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Thermodynamics of Pure Fluids

First of all, let us introduce the notion of *the thermodynamic state*, or *the thermodynamic system*, which is the fundamental concept of thermodynamic formalism. The thermodynamic state is a primitive concept, the existence of which is formally postulated but is not derived from other concepts. As with any other primitive concept, the thermodynamic state cannot be strictly defined, but should be understood as an idealized physical object whose contents are in internal equilibrium, with zero fluxes of all physical quantities inside it and zero fluxes between this object and the surrounding world. Consequently, this object is homogeneous in space and does not evolve in time, such that the spatial gradients and the time derivatives are zero. Therefore, the concepts of space and time become useless for it. This is why one can say that a thermodynamic system exists outside of space and time.

A thermodynamic state is determined by *parameters of state* that are also primitive concepts, not strictly defined but understood as the minimal complete set of parameters capable of describing all the possible thermodynamic states. Usually they are selected as pressure P, temperature T, volume V, and mole fractions of internal components c_k. Instead of volume V we use molar volume $v = V/N$, where N is the number of moles.

In this chapter, all the fluids are considered as thermodynamic systems, i.e. they are always in equilibrium.

The condition of the equilibrium imposes some constraints on the variation of thermodynamic parameters, which cannot be arbitrary. These constraints are formulated mathematically in the form of equations between the parameters of state. They are as follows:

- Equation of state (EOS), for a single-phase one-component fluid,
- EOS and mixing rules, for a single-phase multicomponent fluid,
- Equilibrium equation and EOS, for multiphase one-component fluid,
- Equilibrium equations, EOSs, and mixing rules, for multiphase multicomponent fluid.

Physicochemical Fluid Dynamics in Porous Media: Applications in Geosciences and Petroleum Engineering,
First Edition. Mikhail Panfilov.

1.1 Equilibrium of Single-phase Fluids – Equation of State

A single-phase fluid in equilibrium is completely described by its EOS. An EOS is the result of the homogenization of a physical system consisting of a statistical ensemble of particles (molecules) assumed to be in equilibrium between them and with the external world.

1.1.1 Admissible Classes of EOS

The condition of the equilibrium is stronger than that of stability. And, any thermodynamic system must be necessarily stable. Then any EOS should be consistent with the basic thermodynamic principle which concerns the stability of a single-phase state. It says that a single-phase system is stable if and only if two conditions are satisfied:

$$\left(\frac{\partial P}{\partial V}\right)_T < 0, \qquad C_V > 0 \tag{1.1}$$

where C_V is the isochoric calorific capacity: $C_V = (\partial Q/\partial T)_V$, Q being the heat transmitted to the examined system. The second inequality means that the heat transmitted to the body can only augment its temperature, which is the consequence of the second principle of thermodynamics. For an isolated system, this condition becomes useless.

Consequently, an EOS for a single-phase fluid must describe a continuous monotonically decreasing function $P = P(V)$ (at any fixed temperature T). The best-known example of such an EOS is that of the ideal gas, which results from statistical physics:

$$P = NRT/V = RT/v \tag{1.2}$$

where $v = V/N$ is the molar volume, N is the number of moles, and $R = 8.3144621$ J·mol^{-1}K^{-1} is the universal gas constant.

The ideal gas means the fluid which has particles of zero size and zero energy of interaction between the particles.

If the condition of stability (1.1) is not satisfied, then this means that single-phase state is impossible, and the system is multiphase.

If we desire that the same EOS could be able to describe two different single-phase fluids (liquid and gas), then its solution should necessarily cross the two-phase states of gas–liquid coexistence. Then, in this domain, the function $P(v)$ describing the single-phase states should behave as an unstable function (monotonically increasing). The inverse function $v(P)$ should then have a nonuniqueness in that domain, as shown in Figure 1.1.

In the domain of nonuniqueness shown in Figure 1.1, the function $v(P)$ has three different solutions for a fixed pressure.

Such a behavior is typical for a cubic polynomial with respect to the volume v, which has three different zeros. Such a cubic EOS has been obtained naturally by van der Waals (vdW) as the simplest generalization of the ideal EOS.

