requirement rather than a fitting preference, since a model violating it describes no physical substance; and correct asymptotics at both ends, the second virial coefficient at low density and the repulsive divergence at close packing.

The honest failure mode should be stated plainly, because it is the mode in which such models are most dangerous in practice. A neural network extrapolates confidently and without warning: outside the state space covered by its training data it returns a smooth, plausible number carrying no indication that it is an extrapolation, whereas an analytic model built on physical terms degrades in a way its user can anticipate, since one knows a cubic equation will be poor near the critical point and SAFT poor for an unparameterized associating species. The constraints above are a partial remedy only, and an honest machine-learned equation of state must report the boundary of its training envelope alongside its prediction.

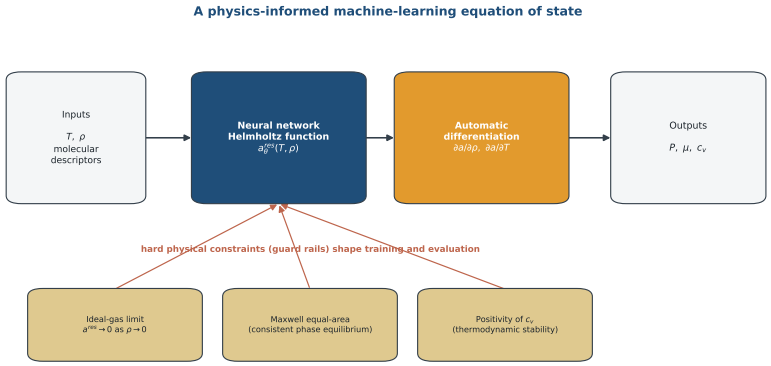

Figure 13.2: Schematic of a physics-informed machine-learned equation of state: state variables and molecular descriptors enter a network representing the residual Helmholtz energy, all derived properties follow by automatic differentiation, and hard physical constraints act as guard rails. The diagram is schematic.

Thread 3: consistency and uncertainty as first-class requirements

Chapters 9 to 12 recorded repeatedly that model parameters are obtained by regression and that the regression is not unique: Chapter 11 noted the correlation between m and ε/k, Chapter 12 that ion parameters absorb errors in the dielectric constant correlation. In each case a range of parameter sets fits the data equally well and extrapolates differently, yet the model as delivered reports a single number. The requirement is that a prediction carry its uncertainty, propagated from the parameter covariance and from the stated uncertainty of the underlying data. Bayesian estimation delivers a posterior rather than a point estimate, and propagating it gives a distribution of predicted properties whose width grows as the data become less constraining, which is precisely the warning a point estimate cannot give. The same discipline applies to consistency: a candidate model should be tested routinely against the Maxwell relations, the Gibbs–Duhem equation and the known limiting behaviours, and those tests should be part of its specification.

Thread 4: electrochemical thermodynamics

Batteries, electrolysers and fuel cells require activity, electric potential and transport in one framework, and at present they usually are not: activity coefficients come from an electrolyte model of the kind discussed in Chapter 12, transport properties from separate correlations, and the electrode potential from a Nernst expression using activities from the first, with no guarantee that the three are mutually consistent. In a concentrated electrolyte, where the activity coefficient may be far from unity and strongly composition-dependent, the inconsistency is not small. The elements of a unified treatment exist. The electrochemical potential $\tilde{\mu}_i = \mu_i + z_i F \phi$ is the correct driving force; the chemical part μ_i follows from the residual Helmholtz energy of Chapter 12 by differentiation; and non-equilibrium thermodynamics relates fluxes to gradients of $\tilde{\mu}_i$ through an Onsager coefficient matrix which is symmetric and, in a concentrated solution, not diagonal, so that the motion of one ion drags the others and the solvent. What is missing is what was missing in every earlier chapter: a tractable model for the coefficients, here the transport coefficients, grounded in the same molecular picture as the thermodynamics.

13.4 Engineering interpretation

Model selection is a statement about physics, not about accuracy. Choosing Peng–Robinson for a natural gas mixture is defensible because the physics of that mixture is excluded volume and dispersion between weakly anisotropic molecules, which is what the model contains. Choosing it for an aqueous glycol system is not, whatever the reported deviation, because the dominant physics there is hydrogen bonding and the model has no representation of it.

The cost hierarchy is real, and accuracy is conditional. A cubic equation costs of the order of a microsecond per state point, SAFT roughly an order of magnitude more, and an electrolyte SAFT more again, so using the most detailed model everywhere in a flowsheet is not thoroughness but poor engineering judgement. Every model in Chapters 8 to 12 also carries parameters fitted to particular substances over particular ranges, so a quoted deviation is a statement about that set. Finally, a flash calculation using one model for the vapour and another for the liquid can violate the phase rule outright, which is the point Chapter 10 made about cubic equations and Chapter 12 about electrolytes, and the reason for building machine-learned models on a learned Helmholtz function.

13.5 Limitations

Limitations

- **Simulation is limited by the force field, not by the sampling.** A converged simulation returns the exact thermodynamics of an assumed potential; if the potential is wrong the answer is precisely wrong, and nothing internal to the calculation reveals it. Simulation is reference data of quality bounded by the underlying potential, not an independent arbiter.
- **Machine-learned models extrapolate confidently and silently.** Outside the training envelope the output remains smooth and plausible and carries no signal that it is unsupported. Such a model is not fit for engineering use unless it reports the boundary of its training data.
- **Descriptors and data limit machine learning as parameters limited SAFT.** A learned model transfers to a new molecule only if the descriptor vector encodes the physics that distinguishes it, and only if molecules of that class appeared in training.
- **Uncertainty quantification is not yet standard practice.** Most published models, and essentially all commercial implementations, report point predictions; parameter covariances are rarely published, and without them a user cannot propagate uncertainty.
- **The electrochemical framework is incomplete.** The thermodynamic side is available in principle from Chapter 12; the transport side lacks a molecular model of comparable standing.

Key idea: what the ladder does and does not do

Figure 13.3 places every model of this course on one vertical ladder, each rung labelled with the physics it added: excluded volume and mean-field attraction (van der Waals), temperature-dependent attraction (Redlich–Kwong), molecular shape through $\alpha(T_r, \omega)$ (Soave), improved volume dependence and a better Z_c (Peng–Robinson), chain connectivity and segment dispersion (SAFT and PC-SAFT), directional association, and electrostatics (ePC-SAFT). The ladder is ordered by physical content and by computational cost, and by nothing else: not by accuracy, because a model containing physics irrelevant to a problem gains nothing from containing it, and not by suitability, because the correct rung is the lowest one whose physics includes the physics of the system at hand.

13.6 Closing the argument

The thesis stated at the beginning of this course was that the sequence from the ideal gas law to modern molecular and electrolyte models is not a catalogue of formulas but a single argument, in which each equation of state exists because its predecessor omitted physics that turned out to matter.

The record supports it in every case. The ideal gas omits molecular size and interaction, and fails wherever the density is appreciable. Van der Waals restores both in the crudest possible form, obtaining the critical point and the two-phase region at the cost of a Z_c of 0.375. Redlich and Kwong impose a $T^{-1/2}$ weakening of the attraction by inspection, improving the vapour phase and nothing else. Soave determines that temperature dependence from the vapour-pressure curve instead of guessing it, making the cubic equation quantitative for phase equilibrium. Peng and Robinson repair the volume dependence Soave left untouched, obtaining usable liquid densities and with them the industrial standard. SAFT observes that none of these contains any representation of the molecule, and rebuilds the equation from a molecular reference, obtaining chain connectivity and, for the first time, directional saturable association. Electrolyte equations

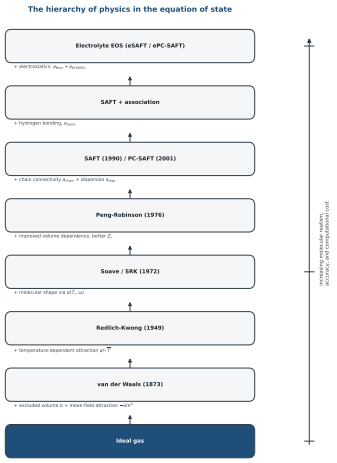

Figure 13.3: The hierarchy of physics in the equation of state: a ladder from the ideal gas upward, each rung labelled with the physics added and the equation that introduced it, with realism, accuracy and cost increasing together. The diagram is schematic.

of state observe that SAFT contains no charge, and add collective screening and dielectric solvation. At each step the new physics is identifiable, the failure it repairs is specific, and the price is explicit.

The corollary is the sentence to carry into your own research. The correct question to ask about a thermodynamic model is not whether it is accurate. Accuracy is a property of a model together with a data set, and a model may be accurate on one system for reasons that guarantee nothing about the next. The correct question is which physics the model contains, and whether that physics is the physics of your problem. If it is, the model will behave predictably and its errors will be interpretable. If it is not, agreement with data is a coincidence of regression, and it will not survive contact with a new system. Every chapter of this course is an instance of that question being asked, answered, and asked again of the answer.