The main cubic EOS used in practice are vdW, Peng–Robinson, and Soawe-Redlish-Kwong (SRK) EOS, (Prausnitz, Lichtenthaler, and de Azevedo (1999)), (Sandler (1999)), and (Tester (1996)).

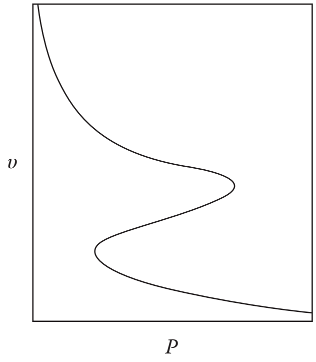

Figure 1.1 Admissible trajectory of EOS capable of describing the thermodynamic state of gas and liquid.

1.1.2 van der Waals EOS

The vdW EOS has the form:

$$P = \frac{RT}{v-b} - \frac{a}{v^2}, \tag{1.3}$$

where coefficients a and b are given in Table 1.1 (Weast 1972).

These coefficients are fit with experimental data to calculate the gas phase.

If we would like to use this equation in the vicinity of the critical point, then parameters a and b can be calculated from the exact relationships obtained from the properties of the critical point:

$$a = \frac{27(RT_c)^2}{64P_c}, \qquad b = \frac{RT_c}{8P_c}$$

where P_c and T_c are the critical pressure and temperature.

vdW EOS was obtained from the ideal EOS by replacing ideal properties by real ones. First of all, we replace the particles with the zero energy of interaction between them by interacting particles. In the first approximation, the energy of interaction is inversely proportional to the volume: $\sim -1/V$ (the higher the volume the lower the energy, the lower the volume the higher the energy). Then the internal energy is $U = U_{\text{ideal}} - A/V$, where U_{ideal} is the energy of the ideal gas (the kinetic energy of particles) and A is a parameter. Then the pressure, defined as $-\partial U/\partial V$, becomes $P = P_{\text{ideal}} - A/V^2$, where P_{ideal} is the pressure of the ideal gas defined as (1.2).

Secondly, we take into account the finite size of particles, b. The volume which is accessible to the fluid is $v - b$, but not v. Then we obtain $P = RT/(V/N - b) - A/V^2$, which is the vdW EOS.

1.1.3 Soave-Redlish-Kwong EOS

The SRK EOS is the empirical generalization of the vdW EOS:

$$P = \frac{RT}{v-b} - \frac{a(T,\omega)}{v(v+b),} \tag{1.4}$$

Table 1.1 Parameters of the van der Waals equation of state.

	a (Pa·m^6 mol^{-2})	b (m^3 mol^{-1})	P_c (bar)	T_c (K)
He	0.00345	23.71×10^{-6}	2.26	5.2
H_2	0.0247	26.61×10^{-6}	12.80	33.2
CO_2	0.3637	42.69×10^{-6}	72.90	304.13
CO	0.1505	39.85×10^{-6}	34.5	132.9
H_2S	0.4544	43.39×10^{-6}	90.04	373.1
H_2O	0.5573	30.52×10^{-6}	218.1	647.3
N_2	0.1408	39.1×10^{-6}	33.9	126.19
O_2	0.1378	31.8×10^{-6}	50.1	154.58
Air (80% N_2, 20% O_2)	0.1358	36.4×10^{-6}		
CH_4	0.225	42.8×10^{-6}	45.8	190.56
C_2H_6	0.5562	63.8×10^{-6}	48.20	305.33
C_3H_8	0.8779	84.45×10^{-6}	42.01	369.83
$C_4H_{10} - n$	1.393	116.8×10^{-6}	38.0	425.13
$C_4H_{10} - i$	1.336	116.8×10^{-6}	35.82	407.82
C_5H_{12}	1.926	146.0×10^{-6}	33.7	469.7
C_6H_{14}	2.471	173.1×10^{-6}	29.94	507.85
C_7H_{16}	3.089	203.8×10^{-6}	27.4	540.2
C_8H_{18}	3.784	237.2×10^{-6}	24.9	568.7
C_9H_{20}	4.511	20.2×10^{-6}	24.9	568.
$C_{10}H_{22}$	5.288	305.1×10^{-6}	21.1	617.7
$C_{15}H_{32}$	9.650	485.7×10^{-6}	14.80	707.0

Table 1.2 Pitzer's acentric factor.