Student handout: Chapter 13

Summary

- By Chapter 12 the binding constraint had moved from missing physics to parameterization and evidence: dielectric correlations, scarce data at high concentration, non-unique regressions and an arbitrary split between terms.
- *Molecular simulation* supplies reference data where experiment cannot, including individual terms of a decomposed free energy, using free-energy methods rather than simple averaging; its limiting factor is the force field, not the sampling.
- *Physics-informed machine learning* must learn the residual Helmholtz energy, not the pressure, and obtain all derived properties by automatic differentiation, so that consistency is structural. Hard constraints are imposed for the ideal-gas limit, the Maxwell equal-area condition, positivity of c_V and correct asymptotics; the failure mode is confident, silent extrapolation outside the training envelope.
- *Consistency and uncertainty* must be first-class requirements: posterior parameter distributions rather than point estimates, propagated to predictions, and routine testing against the Maxwell relations, Gibbs–Duhem and known limits. *Electrochemical thermodynamics* requires activity, potential and transport in one framework, built on $\tilde{\mu}_i = \mu_i + z_i F \phi$ and an Onsager description of coupled fluxes: the thermodynamic half exists, the transport half does not.
- The corollary: the correct question about a model is not whether it is accurate but which physics it contains and whether that physics is the physics of the problem.

Key equations

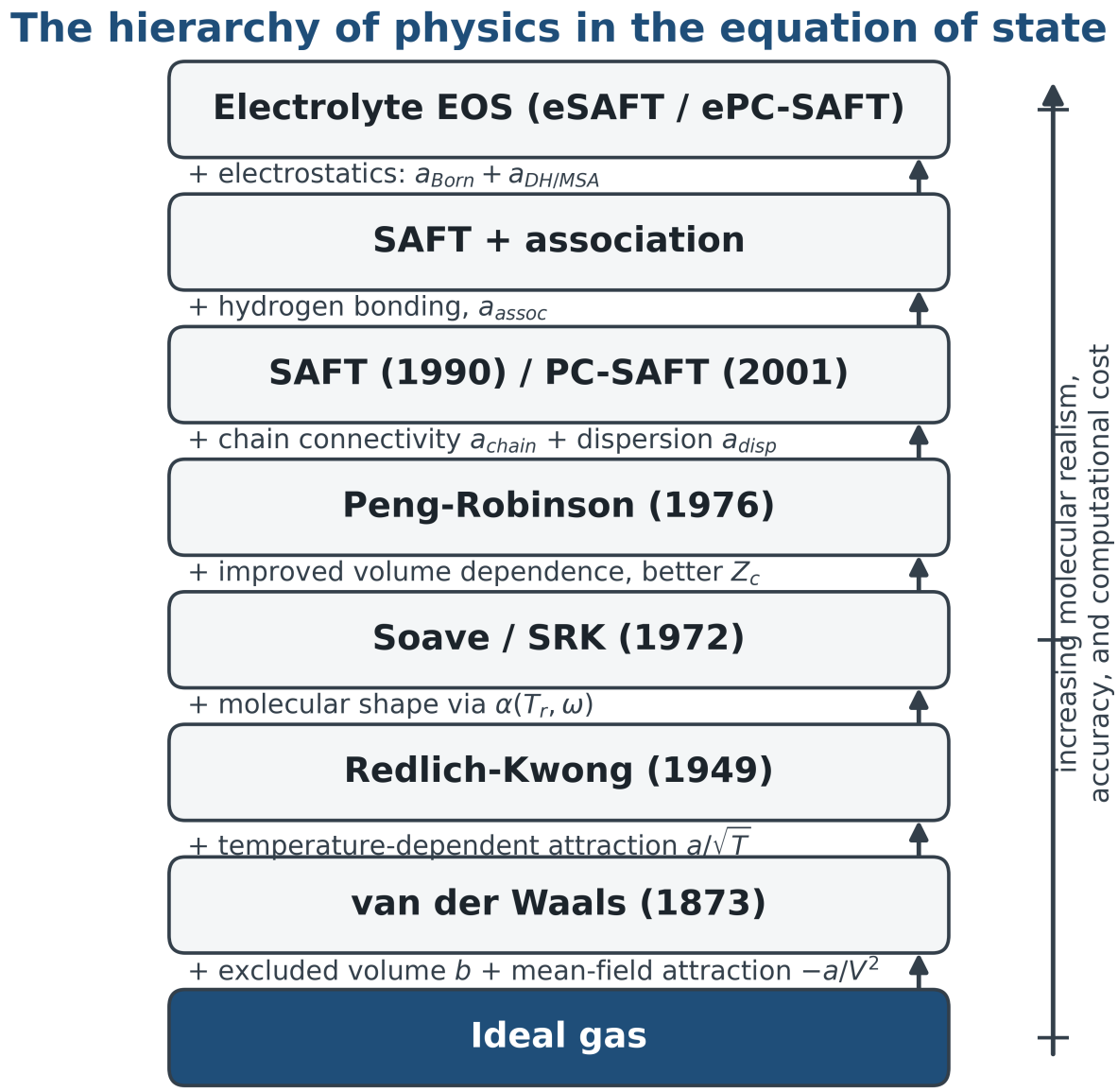

Figure 13.3 (enlarged). The hierarchy of physics in the equation of state.

$$\tilde{a}^{\mathrm{res}}_\theta = \tilde{a}^{\mathrm{res}}_\theta(T,\rho,\mathbf{d}), \qquad Z = 1+\rho\left(\frac{\partial \tilde{a}^{\mathrm{res}}_\theta}{\partial \rho}\right)_T \tag{13.2}$$

$$\frac{H^{\mathrm{res}}}{RT} = -T\left(\frac{\partial \tilde{a}^{\mathrm{res}}_\theta}{\partial T}\right)_\rho + Z - 1, \qquad \ln\varphi_i = \left(\frac{\partial\, n\tilde{a}^{\mathrm{res}}_\theta}{\partial n_i}\right)_{T,V,n_{j\neq i}} - \ln Z \tag{13.3}$$

$$\tilde{a}^{\mathrm{res}}_\theta \to 0 \;\; (\rho \to 0), \qquad c_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_V > 0, \qquad \oint V\,\mathrm{d}P = 0 \;\; \text{(equal area)} \tag{13.4}$$

$$\tilde{\mu}_i = \mu_i + z_i F\phi, \qquad \mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} \tag{13.5}$$

Concept map

Remaining errors come from parameters and missing data rather than from missing terms → simulated reference data, learned functional form, explicit uncertainty, coupled electrochemistry → constrained neural Helmholtz functions differentiated automatically, with Bayesian parameter posteriors → force-field quality, silent extrapolation, descriptor coverage, and no molecular transport model

Practice questions

1. Explain why a machine-learned model of $Z(T,\rho)$ can violate the Maxwell relations while a model of $\tilde{a}^{\mathrm{res}}(T,\rho)$ cannot, and identify which phase-equilibrium calculation the violation would corrupt first.
2. State the four hard constraints listed in this chapter and, for each, name a physical consequence of violating it.
3. Molecular simulation is described as a source of reference data rather than an independent arbiter. Justify this, and describe a case in which simulation can test a single term of Equation (11.2) in isolation.
4. Take a system from your own field and identify the dominant physics: excluded volume, anisotropic dispersion, chain connectivity, hydrogen bonding, electrostatics. Select the lowest rung of Figure 13.3 that contains it, and justify the choice against both a simpler and a more detailed alternative.
5. Explain why an average deviation reported on a given data set is not by itself evidence that a model is suitable for a new system, and state what further information is required.

Recommended references

- D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, 3rd ed., Academic Press, 2023.
- J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 4th ed., Academic Press, 2013.
- G. M. Kontogeorgis and G. K. Folas, *Thermodynamic Models for Industrial Applications*, Wiley, 2010.
- J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, 1999.

Chapter 14

Worked examples

This chapter works ten problems in full. They are ordered so that each uses the result of the previous one: a compressibility factor, then the cubic that produces it, then the selection of the correct root, then the comparison of models, then the temperature dependence that separates them, then the fugacity coefficient, then the saturation pressure, then the mixture, then the departure functions, and finally the corresponding-states framework in which all of it sits.

Three conventions apply throughout. First, all critical constants and acentric factors are taken from §8 of the design specification, and the gas constant is $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}} = 83.14\,\mathrm{bar\,cm^3\,mol^{-1}\,K^{-1}}$; the second form is used wherever pressures are in bar and volumes in $\mathrm{cm^3\,mol^{-1}}$, and the two are the same constant because $1\,\mathrm{bar\,cm^3} = 0.1\,\mathrm{J}$. Second, every numerical value printed below is produced by `code/worked_examples.py`; nothing is estimated. Third, results are quoted to four significant figures, which is well beyond the accuracy of the models but is necessary if a reader is to reproduce the arithmetic exactly.

Example 1: Compressibility factor and its engineering consequence

Problem. Methane is stored and transported at $T = 300\,\mathrm{K}$ and $P = 100\,\mathrm{bar}$. Using $T_\mathrm{c} = 190.6\,\mathrm{K}$, $P_\mathrm{c} = 45.99\,\mathrm{bar}$ and $\omega = 0.012$, compute the compressibility factor and molar volume from the ideal gas law and from the Peng–Robinson equation. Convert the difference into (i) the error in the mass of methane held in a $50\,\mathrm{m^3}$ vessel at that condition, taking the molar mass as $16.043\,\mathrm{g\,mol^{-1}}$, and (ii) the error in the volumetric flow that a compressor handling $100\,\mathrm{kmol\,h^{-1}}$ must accept.

Strategy. The ideal gas law gives $Z = 1$ directly. The Peng–Robinson equation is solved in the dimensionless form $Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0$ with $A = a(T)P/(RT)^2$ and $B = bP/(RT)$. Because $Z = PV/(RT)$ is exactly the ratio of the real to the ideal molar volume, every volumetric quantity scales with Z and every quantity inversely proportional to volume scales with $1/Z$; the two engineering consequences are therefore obtained without further modelling.

Solution.

1. Reduced state: $T_\mathrm{r} = T/T_\mathrm{c} = 300/190.6 = 1.574$ and $P_\mathrm{r} = P/P_\mathrm{c} = 100/45.99 = 2.174$. The fluid is supercritical and strongly compressed.
2. Ideal gas: $V^{ig} = RT/P = (83.14)(300)/100 = 249.4\,\mathrm{cm^3\,mol^{-1}}$ with $Z = 1$ by definition.
3. Peng–Robinson constants: $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 = 0.3931$, $\alpha = [1 + \kappa(1 - \sqrt{T_\mathrm{r}})]^2 = 0.8099$, $a(T) = 0.45724\,R^2T_\mathrm{c}^2\alpha/P_\mathrm{c} = 2.022 \times 10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$ and $b = 0.07780\,RT_\mathrm{c}/P_\mathrm{c} = 26.81\,\mathrm{cm^3\,mol^{-1}}$.
4. Dimensionless groups: $A = aP/(RT)^2 = 0.3250$ and $B = bP/(RT) = 0.1075$, so the cubic reads

$$Z^3 - 0.8925\,Z^2 + 0.07540\,Z - 0.02214 = 0.$$

   It has one real root, $Z = 0.8339$, and one complex conjugate pair.
5. Molar volume: $V = ZRT/P = (0.8339)(83.14)(300)/100 = 208.0\,\mathrm{cm^3\,mol^{-1}}$, smaller than the ideal-gas value by $41.42\,\mathrm{cm^3\,mol^{-1}}$.
6. Vessel inventory: $n = V_\mathrm{vessel}/V$. The ideal gas law gives $n^{ig} = 50\,\mathrm{m^3}/V^{ig} = 200.5\,\mathrm{kmol}$ and $m^{ig} = 3216\,\mathrm{kg}$, whereas Peng–Robinson gives $n = 240.4\,\mathrm{kmol}$ and $m = 3856\,\mathrm{kg}$. The ideal gas law understates the inventory by $640.4\,\mathrm{kg}$, that is by $1 - Z = 16.61\,\%$.
7. Compressor suction: $\dot{Q} = \dot{n}V$. The ideal gas law gives $\dot{Q}^{ig} = 24.94\,\mathrm{m^3\,h^{-1}}$ against the real $20.80\,\mathrm{m^3\,h^{-1}}$, so a machine sized on the ideal gas law is oversized by $1/Z - 1 = 19.91\,\%$.
8. Summary of the two routes:

quantity	ideal gas	Peng–Robinson	error of the ideal gas law
Z	1	0.8339	+0.1661
V / cm^3 mol^{-1}	249.4	208.0	19.91 %
inventory in 50 m^3 / kg	3216	3856	−16.61 %
suction volume / m^3 h^{-1}	24.94	20.80	19.91 %

The two percentages differ because one is referred to the real state and the other to the ideal state; the underlying error is the same single factor Z.

Check. Back-substituting $V = 208.0\,\mathrm{cm^3\,mol^{-1}}$ into the pressure-explicit form of the equation returns 100.0000 bar, so the root is exact. As an independent route, the second virial coefficient implied by the Peng–Robinson equation is $B_2 = b - a/(RT) = -54.26\,\mathrm{cm^3\,mol^{-1}}$, and the two-term virial expansion gives $Z = 1 + B_2P/(RT) = 0.7825$. This has the correct sign and the correct order of magnitude but is 0.0515 too low, which is the expected behaviour of a density expansion truncated after one term at $P_\mathrm{r} = 2.174$.

Engineering comment. A single number, $Z = 0.8339$, moves the vessel inventory by 640 kg and the compressor suction volume by one fifth. In custody transfer the first figure is a direct financial error repeated on every transaction; in machine selection the second is a capital error frozen at the purchase order. Neither can be recovered by tuning downstream, which is why the volumetric closure is chosen before any unit operation is sized.

Example 2: van der Waals parameters and the cubic in V

Problem. For carbon dioxide at $T = 300\,\mathrm{K}$ and $P = 60\,\mathrm{bar}$, with $T_\mathrm{c} = 304.2\,\mathrm{K}$ and $P_\mathrm{c} = 73.83\,\mathrm{bar}$, obtain the van der Waals constants a and b from the critical constants, write the resulting cubic in molar volume, find all its real roots, and select the physically correct one by an explicit criterion. Compare the van der Waals critical compressibility factor with the measured value, taking $V_\mathrm{c} = 94.0\,\mathrm{cm^3\,mol^{-1}}$ from the literature.

Strategy. Imposing $(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0$ at the critical point gives $a = 27R^2T_\mathrm{c}^2/(64P_\mathrm{c})$ and $b = RT_\mathrm{c}/(8P_\mathrm{c})$. Multiplying $P = RT/(V-b) - a/V^2$ by $V^2(V-b)$ produces a cubic in V that is solved numerically. Root selection uses three tests in order: physical admissibility $V > b$, mechanical stability $(\partial P/\partial V)_T < 0$, and, if two roots survive, the lower molar Gibbs energy, which because $G - G^{ig} = RT\ln\varphi$ at fixed T and P is the smaller $\ln\varphi$.

Solution.

1. Constants: $a = 27(83.14)^2(304.2)^2/[64(73.83)] = 3.655 \times 10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$ and $b = (83.14)(304.2)/[8(73.83)] = 42.82\,\mathrm{cm^3\,mol^{-1}}$.
2. Reduced state: $T_\mathrm{r} = 0.9862$, $P_\mathrm{r} = 0.8127$. The state is subcritical and close to the critical point.
3. The cubic. With $RT/P = 415.7\,\mathrm{cm^3\,mol^{-1}}$,
$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0 \implies V^3 - 458.5\,V^2 + 6.092\times10^4\,V - 2.608\times10^6 = 0,$$
with V in $\mathrm{cm^3\,mol^{-1}}$.
4. Roots: one real root $V = 266.9\,\mathrm{cm^3\,mol^{-1}}$ and one complex conjugate pair $95.81 \pm 24.36\,i$, which has no physical meaning. Hence $Z = PV/(RT) = 0.6420$, $\ln\varphi = -0.2890$ and $\varphi = 0.7490$.
5. Selection. The single real root satisfies $V > b$ and $(\partial P/\partial V)_T = -0.1123\,\mathrm{bar\,mol\,cm^{-3}}$, so it is admissible and mechanically stable; with only one root the choice is forced. The van der Waals saturation pressure at this temperature, obtained from the isofugacity condition, is 69.82 bar, so $P = 60\,\mathrm{bar}$ lies below it and the fluid is a vapour, consistent with the single vapour-like root. For comparison the Peng–Robinson equation gives $P^{sat} = 67.22\,\mathrm{bar}$ at the same temperature, and at the specified state it gives $Z = 0.5663$ and $V = 235.4\,\mathrm{cm^3\,mol^{-1}}$, so the van der Waals molar volume is high by 13.38 % even in the vapour.

6. The criterion exercised. At 70 bar and the same temperature the same cubic has three real roots, so the selection rule has work to do:

branch	Z	V / cm^3 mol^{-1}	$\ln\varphi$
liquid	0.2882	102.7	−0.355182
middle	0.3766	134.2	−0.354537
vapour	0.4554	162.3	−0.354739

   The middle root is discarded on mechanical stability grounds, and $G^V - G^L = RT(\ln\varphi^V - \ln\varphi^L) = 1.104\,\mathrm{J\,mol^{-1}} > 0$ selects the liquid, consistent with $P > P^{sat}$. The three fugacity coefficients agree to three decimal places because 70 bar is only 0.18 bar above the saturation pressure of the model at this temperature; the discrimination between phases becomes numerically delicate near saturation, and more so near the critical point, which is one reason flash algorithms are written in terms of $\ln\varphi$ rather than φ.

7. Critical compressibility: van der Waals predicts $Z_c = 3/8 = 0.3750$, whereas $P_cV_c/(RT_c) = (73.83)(94.0)/[(83.14)(304.2)] = 0.2744$. The model overpredicts Z_c, and equivalently $V_c = 3b = 128.5\,\mathrm{cm^3\,mol^{-1}}$ against $94.0\,\mathrm{cm^3\,mol^{-1}}$, by 36.66 %.