	He	Ar	H_2	CO_2	CO	N_2	O_2	H_2O	CH_4	C_2H_6	C_3H_8
ω	−0.390	0.000	−0.220	0.228	0.049	0.040	0.022	0.344	0.010	0.100	0.152

	$C_4H_{10} - n$	$C_4H_{10} - i$	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$	$C_{12}H_{26}$
ω	0.193	0.176	0.251	0.296	0.350	0.394		0.490	0.562

where $a(T,\omega) = \alpha[1 + (0.48508 + 1.55171\omega - 0.156613\omega^2)(1 - \sqrt{T/T_c})]^2$, $\alpha = 0.427480\frac{R^2T_c^2}{P_c}$, and $b = 0.086640\frac{RT_c}{P_c}$, ω is the Pitzer's acentric factor responsible for the degree of nonsphericity of molecules. The acentric factor is zero for all spherical molecules. Several examples of nonspherical molecules are given in Table 1.2.

1.1.4 Peng–Robinson EOS

The Peng–Robinson EOS is

$$P = \frac{RT}{v-b} - \frac{a(T,\omega)}{v^2+2bv-b^2}, \tag{1.5}$$

where $a(T,\omega) = \alpha[1+m(1-\sqrt{T/T_c})]^2$, $\alpha = 0.45724\frac{R^2T_c^2}{P_c}$, $b = 0.07780\frac{RT_c}{P_c}$, ω is the Pitzer's acentric factor, and $m = \begin{cases} 0.37464 + 1.54226\omega - 0.26992\omega^2, & \omega \leq 0.49 \\ 0.379642 + 1.48503\omega - 0.164423\omega^2, & \omega > 0.49 \end{cases}$

1.1.5 Mixing Rules for Multicomponent Fluids

For single-phase mixtures, the EOSs are assumed to keep the same form, but the efficient parameters a, b, and α are calculated using some rules of averaging over all the components, which are called *the mixing rules*.

For VdW, SRK, and Peng–Robinson EOSs, the mixing rules are identical:

$$a = \sum_{k=1}^{n}\sum_{j=1}^{n} a_{kj}C_kC_j, \quad b = \sum_{k=1}^{n} b_kC_k, \quad a_{kk} = a_k, \quad a_{kj} = (1-k_{kj})\sqrt{a_ka_j}$$

where C_k is the mole fraction of component k in the mixture.

Coefficients of binary interaction, $k_{kj} = k_{jk}$, are determined in Table 1.3.

1.2 Two-phase Equilibrium of Pure Fluids

For two-phase fluids, the EOS for each phase is not sufficient to describe the equilibrium. The main equilibrium relationships are formulated through *chemical*

Table 1.3 Coefficients of binary interaction, k_{kj}.

	N_2	CO_2	H_2S	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$
N_2	0	0	0.13	0.025	0.01	0.09	0.095	0.1	0.11	0.115	0.12	0.12	0.125
CO_2		0	0.135	0.105	0.130	0.125	0.115	0.115	0.115	0.115	0.115	0.115	0.115
H_2S			0	0.07	0.085	0.08	0.075	0.07	0.07	0.6	0.6	0.6	0.055
CH_4				0	0.005	0.01	0.025	0.03	0.03	0.035	0.04	0.04	0.045
C_2H_6					0	0.005	0.01	0.01	0.02	0.02	0.02	0.02	0.02
C_3H_8						0	0	0.002	0.01	0.005	0.005	0.005	0.005
C_4H_{10}							0	0.005	0.005	0.005	0.005	0.005	0.005
C_5H_{12}								0	0	0	0	0	0
C_6H_{14}									0	0	0	0	0
C_7H_{16}										0	0	0	0
C_8H_{18}											0	0	0
C_9H_{20}												0	0
$C_{10}H_{22}$													0

potential, which is the specific energy of molecular interaction per one molecule. As this is the intensive parameter, it can depend only on intensive thermodynamic parameters of state such as pressure, temperature, and fluid composition. Consequently, we start this chapter with the general relationships which can be obtained for the chemical potential in terms of these thermodynamic parameters.