Check. Evaluating the cubic in Z at the critical point using the same constants returns $Z = 0.374997$ against the analytic $3/8 = 0.375000$, so the parameter set is internally consistent and the residual is the accuracy attainable at a triple root. The units check as well: a has the dimensions of pressure times volume squared, so a/P has those of $(\mathrm{cm^3\,mol^{-1}})^2$ and ab/P those of $(\mathrm{cm^3\,mol^{-1}})^3$, which are exactly the dimensions required of the coefficients of V and of V^0 in a cubic whose leading term is V^3.
Engineering comment. The van der Waals equation places the fluid on the correct side of the saturation curve and returns a vapour volume of the right order, but its critical volume is too large by more than a third. Since V_c sets the scale of the entire liquid branch, any liquid density taken from this equation is unusable for sizing, inventory or pump calculations. That single defect, and not the vapour-phase behaviour, is what drove the developments of Chapters 8 to 10.

Example 3: Three real roots and the selection of the stable branch

Problem. *n*-butane at $T = 350\,\mathrm{K}$ and $P = 10\,\mathrm{bar}$, with $T_c = 425.1\,\mathrm{K}$, $P_c = 37.96\,\mathrm{bar}$ and $\omega = 0.200$, is described by the Peng–Robinson equation. Obtain all three real roots of the cubic in Z, identify the vapour, unstable and liquid branches, and decide which phase is thermodynamically stable by comparing $\ln\varphi$, equivalently the molar Gibbs energy.
Strategy. At $T_r = 0.8233$ the isotherm is subcritical, so the cubic may have three real roots. The smallest and largest are the liquid and vapour branches; the middle root lies on the segment where $(\partial P/\partial V)_T > 0$ and is mechanically unstable, hence never physical. Between the two admissible roots the stable phase is the one with the lower molar Gibbs energy, and since both are evaluated at the same T and P, comparing $G - G^{ig} = RT\ln\varphi$ is equivalent to comparing G itself.
Solution.

1. Parameters: $\kappa = 0.6723$, $\alpha = 1.1284$, $a(T) = 1.698\times10^7\,\mathrm{bar\,cm^6\,mol^{-2}}$ and $b = 72.44\,\mathrm{cm^3\,mol^{-1}}$, hence $A = 0.2005$ and $B = 0.02489$.
2. The cubic: $Z^3 - 0.9751\,Z^2 + 0.1489\,Z - 0.004356 = 0$, with the three real roots listed below.
3. Branch properties, with $V = ZRT/P$ and $\ln\varphi$ from the Peng–Robinson expression of Chapter 10:

branch	Z	V / cm^3 mol^{-1}	$\ln\varphi$	φ	$(\partial P/\partial V)_T$ / bar mol cm^{-3}
liquid	0.03867	112.5	−0.2301	0.7944	−6.942
middle (unstable)	0.1418	412.5	+0.06694	1.069	+0.07460
vapour	0.7947	2312	−0.1885	0.8282	−0.003287

   The middle root is eliminated at once: its $(\partial P/\partial V)_T$ is positive, so a fluctuation that compresses it

lowers its pressure and the compression runs away.

4. Stability test between the survivors:

$$G^V - G^L = RT\left(\ln\varphi^V - \ln\varphi^L\right) = (8.314)(350)\left[-0.1885-(-0.2301)\right] = 121.2\,\mathrm{J\,mol^{-1}} > 0,$$

so the liquid has the lower molar Gibbs energy and is the stable phase.

Check. Solving the isofugacity condition independently gives $P^{sat}(350\,\mathrm{K}) = 9.469\,\mathrm{bar}$ for this model. The state pressure 10 bar exceeds it, so the fluid must be a subcooled liquid; this is exactly what the Gibbs comparison returned, by a different route.

Engineering comment. Selecting the vapour root here would put $V = 2312\,\mathrm{cm^3\,mol^{-1}}$ in place of $112.5\,\mathrm{cm^3\,mol^{-1}}$, a factor of 20.55 in molar volume and therefore in density. A $50\,\mathrm{m^3}$ drum would be reported as holding 1.257 t instead of 25.83 t. This is the single most common practical error in equation-of-state work, and it is not an error of the model but of its use: the cubic returns three mathematically valid numbers and the code must decide. Any implementation that simply takes the largest root, or the root closest to the previous iterate, will silently produce this failure somewhere near the saturation curve, which is precisely where process equipment operates.

Example 4: Redlich–Kwong, Soave and Peng–Robinson at one state point

Problem. Propane at $T = 350\,\mathrm{K}$ and $P = 15\,\mathrm{bar}$, with $T_c = 369.8\,\mathrm{K}$, $P_c = 42.48\,\mathrm{bar}$ and $\omega = 0.152$. Tabulate $a(T)$, b, A, B, Z, V and φ from the Redlich–Kwong, Soave–Redlich–Kwong and Peng–Robinson equations, and account physically for the ordering of the results.

Strategy. All three models share the form $P = RT/(V-b) - a(T)/[(V+\delta_1 b)(V+\delta_2 b)]$ with $(\delta_1,\delta_2) = (1,0)$ for the first two and $(1+\sqrt{2}, 1-\sqrt{2})$ for the third, so one cubic solver and one fugacity expression serve all three. The models differ in two independent places: the temperature dependence of the attraction, which is $T_r^{-1/2}$ for Redlich–Kwong and a fitted $\alpha(T_r,\omega)$ for the other two, and the volume dependence of the attraction, which Peng and Robinson alone modified. At $T_r = 0.9465$ the model saturation pressure is 29.71 bar, so the state is a superheated vapour and each cubic has a single real root.

Solution.

1. Alpha functions at $T_r = 0.9465$: $\alpha^{RK} = T_r^{-1/2} = 1.0279$, $\alpha^{SRK} = 1.0392$ with $m = 0.7152$, and $\alpha^{PR} = 1.0330$ with $\kappa = 0.6028$.
2. Dimensionless groups and roots, with $A = a(T)P/(RT)^2$, $B = bP/(RT)$ and $V = ZRT/P$:

Model	$a(T)$ / bar cm^6 mol^{-2}	b / cm^3 mol^{-1}	A	B	Z	V / cm^3 mol^{-1}	φ
RK	9.778×10^6	62.71	0.1732	0.03232	0.8418	1633	0.8618
SRK	9.885×10^6	62.71	0.1751	0.03232	0.8391	1628	0.8599
PR	1.051×10^7	56.31	0.1862	0.02903	0.8255	1601	0.8479

3. Comparison with the ideal gas, for which $V^{ig} = 1939.9\,\mathrm{cm^3\,mol^{-1}}$: the three models place $Z-1$ at -0.1582, -0.1609 and -0.1745 respectively, so all three agree that attraction dominates, and they differ among themselves by 0.01631 in Z, that is 1.975 % of the Peng–Robinson value, and by 1.638 % in φ.
4. Physical ordering. Redlich–Kwong and Soave share the same b, because both use $\Omega_b = 0.08664$, and differ only through α; at $T_r = 0.9465$ the Soave alpha is 1.1 % larger, its attraction term is correspondingly larger and its Z smaller. Peng–Robinson uses $\Omega_b = 0.07780$, so its co-volume is smaller by the factor $0.07780/0.08664 = 0.8980$, and its larger $\Omega_a = 0.45724$ raises $a(T)$ by roughly six percent; both changes act in the same direction, weakening repulsion and strengthening attraction, and Z falls furthest. The fugacity coefficients follow Z monotonically, which they must, since $\ln\varphi = \int_0^P (Z-1)\,\mathrm{d}P/P$ and the three isotherms do not cross below 15 bar.

Check. For each model $\ln\varphi$ was computed twice, once from the closed-form expression and once

by numerically integrating $(Z-1)\,\mathrm{d}P/P$ from zero pressure along the isotherm. The results are -0.1487397, -0.1509628 and -0.1649880 by both routes, agreeing to better than 1×10^{-15}, which confirms both the algebra of the fugacity expressions and the root selection at every pressure on the integration path.

Engineering comment. The three models disagree by 0.01631 in Z and 1.638 % in the vapour-phase fugacity coefficient, which for a distillation or absorption calculation is immaterial, since equilibrium depends on ratios of fugacities and the discrepancy largely cancels between the components. The reason to prefer Peng–Robinson is not visible at this state point at all: it appears on the liquid branch, where the smaller $b = 56.31\,\mathrm{cm^3\,mol^{-1}}$ against $62.71\,\mathrm{cm^3\,mol^{-1}}$ and the modified volume dependence displace the saturated liquid molar volume by roughly twelve percent, as recorded in Chapter 10. Choosing between cubics on vapour-phase evidence is therefore a common and misleading exercise, and a comparison table of this kind should always be read with the question of which branch is being tested kept in view.

Example 5: The alpha function and the sensitivity to ω

Problem. For propane ($T_c = 369.8\,\mathrm{K}$, $P_c = 42.48\,\mathrm{bar}$, $\omega = 0.152$) compute α and $a(T)$ at $T_r = 0.6$, 0.8, 1.0 and 1.3 for the Redlich–Kwong, Soave–Redlich–Kwong and Peng–Robinson equations. Then quantify how a 5 % error in ω propagates into the saturation pressure predicted by the Peng–Robinson equation between $T_r = 0.6$ and 0.95.