Such a relationship for the chemical potential can be obtained in two different ways:

- By developing a differential equation for the chemical potential directly from its definition through the Gibbs free energy; or
- By using the property of the homogeneity of the free energy with respect to the number of particles N.

1.2.1 Pseudo-liquid/pseudo-gas and True liquid/gas

Before determining the equilibrium conditions between a gas and a liquid, we should introduce the definition of gas and liquid in terms of intensive parameters used in thermodynamics: P, v, T. As long as any phase is defined only by its EOS, we can introduce the concept of pseudo-gas and pseudo-liquid in the following way:

The pseudo-liquid and the pseudo-gas: they are hypothetical fictitious fluids, each of them being defined only by a formal EOS ($v = v(P, T)$, or $P = P(v, T)$), and each of them exists formally at any P, T. The difference between the pseudo-gas and the pseudo-liquid is determined only by the different EOSs used for them. If we use the same EOS for both phases, then the pseudo-gas and the pseudo-liquid are identical at all P, T.

Along with pseudo-gas and pseudo-liquid, we can also introduce the concepts of the following:

The true coexisting (equilibrium) gas and liquid: they are the fluids which are determined by the system of EOS and the phase equilibrium equations. It will be shown that, for a fixed T, the true gas and liquid have the same pressure, but differ in molar volumes: $v_{\min}$ for liquid and $v_{\max}$ for gas.

The true single-phase gas and true single-phase liquid: they are the fluids which are determined by EOS only and exist outside the two-phase coexistence domain, such that gas exists at $v > v_{\max}$, while liquid exists at $v < v_{\min}$, for a given T.

So the true phases exist in some limited domains, while the pseudo-phases exist everywhere.

The pseudo-phases do not exist in reality; they are some purely mathematical objects, but are necessary to formulate the equilibrium equations.

1.2.2 Equilibrium Conditions in Terms of Chemical Potentials

The equilibrium conditions for gas and liquid coexistence result from the minimization of the fluid energy or from the maximization of fluid entropy. Let us examine an isolated system consisting of a pseudo-gas and a pseudo-liquid defined by their EOSs (different or identical). The differential thermodynamic relationship, which defines the internal energy U of each phase, is

$$\mathrm{d}U_i = T_i\mathrm{d}S_i - P_i\mathrm{d}V_i + \mu_i\mathrm{d}N_i, \quad i = g, l$$

where S is the entropy.

For an isolated system, the total internal energy $U = U_g + U_l$, the total volume $V = V_g + V_l$, and the total number of particles $N = N_g + N_l$ are constant. Then $\mathrm{d}V_g = -\mathrm{d}V_l$, $\mathrm{d}U_g = -\mathrm{d}U_l$, $\mathrm{d}N_g = -\mathrm{d}N_l$, and we obtain for the total entropy of the system:

$$\mathrm{d}S = \mathrm{d}S_g + \mathrm{d}S_l = \left(\frac{1}{T_g} - \frac{1}{T_l}\right)\mathrm{d}U_g + \left(\frac{1}{P_g} - \frac{1}{P_l}\right)\mathrm{d}V_l + \left(\frac{\mu_g}{T_g} - \frac{\mu_l}{T_l}\right)\mathrm{d}N_g.$$

In the equilibrium, the entropy of an isolated system reaches the maximum; then $\mathrm{d}S = 0$, which yields the equilibrium equations in the following form:

$$P_g = P_l \equiv P, \quad T_g = T_l \equiv T, \quad \mu_g(P, T) = \mu_l(P, T) \tag{1.6}$$

The last relationship in (1.6) is not an identity, i.e. it cannot by satisfied at any P and T, but is an equation which determines a unique function

$$P = P^{\mathrm{sat}}(T) \tag{1.7}$$

which is the equilibrium gas–liquid curve, or the curve of gas–liquid coexistence. Pressure (1.7) is called the saturation pressure.

The physical meaning of (1.6) follows from the meaning of the chemical potential μ^k, which is the energy of interaction of the molecules of type k with all other molecules of the mixture, per one molecule k ("the specific energy"). Then (1.6) says the equilibrium is reached when the specific energy of interaction in the gas phase is the same as that in liquid phase.

The objective of the phase equilibrium theory consists exactly in constructing the coexistence curve (1.7) for different models (EOSs) of gases and liquids.