Strategy. The attraction parameter factorizes as $a(T) = a_c\alpha$, where a_c depends only on the critical constants and α carries all the temperature dependence. Redlich–Kwong uses $\alpha = T_r^{-1/2}$, a universal function with no adjustable content; Soave and Peng–Robinson use $\alpha = [1 + m(1-\sqrt{T_r})]^2$ with m a fitted function of ω. The saturation pressure is then obtained from the isofugacity condition $\varphi^L = \varphi^V$ for the nominal and the perturbed acentric factor, and the ratio of fractional changes is reported as an amplification factor.

Solution.

1. Reference constants: $a_c = 0.42748\,R^2T_c^2/P_c = 9.512\times10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$ for Redlich–Kwong and Soave, $a_c = 0.45724\,R^2T_c^2/P_c = 1.017\times10^7\,\mathrm{bar\,cm^6\,mol^{-2}}$ for Peng–Robinson; $m = 0.480 + 1.574\omega - 0.176\omega^2 = 0.7152$ and $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 = 0.6028$.
2. Alpha functions and $a(T)$, with $a(T)$ in $10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$:

T_r	T / K	α^{RK}	α^{SRK}	α^{PR}	a^{RK}	a^{SRK}	a^{PR}
0.6	221.88	1.2910	1.3484	1.2902	12.28	12.83	13.13
0.8	295.84	1.1180	1.1567	1.1313	10.64	11.00	11.51
1.0	369.80	1.0000	1.0000	1.0000	9.512	9.512	10.17
1.3	480.74	0.8771	0.8095	0.8381	8.343	7.701	8.528

   All three coincide at $T_r = 1$ by construction. Below the critical temperature the three-parameter forms rise faster than $T_r^{-1/2}$, and above it they fall faster; at $T_r = 1.3$ the Soave alpha is 7.7 % below the Redlich–Kwong value, which is the entire content of Soave's correction expressed as a number.
3. Perturbing the acentric factor by 5 %, $\omega' = 1.05\omega = 0.1596$, moves κ from 0.6028 to 0.6139, an increase of 1.838 %: the correlation is already strongly damping.
4. Propagation into the saturation pressure:

T_r	T / K	$P^{sat}(\omega)$ / bar	$P^{sat}(\omega')$ / bar	change / %	$\lvert\Delta P^{sat}/P^{sat}\rvert/\lvert\Delta\omega/\omega\rvert$
0.60	221.88	0.6703	0.6505	−2.955	0.5910
0.70	258.86	2.987	2.934	−1.760	0.3519
0.80	295.84	8.978	8.891	−0.9713	0.1943
0.90	332.82	21.14	21.05	−0.4177	0.08353
0.95	351.31	30.45	30.39	−0.1962	0.03924

The sensitivity is largest at low reduced temperature and decays monotonically toward the critical point.

Check. At $T_\mathrm{r}=1$ the alpha function equals unity for every ω, so $a(T_\mathrm{c})$ must be independent of the acentric factor; the computation returns $1.017\,451\,1\times10^{7}\,\mathrm{bar\,cm^{6}\,mol^{-2}}$ for both ω and ω'. The saturation pressure at T_c is P_c for both, so the sensitivity is required to vanish as $T_\mathrm{r}\to1$, and the tabulated amplification does fall monotonically from 0.5910 to 0.03924 across the range. This is a limiting-case verification of the whole table.

Engineering comment. A 5 % error in ω produces at most a 3 % error in the predicted vapour pressure, so the acentric factor is a robust input: tabulated values differing in the third decimal place between sources are of no consequence. The result also shows why Soave's correlation mattered. The quantity being predicted, the vapour pressure, varies by a factor of 45.43 between $T_\mathrm{r}=0.60$ and 0.95, and the two-parameter Redlich–Kwong alpha cannot follow it for a non-spherical molecule at all; introducing ω into α converts a qualitative curve into a quantitative one, at the cost of one tabulated number per compound whose accuracy barely matters.

Example 6: Fugacity coefficient from the Peng–Robinson equation

Problem. State the Peng–Robinson fugacity coefficient in full, evaluate it for carbon dioxide at $T=320\,\mathrm{K}$ and $P=70\,\mathrm{bar}$ with $T_\mathrm{c}=304.2\,\mathrm{K}$, $P_\mathrm{c}=73.83\,\mathrm{bar}$ and $\omega=0.224$, and verify the result independently by integrating $\ln\varphi=\int_0^P(Z-1)\,\mathrm{d}P/P$ numerically along the isotherm.

Strategy. Integrating $(Z-1)\,\mathrm{d}P/P$ analytically for a cubic with denominator $(V+\delta_1 b)(V+\delta_2 b)$ gives a closed form; with $\delta_1-\delta_2=2\sqrt{2}$ it reads

$$\ln\varphi = Z-1-\ln(Z-B)-\frac{A}{2\sqrt{2}\,B}\ln\left(\frac{Z+\left(1+\sqrt{2}\right)B}{Z+\left(1-\sqrt{2}\right)B}\right),\qquad A=\frac{a(T)P}{R^2T^2},\quad B=\frac{bP}{RT}. \tag{14.1}$$

The state is supercritical ($T_\mathrm{r}=1.052$), so a single root exists at every pressure between zero and 70 bar and the integration path is unambiguous. The integrand is finite at the lower limit, where $(Z-1)/P\to B_2/(RT)$ with $B_2=b-a/(RT)$ the second virial coefficient of the model.

Solution.

1. Parameters: $\kappa=0.7066$, $\alpha=0.9641$, $a(T)=3.819\times10^{6}\,\mathrm{bar\,cm^{6}\,mol^{-2}}$, $b=26.65\,\mathrm{cm^{3}\,mol^{-1}}$, hence $A=0.3777$ and $B=0.07012$.
2. Root: $Z=0.6298$, so $V=ZRT/P=239.3\,\mathrm{cm^{3}\,mol^{-1}}$. The state is $T_\mathrm{r}=1.052$, $P_\mathrm{r}=0.9481$, just above the critical point, where the fluid is dense but single phase.
3. Term by term in Equation (14.1), with $A/(2\sqrt{2}B)=1.904357$ and the logarithm argument $[Z+(1+\sqrt{2})B]/[Z+(1-\sqrt{2})B]=1.330168$, whose natural logarithm is 0.2853054:

$$\underbrace{Z-1}_{-0.3702461}\quad\underbrace{-\ln(Z-B)}_{+0.5804760}\quad\underbrace{-\frac{A}{2\sqrt{2}B}\ln(\cdot)}_{-0.5433233}\;=\;\ln\varphi=-0.3330935.$$

4. Hence $\varphi=\exp(-0.3330935)=0.7167$, and the fugacity is $f=\varphi P=(0.7167)(70)=50.17\,\mathrm{bar}$. The three terms of Equation (14.1) have a clear reading: the first two are the repulsive contribution,

positive in sum here because $-\ln(Z-B)$ dominates $Z-1$, and the third is the attractive contribution, always negative for a positive a. Their near cancellation is typical: the fugacity coefficient of a dense fluid is a small residue of two large opposing effects, which is why the algebra must be carried at full precision even though the answer is quoted to four figures.

5. The integrand of the verification integral, sampled along the isotherm:

P / bar	0	17.5	35.0	52.5	70.0
$(Z-1)/P$ / bar^{-1}	−0.004394	−0.004539	−0.004720	−0.004956	−0.005289

The integrand is smooth, finite at the origin and monotone, so the quadrature converges rapidly and no root switching can have occurred on the path.

Check. Numerical quadrature of $(Z-1)\,\mathrm{d}P/P$ from $P=0$ to 70 bar, with Z obtained by solving the cubic at each quadrature node, gives $\ln\varphi = -0.3330935$ with an estimated quadrature error of 3.7×10^{-15}. The two routes differ by 8.3×10^{-16} in $\ln\varphi$ and by 7.7×10^{-16} relative in φ, that is at the level of double-precision rounding. The integrand behaves as it must: at $P\to0$ it equals $B_2/(RT)$ with $B_2 = b - a/(RT) = -116.9\,\mathrm{cm^3\,mol^{-1}}$, giving $-0.004\,394\,\mathrm{bar^{-1}}$, and it varies smoothly to $-0.005\,289\,\mathrm{bar^{-1}}$ at 70 bar, so no root switching occurred anywhere on the path.

Engineering comment. At this condition $\varphi = 0.7167$, so treating carbon dioxide as an ideal gas would overstate its fugacity, and therefore its escaping tendency in any phase or reaction equilibrium, by 40 %. The agreement between the closed form and the quadrature is not a formality: it is the standard acceptance test for an equation-of-state implementation, because it exercises the cubic solver, the root selection and the fugacity algebra simultaneously, and it fails loudly if any of the three is wrong.

Example 7: Vapour pressure of propane by the isofugacity condition

Problem. For propane at $T = 300\,\mathrm{K}$ ($T_\mathrm{c} = 369.8\,\mathrm{K}$, $P_\mathrm{c} = 42.48\,\mathrm{bar}$, $\omega = 0.152$), solve $\varphi^L P = \varphi^V P$ for the saturation pressure with the Peng–Robinson equation. Show the first iterations explicitly, report the converged P^{sat} and the saturated liquid and vapour molar volumes, and obtain the enthalpy of vaporization from the Clapeyron equation with $\mathrm{d}P^{sat}/\mathrm{d}T$ evaluated numerically.

Strategy. At equilibrium the fugacities of the two phases are equal; at a common pressure this reduces to $\varphi^L = \varphi^V$, where both fugacity coefficients come from Equation (14.1) evaluated at the smallest and largest roots of the same cubic. The condition is solved by successive substitution, $P_{k+1} = P_k\,\varphi_k^L/\varphi_k^V$, which is the classical scheme because the ratio is the factor by which the pressure must move to equalize the fugacities. The starting estimate is the Wilson expression $P_0 = P_\mathrm{c}\exp[5.373(1+\omega)(1-T_\mathrm{c}/T)]$. The Clapeyron equation $\mathrm{d}P^{sat}/\mathrm{d}T = \Delta H^{vap}/[T(V^V - V^L)]$ then gives the latent heat without any further model.

Solution.

1. $T_\mathrm{r} = 0.8112$ and $P_0 = 42.48\exp[5.373(1.152)(1-369.8/300)] = 10.06\,\mathrm{bar}$.
2. Successive substitution:

k	P_k / bar	Z^L	Z^V	φ^L	φ^V	φ^L/φ^V
0	10.06332	0.035005	0.813278	0.836232	0.841165	0.9941350
1	10.00430	0.034802	0.814582	0.840992	0.842086	0.9987010
2	9.991306	0.034757	0.814869	0.842048	0.842289	0.9997140
3	9.988448	0.034747	0.814932	0.842281	0.842334	0.9999371
4	9.987820	0.034745	0.814946	0.842332	0.842344	0.9999862
5	9.987682	0.034744	0.814949	0.842343	0.842346	0.9999970

The iteration is linearly convergent: the relative errors of the successive iterates are 7.577×10^{-3}, 1.668×10^{-3}, 3.667×10^{-4}, 8.060×10^{-5}, 1.772×10^{-5} and 3.894×10^{-6}, whose ratios are 0.2201, 0.2199, 0.2198, 0.2198 and 0.2198. Each iteration therefore gains rather more than half a

decimal digit, and the contraction factor is constant, which is the signature of a fixed-point scheme rather than a Newton scheme.

3. Converged result, refined by a bracketed root solve on $\ln\varphi^V - \ln\varphi^L$:

$$P^{sat}(300\,\mathrm{K}) = 9.988\,\mathrm{bar}, \qquad Z^L = 0.03474, \qquad Z^V = 0.8150,$$

with a residual $|\ln\varphi^V - \ln\varphi^L| = 3.6\times10^{-13}$.

4. Saturated molar volumes: $V^L = Z^L RT/P^{sat} = 86.77\,\mathrm{cm^3\,mol^{-1}}$ and $V^V = 2035\,\mathrm{cm^3\,mol^{-1}}$, so $V^V - V^L = 1948\,\mathrm{cm^3\,mol^{-1}}$. The saturated liquid density is $M/V^L = 508.2\,\mathrm{kg\,m^{-3}}$ with $M = 44.097\,\mathrm{g\,mol^{-1}}$.

5. Quality of the initial estimate. The Wilson expression gave 10.06 bar against the converged 9.988 bar, an error of 0.7577 %. That is why the successive substitution needed only five steps: the correlation is designed to be accurate enough to place the starting pressure inside the three-root window, which is the only requirement the scheme imposes on it.

6. Clapeyron slope by central difference: $P^{sat}(299.5\,\mathrm{K}) = 9.862\,\mathrm{bar}$ and $P^{sat}(300.5\,\mathrm{K}) = 10.11\,\mathrm{bar}$, so $\mathrm{d}P^{sat}/\mathrm{d}T = 0.2523\,\mathrm{bar\,K^{-1}}$.

7. Enthalpy of vaporization, using $1\,\mathrm{bar\,cm^3} = 0.1\,\mathrm{J}$:

$$\Delta H^{vap} = T\left(V^V - V^L\right)\frac{\mathrm{d}P^{sat}}{\mathrm{d}T} = (300)(1948.4)(0.25230)(0.1) = 14\,747\,\mathrm{J\,mol^{-1}} = 14.75\,\mathrm{kJ\,mol^{-1}}.$$

Check. Two independent verifications agree. First, the Maxwell equal-area construction: integrating $P(V) - P^{sat}$ along the model isotherm from V^L to V^V gives a residual of $9.1\times10^{-9}\,\mathrm{bar\,cm^3\,mol^{-1}}$, that is 4.7×10^{-11} percent of $P^{sat}(V^V - V^L)$, confirming that the isofugacity root is also the equal-area root, as it must be. Second, the latent heat computed from the Peng–Robinson residual enthalpies of the two saturated phases, $H^{res,V} = -1288\,\mathrm{J\,mol^{-1}}$ and $H^{res,L} = -16\,035\,\mathrm{J\,mol^{-1}}$, is their difference, $14\,747\,\mathrm{J\,mol^{-1}}$, which differs from the Clapeyron value by 0.0009 %; the residual is entirely attributable to the finite difference used for the slope.

Engineering comment. A saturation pressure of 9.988 bar at ambient temperature fixes the design pressure of every propane storage vessel, and the saturated liquid density of $508.2\,\mathrm{kg\,m^{-3}}$ fixes the mass in it. The latent heat obtained here comes from the same equation and the same two roots, with no separate correlation, which is exactly the economy that made a single cubic acceptable for whole flowsheets: pressure, density and latent heat are three consequences of one PVT surface, and they cannot become mutually inconsistent.

Example 8: Binary vapour–liquid equilibrium and K-values

Problem. An equimolar mixture of methane and *n*-butane is at $T = 350\,\mathrm{K}$ and $P = 20\,\mathrm{bar}$. Using the Peng–Robinson equation with the van der Waals one-fluid mixing rules

$$a_{mix} = \sum_i\sum_j y_i y_j \sqrt{a_i a_j}\,(1 - k_{ij}), \qquad b_{mix} = \sum_i y_i b_i,$$

and with $k_{ij} = 0$ assumed for this pair, compute the K-values of both components and perform one Rachford–Rice iteration, reporting the residual function and the updated vapour fraction. State what changes if $k_{ij} \neq 0$.

Strategy. For a mixture the fugacity coefficient of a component follows from the same integration as Equation (14.1) applied to the partial molar residual Gibbs energy:

$$\ln\hat{\varphi}_i = \frac{b_i}{b_{mix}}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}\,B}\left(\frac{2\sum_j y_j a_{ij}}{a_{mix}} - \frac{b_i}{b_{mix}}\right)\ln\left(\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right), \tag{14.2}$$

and $K_i = \hat{\varphi}_i^L/\hat{\varphi}_i^V$. Trial phase compositions are needed before Equation (14.2) can be evaluated, so the Wilson expression $K_i = (P_{c,i}/P)\exp[5.373(1+\omega_i)(1 - T_{c,i}/T)]$ initializes the calculation. The vapour

fraction ψ then follows from the Rachford–Rice residual $F(\psi) = \sum_i z_i(K_i - 1)/[1 + \psi(K_i - 1)] = 0$, which is monotonically decreasing in ψ and therefore has at most one root in $[0, 1]$.

Solution.

1. Pure-component parameters at 350 K: $a_1 = 1.848 \times 10^6$ and $a_2 = 1.698 \times 10^7\,\mathrm{bar\,cm^6\,mol^{-2}}$, $b_1 = 26.81$ and $b_2 = 72.44\,\mathrm{cm^3\,mol^{-1}}$, with the cross term $a_{12} = \sqrt{a_1 a_2}(1 - k_{12}) = 5.602 \times 10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$.
2. Initialization: the Wilson expression gives $K_1 = 27.36$ and $K_2 = 0.4758$, and solving $F(\psi) = 0$ with these values returns $\psi = 0.9349$, hence trial compositions $x = (0.01950, 0.9805)$ and $y = (0.5334, 0.4666)$.
3. Mixture parameters and roots. For the liquid trial phase, $a_{mix} = 1.654 \times 10^7\,\mathrm{bar\,cm^6\,mol^{-2}}$, $b_{mix} = 71.55\,\mathrm{cm^3\,mol^{-1}}$, $A = 0.3906$, $B = 0.04917$ and $Z^L = 0.07640$, that is $V^L = 111.2\,\mathrm{cm^3\,mol^{-1}}$. For the vapour trial phase, $a_{mix} = 7.010 \times 10^6\,\mathrm{bar\,cm^6\,mol^{-2}}$, $b_{mix} = 48.10\,\mathrm{cm^3\,mol^{-1}}$, $A = 0.1656$, $B = 0.03306$ and $Z^V = 0.8611$, that is $V^V = 1253\,\mathrm{cm^3\,mol^{-1}}$.
4. Fugacity coefficients from Equation (14.2) and the resulting K-values:

component	$\hat{\varphi}_i^L$	$\hat{\varphi}_i^V$	K_i
methane	9.277	1.025	9.055
n-butane	0.4128	0.7274	0.5675

5. One Rachford–Rice iteration at $\psi = 0.9349$ with these K-values:

$$F(\psi) = \underbrace{\frac{0.5(9.055-1)}{1+0.9349(9.055-1)}}_{+0.4721} + \underbrace{\frac{0.5(0.5675-1)}{1+0.9349(0.5675-1)}}_{-0.3630} = +0.1091, \qquad \frac{\mathrm{d}F}{\mathrm{d}\psi} = -0.7093,$$

   so the Newton update is $\psi_{new} = 0.9349 - (0.1091)/(-0.7093) = 1.089$.
6. Interpretation of the update. The residual is positive at both ends of the interval, $F(0) = 3.811$ and $F(1) = 0.06380$, so F has no root in $[0, 1]$ and the Newton step correctly leaves the interval. The Peng–Robinson K-values therefore state that the equimolar feed at 350 K and 20 bar is a single superheated vapour, not a two-phase mixture.