1.2.3 Explicit Relationship for Chemical Potential

Let us use the definition of the free Gibbs energy G:

$$\mathrm{d}G \equiv -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N, \tag{1.8}$$

where S is the entropy and N is the number of moles. Then we obtain the definition for chemical potential:

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}, \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}. \tag{1.9}$$

Assuming that the Gibbs energy is a continuous and differentiable function of its arguments, we can use the property of commutation for the operation of differentiation:

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial N}\right)_{T,P}\right)_{T,N} = \left(\frac{\partial}{\partial N}\left(\frac{\partial G}{\partial P}\right)_{T,N}\right)_{T,P}$$

Then:

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,N} = v. \tag{1.10}$$

The value $v = \left(\frac{\partial V}{\partial N}\right)_{T,P}$ is the molar volume ($\mathrm{m}^3\ \mathrm{mol}^{-1}$).

Chemical potential and molar volume are intensive parameters; they cannot then depend on the particle number N. Then Equation (1.10) becomes

$$\begin{cases} \dfrac{\partial \mu(P,T)}{\partial P} = v(P,T), \\ \mu|_{P=P_*} = \mu(P_*,T) \end{cases} \tag{1.11}$$

where the second relationship represents the initial condition taken at a special point P_* at which the chemical potential is known a priori (frequently $P_* = P_{\mathrm{at}}$). The integration of (1.11) leads to

$$\mu(P,T) = \int_{P_*}^{P} v(\overline{P},T)\mathrm{d}\overline{P} + \mu(P_*,T) \tag{1.12}$$

or if we change the variables of integration (integrating by parts):

$$\mu(P,T) = vP - v_*P_* - \int_{v_*}^{v} P(\overline{v},T)\mathrm{d}\overline{v} + \mu(P_*,T), \tag{1.13}$$

where $v_* = v(P_*)$.

Another method can be used to obtain the same relationship for the chemical potential, which is based on the homogeneity of the Gibbs free energy. It leads directly to the explicit algebraic relationship without obtaining the differential equation (1.11). This method is presented in Appendix A.

In particular, for an ideal gas, using (1.12) and the EOS (1.2), we obtain

$$\mu(P,T) = RT\ln\frac{P}{P_*} + \mu(P_*,T) \tag{1.14}$$

Chemical potential for cubic equations, obtained from (1.13), is given in Appendix B.

1.2.4 Equilibrium Conditions in Terms of Pressure and Volumes

The equilibrium condition that results from (1.10) and (1.12) is

$$\int_{P_*}^{P} v_g(\overline{P},T)\mathrm{d}\overline{P} + \mu_g(P_*,T) = \int_{P_*}^{P} v_l(\overline{P},T)\mathrm{d}\overline{P} + \mu_l(P_*,T) \tag{1.15}$$

which should be complemented with two EOSs for two pseudo-phases:

$$v_g = v_g(P,T), \quad \text{and} \quad v_l = v_l(P,T) \tag{1.16}$$

(we can only operate with pseudo-phases until the volumes $v_{\min}$ and $v_{\max}$ of true coexisting gas and liquid are defined).

Let us determine the pseudo-liquid and the pseudo-gas by the same EOS; then the chemical potentials $\mu_g(P_*, T)$ and $\mu_l(P_*, T)$ are identical, since they correspond to the same pseudo-fluid. Then, for any P_*, we obtain from (1.15):

$$\int_{P_*}^{P} [v_g(\overline{P}, T) - v_l(\overline{P}, T)]\mathrm{d}\overline{P} = 0 \tag{1.17}$$

The solution to this equation is the pressure of gas–liquid coexistence: $P = P^{\mathrm{sat}}$.