Check. Three verifications were performed. First, setting the composition of either component to unity in Equation (14.2) reproduces the pure-component fugacity coefficient of Chapter 10 exactly, $\hat{\varphi} = 0.9757409$ for methane and 0.4127765 for *n*-butane, to 2×10^{-16}. Second, the dew-point pressure of this feed at 350 K, obtained by solving $\sum_i y_i/K_i = 1$ with the same model, is 22.77 bar, above the specified 20 bar, which confirms the single-phase verdict by an independent route. Third, the identical procedure applied at 40 bar, inside the two-phase region, converges to $\psi = 0.6930$, $K = (4.372, 0.4057)$, $x = (0.1498, 0.8502)$ and $y = (0.6551, 0.3449)$, with an isofugacity residual $\max_i |x_i\hat{\varphi}_i^L - y_i\hat{\varphi}_i^V| = 7.3 \times 10^{-14}$ and a material balance residual of 1.1×10^{-16}.

Engineering comment. Two lessons follow. The first is that the bracketing test on $F(\psi)$, and not the Newton step, is what detects a single-phase feed; a flash routine that iterates without testing $F(0)$ and $F(1)$ will either diverge or return a physically meaningless negative-flow split. The second concerns k_{12}. Setting it to zero is an assumption, not a neutral choice:

k_{12}	K_1	K_2	change in K_2	converged ψ at 40 bar
0	9.055	0.5675	reference	0.6930
0.02	8.919	0.6043	6.472 %	0.7359
0.05	8.671	0.6627	16.76 %	0.8177

A binary interaction parameter of a few hundredths, well within the range regressed for light hydrocarbon pairs, moves the vapour fraction by 6.19 % and 17.99 % respectively, which is the difference

between a column that meets specification and one that does not. The geometric mean $\sqrt{a_1 a_2}$ is a statement about the unlike pair potential, and setting $k_{12} = 0$ asserts that the methane to *n*-butane attraction is exactly the geometric mean of the like attractions; for molecules of such different size that assertion is optimistic, and it must be recorded in the calculation basis rather than left implicit.

Example 9: Departure functions and a compressor duty

Problem. For carbon dioxide ($T_c = 304.2\,\mathrm{K}$, $P_c = 73.83\,\mathrm{bar}$, $\omega = 0.224$) at $T = 350\,\mathrm{K}$ and $P = 80\,\mathrm{bar}$, evaluate $H - H^{ig}$ and $S - S^{ig}$ from the Peng–Robinson equation. Then compute the isentropic duty of a compressor handling $100\,\mathrm{kmol\,h^{-1}}$ of carbon dioxide from 10 bar to 80 bar with an inlet temperature of 350 K, and compare with the answer obtained by neglecting the departure functions. Assume a constant ideal-gas heat capacity $C_P^{ig} = 42.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$, representative of carbon dioxide between 350 K and 541 K; the reference state for both routes is the ideal gas at the same temperature and pressure, so it cancels from every difference taken below.

Strategy. Applying the departure-function chain of Chapter 1 to the Peng–Robinson equation gives, with $\mathscr{L} = \ln\{[Z + (1+\sqrt{2})B]/[Z + (1-\sqrt{2})B]\}$,

$$H - H^{ig} = RT\,(Z-1) + \frac{T\,\mathrm{d}a/\mathrm{d}T - a}{2\sqrt{2}\,b}\,\mathscr{L}, \qquad S - S^{ig} = R\ln(Z-B) + \frac{\mathrm{d}a/\mathrm{d}T}{2\sqrt{2}\,b}\,\mathscr{L}, \tag{14.3}$$

with $\mathrm{d}a/\mathrm{d}T = -a_c\kappa\left[1 + \kappa(1-\sqrt{T_r})\right]/\sqrt{T T_c}$. An isentropic compression is then located by solving $C_P^{ig}\ln(T_2/T_1) - R\ln(P_2/P_1) + S^{res}(T_2,P_2) - S^{res}(T_1,P_1) = 0$ for T_2, and the duty follows from $W_s = C_P^{ig}(T_2 - T_1) + H^{res}(T_2,P_2) - H^{res}(T_1,P_1)$.

Solution.

1. Parameters in SI units: $a_c = 0.396\,141\,\mathrm{Pa\,m^6\,mol^{-2}}$, $b = 2.665\,115 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$, $\kappa = 0.7066$. At $350\,\mathrm{K}$, $T_r = 1.151$, $a = 0.355\,203\,\mathrm{Pa\,m^6\,mol^{-2}}$ and $\mathrm{d}a/\mathrm{d}T = -8.137\,746 \times 10^{-4}\,\mathrm{Pa\,m^6\,mol^{-2}\,K^{-1}}$.
2. State: $A = 0.3368$, $B = 0.07327$, $Z = 0.7217$ and $V = 262.5\,\mathrm{cm^3\,mol^{-1}}$, with $\mathscr{L} = 0.2622$.
3. Prefactors in Equation (14.3): $(T\,\mathrm{d}a/\mathrm{d}T - a)/(2\sqrt{2}b) = -8508\,\mathrm{J\,mol^{-1}}$ and $(\mathrm{d}a/\mathrm{d}T)/(2\sqrt{2}b) = -10.80\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Hence

$$H - H^{ig} = (8.314)(350)(0.7217-1) + (-8508)(0.26218) = -3041\,\mathrm{J\,mol^{-1}} = -3.041\,\mathrm{kJ\,mol^{-1}},$$

$$S - S^{ig} = (8.314)\ln(0.72169 - 0.07327) + (-10.7955)(0.26218) = -6.432\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

4. Inlet state and isentropic outlet. The entropy balance $C_P^{ig}\ln(T_2/T_1) - R\ln 8 + \Delta S^{res} = 18.2844 - 17.2885 - 0.9959 = 0$ is satisfied at $T_2 = 540.9\,\mathrm{K}$. The two states are

state	T / K	P / bar	Z	H^{res} / J mol^{-1}
suction	350.0	10	0.9668	−322.4
discharge	540.9	80	0.9651	−1066

   with $S^{res} = -0.6462\,\mathrm{J\,mol^{-1}\,K^{-1}}$ at suction and $-1.642\,\mathrm{J\,mol^{-1}\,K^{-1}}$ at discharge. Both compressibility factors are close to unity because the discharge is hot; the residual properties are nevertheless not negligible, which is the point of the example.
5. Duty:

$$W_s = (42.0)(540.92 - 350.00) + (-1066.17) - (-322.39) = 7275\,\mathrm{J\,mol^{-1}},$$

   and with $\dot{n} = 100\,\mathrm{kmol\,h^{-1}} = 27.78\,\mathrm{mol\,s^{-1}}$ the shaft power is 202.1 kW.
6. Ideal-gas-only route: $R/C_P^{ig} = 0.19795$, so $T_2 = 350 \times 8^{0.19795} = 528.2\,\mathrm{K}$ and $W_s = C_P^{ig}(T_2 - T_1) = 7486\,\mathrm{J\,mol^{-1}}$, that is 207.95 kW.
7. Comparison of the two routes:

route	T_2 / K	W_s / J mol^{-1}	duty / kW
ideal gas only	528.2	7486	207.95
Peng–Robinson departures	540.9	7275	202.08
difference	−12.68	−211.4	−5.872

The ideal-gas answer is 2.824 % high in duty and 12.68 K high in discharge temperature.

Check. The three departure functions are derived separately and must satisfy $H^{res} - TS^{res} = G^{res} = RT\ln\varphi$. Evaluating each independently gives $-3040.52 - (350)(-6.432194) = -789.26\,\mathrm{J\,mol^{-1}}$ against $RT\ln\varphi = -789.26\,\mathrm{J\,mol^{-1}}$, agreeing to 9×10^{-13}. As a second and stronger test, S^{res} was recomputed as $-(\partial G^{res}/\partial T)_P$ by central difference on $RT\ln\varphi$, giving $-6.4322\,\mathrm{J\,mol^{-1}\,K^{-1}}$ against the analytic $-6.4322\,\mathrm{J\,mol^{-1}\,K^{-1}}$, a difference of 8×10^{-7}; this exercises the temperature derivative of the alpha function, which is where errors in departure functions usually hide.

Engineering comment. The residual enthalpy at the discharge condition is $-1.066\,\mathrm{kJ\,mol^{-1}}$ and at suction $-0.322\,\mathrm{kJ\,mol^{-1}}$; the difference is only about ten percent of the shaft work, yet it moves the duty by 5.9 kW on a 202 kW machine. Two consequences follow. The ideal-gas calculation is conservative here, so it does not create a safety problem, but it does create a capital one, since a machine specified 2.8 % large is paid for. More seriously, the predicted discharge temperature is 12.7 K too high, which propagates into intercooler duty, material selection and, on a multistage machine, into the stage distribution itself.

Example 10: Corresponding states and the acentric factor in practice

Problem. For *n*-butane ($T_c = 425.1$ K, $P_c = 37.96$ bar, tabulated $\omega = 0.200$), recover the acentric factor from the Peng–Robinson saturation curve at $T_r = 0.7$ and compare with the tabulated value. Then estimate Z at $T_r = 1.2$ and $P_r = 1.5$ from three-parameter corresponding states, compare with the direct Peng–Robinson result, and discuss the discrepancy.

Strategy. The acentric factor is defined by $\omega = -1 - \log_{10} P_r^{sat}$ evaluated at $T_r = 0.7$, so any model that predicts a saturation curve also predicts an acentric factor, and the comparison with the tabulated value measures how faithfully the $\kappa(\omega)$ correlation inverts. For the second part the three-parameter corresponding-states expansion $Z = Z^{(0)} + \omega Z^{(1)}$ is used, with $Z^{(0)}$ from the Lee–Kesler simple fluid and $Z^{(1)} = (Z^{(r)} - Z^{(0)})/\omega^{(r)}$ from its *n*-octane reference fluid, $\omega^{(r)} = 0.3978$. This is a genuinely independent model, fitted to experimental PVT data rather than derived from a cubic, so the comparison is a test and not a tautology.

Solution.

1. At $T_r = 0.7$, $T = 0.7(425.1) = 297.6$ K. The Peng–Robinson isofugacity solution gives $P^{sat} = 2.387$ bar, hence $P_r^{sat} = 2.38678/37.96 = 0.06288$ and $\log_{10} P_r^{sat} = -1.2015$.
2. Recovered acentric factor: $\omega = -1 - (-1.20151) = 0.2015$, against the tabulated 0.200. The deviation is $+0.001514$, that is 0.7570 %.
3. Three-parameter corresponding states at $T_r = 1.2$, $P_r = 1.5$: the Lee–Kesler simple fluid gives $Z^{(0)} = 0.6605$ and the reference fluid gives $Z^{(r)} = 0.7193$, hence

$$Z^{(1)} = \frac{Z^{(r)} - Z^{(0)}}{\omega^{(r)}} = \frac{0.71927 - 0.66052}{0.3978} = 0.1477,$$

$$Z = Z^{(0)} + \omega Z^{(1)} = 0.66052 + (0.200)(0.14769) = 0.6901.$$

4. Direct Peng–Robinson result at the same reduced state, that is $T = 510.1$ K and $P = 56.94$ bar: $Z = 0.6831$, corresponding to $V = 508.8\,\mathrm{cm^3\,mol^{-1}}$ against $514.0\,\mathrm{cm^3\,mol^{-1}}$ from the corresponding-states estimate.
5. Summary of the estimates at $T_r = 1.2$, $P_r = 1.5$:

route	Z	V / cm^3 mol^{-1}
two-parameter corresponding states, $Z^{(0)}$ only	0.6605	492.0
three-parameter corresponding states, $Z^{(0)} + \omega Z^{(1)}$	0.6901	514.0
Peng–Robinson, direct	0.6831	508.8

6. Discrepancy: $Z^{PR} - Z^{CS} = -0.006991$, that is $-1.013\,\%$. For perspective, dropping the acentric term entirely and using two-parameter corresponding states would give $Z = Z^{(0)} = 0.6605$, an error of $-4.281\,\%$; the acentric correction is worth $\omega Z^{(1)} = +0.02954$ in Z, four times the residual disagreement between the two models.

Check. The Lee–Kesler implementation was verified in three ways. At $T_\mathrm{r} = 2$ and $P_\mathrm{r} = 1 \times 10^{-4}$ it returns $Z^{(0)} = 0.99999714$, and the implied second virial coefficient $(Z^{(0)} - 1)T_\mathrm{r}/P_\mathrm{r} = -0.057232$ reproduces the analytic $B(T_\mathrm{r})$ of the same correlation, -0.057233. At its own critical point it returns 0.2918 against the correlation's stated $Z_\mathrm{c} = 0.2901$, the residual being the accuracy attainable at a triple root. The corresponding test on the Peng–Robinson cubic, whose three roots at the critical point have mean $(1 - B)/3$, returns 0.307400 against the design value 0.30740. A truncated virial route is not available as a check here: the Pitzer correlation $B^{(0)} = -0.2322$, $B^{(1)} = 0.05902$ would give $Z = 0.7245$, but its validity criterion $P_\mathrm{r} < T_\mathrm{r}/2 = 0.60$ is violated at $P_\mathrm{r} = 1.5$, which is exactly the reason a full corresponding-states correlation is needed at this density.

Engineering comment. Two conclusions of different kinds follow. The recovered acentric factor differs from the tabulated one by less than one percent, which shows that the $\kappa(\omega)$ correlation inverts almost exactly, and repeating the calculation for propane gives $\omega = 0.1530$ against a tabulated 0.152, so the small positive offset is a property of the correlation and not of one substance. The one percent disagreement in Z at $T_\mathrm{r} = 1.2$, $P_\mathrm{r} = 1.5$ is of a different nature. It is not an arithmetic residual but a genuine model difference: the Lee–Kesler correlation is a multiparameter fit to measured volumetric data, whereas the cubic carries only two substance constants and a mean-field attraction. In the dense near-critical region the two constructions cannot agree better than this, and a one percent uncertainty in Z is a reasonable expectation for any cubic equation there, which is the practical warning to carry away from all ten examples.

Closing remarks on the ten examples

Three threads run through the set. The first is that a single dimensionless number, the compressibility factor, converts directly into money and metal: 640 kg of methane in Example 1, 25.8 t of misassigned *n*-butane in Example 3, 5.9 kW of compressor duty in Example 9. None of these errors announces itself; each is simply carried forward.

The second is that almost every quantity a process calculation needs is a functional of the same PVT surface. The fugacity coefficient of Example 6, the saturation pressure and latent heat of Example 7, the K-values of Example 8 and the departure functions of Example 9 were all obtained from one cubic with three tabulated constants per substance. This is the economy that made the cubic equation of state the industrial standard, and it is also the reason an error in the volumetric closure cannot be confined: it reappears in the enthalpy balance, the phase split and the equipment size at the same time.

The third is that verification is cheap and non-negotiable. Every example above carries an independent check, and the checks used only four techniques: a limiting case, a second analytic route, a numerical quadrature or derivative, and a units argument. Where the closed form and the quadrature agreed to 1×10^{-15} the implementation may be trusted; where the two routes agreed only to one percent, as in Example 10, the residual is a real difference between models and must be reported as an uncertainty rather than resolved by refining the arithmetic.

The examples also record, in one place, the numerical acceptance criteria a working implementation should meet. The closed-form and quadrature routes to $\ln\varphi$ must agree to machine precision, as they did in Examples 4 and 6 at the level of 1×10^{-15}. The isofugacity saturation pressure must satisfy the Maxwell

equal-area construction, as in Example 7, where the residual was $9.1 \times 10^{-9}\,\mathrm{bar\,cm^3\,mol^{-1}}$. The three departure functions must satisfy $H^{res} - TS^{res} = RT\ln\varphi$ and $S^{res} = -(\partial G^{res}/\partial T)_P$, as in Example 9. The mixture fugacity coefficient must reduce to the pure-component value when a mole fraction is set to unity, as in Example 8. A flash must close its material balance and its isofugacity condition simultaneously. None of these tests requires experimental data, and each one fails loudly when an implementation is wrong; together they are cheaper than a single misdiagnosed simulation.

Chapter 15

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Chapter 16

Answers to selected practice questions

Numerical answers to the quantitative practice questions are given below. Full solutions to the worked examples appear in the examples chapter; students should attempt the practice questions before consulting these values.

Because the practice questions are designed to be solved with the accompanying Python routines, answers are quoted to four significant figures. A discrepancy in the fourth figure usually indicates a different value of R or a different unit convention, not a conceptual error. A discrepancy in the second figure usually indicates selection of the wrong root of the cubic.

Instructors: a complete solution key, including the alpha-function sensitivity studies and the flash-calculation convergence traces, is distributed separately with the instructor package.