All cubic EOSs are formulated explicitly with respect to function $P(v)$ and not $v(P)$; this is why it is preferable to change the variables of integration in (1.17), integrating it by parts: $(v_g - v_l)P^{\mathrm{sat}} - (v_* - v_*)P_* - \int_{v_*}^{v_g} P(v)\mathrm{d}v + \int_{v_*}^{v_l} P(v)\mathrm{d}v = 0$, where $v_* = v(P_*)$. Definitely, we obtain the system of the equilibrium equation and two EOSs:

$$\begin{cases} (v_g - v_l)P^{\mathrm{sat}} = \displaystyle\int_{v_l}^{v_g} P(v)\mathrm{d}v, \\ v_g = \text{maximal solution of } P^{\mathrm{sat}} = P(v), \\ v_l = \text{minimal solution of } P^{\mathrm{sat}} = P(v) \end{cases} \tag{1.18}$$

This system of three equations determines a unique nontrivial solution in terms of pressure P^{sat} of gas–liquid coexistence and two different volumes v_g and v_l of coexisting phases. The existence of this nontrivial solution is shown in the next section.

1.2.5 Solvability of the Equilibrium Equation – Maxwell's Rule

Let us consider a cubic EOS which has the typical form presented in Figure 1.2. Let us select points A and B in such a way that the surfaces AGM and MHB are equivalent. Then the coordinates of points A and B, i.e. the pressure P^{sat} and the volumes v_{min} and v_{max}, represent the desired nontrivial solution to the problem of gas–liquid coexistence.

Proof: The left-hand side of (1.18) is equal to the surface of the rectangle $AFEB$. The right-hand side is the surface of the area $FAGMHBE$ under the curve. These areas are identical, as the areas of AGM and MHB are equivalent. Then Equation (1.18) is satisfied, if $v_g = v_{\mathrm{max}}$ and $v_l = v_{\mathrm{min}}$. □

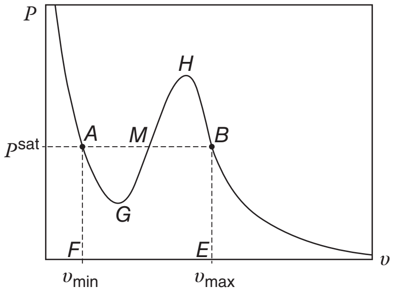

Figure 1.2 Graphical illustration of the solvability of the equilibrium equation.

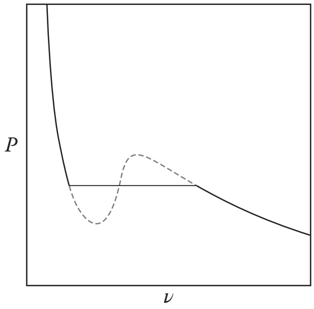

Figure 1.3 The true phase diagram of a one-component fluid.

Corollaries:

(1) The cubic (with respect to the volume) EOSs, which have the typical shape presented in Figure 1.2, are capable of describing the nontrivial gas–liquid coexistence.
(2) The line *AB*, corresponding to the nontrivial gas–liquid coexistence and called Maxwell's line, is constructed in such a way that the surfaces *AGM* and *MHB* would be identical. Such a graphical technique is equivalent to the analytical technique of solving the equilibrium equation.
(3) The true curve $P(v)$, which corresponds to the two-phase equilibrium, is the horizontal Maxwell's straight line that defines the unique pressure of two-phase coexistence, as shown in Figure 1.3.

1.2.6 Calculation of Gas–Liquid Coexistence

As an example we illustrate the technique of solving the equilibrium equation in the case of the Peng–Robinson EOS applied to both pseudo-phases. Substituting (1.5) into (1.18) and integrating it, we obtain the equilibrium equation complemented with two EOSs:

$$\begin{cases} (v_g - v_l)P^{\text{sat}} = \text{RT} \ln \dfrac{(v_g - b)}{(v_l - b)} - \dfrac{a}{2\sqrt{2}b} \ln \dfrac{(v_g - v_1)(v_l - v_2)}{(v_g - v_2)(v_l - v_1)}, \\ v_g = \text{maximal solution of } \left\{ P^{\text{sat}} = \dfrac{RT}{v - b} - \dfrac{a}{v^2 + 2bv - b^2} \right\}, \\ v_l = \text{minimal solution of } \left\{ P^{\text{sat}} = \dfrac{RT}{v - b} - \dfrac{a}{v^2 + 2bv - b^2} \right\} \end{cases} \tag{1.19}$$

where $v_1 = b(-1 + \sqrt{2}), \qquad v_2 = b(-1 - \sqrt{2})$.

This system of three equations has a unique nontrivial solution (at a fixed T) with respect to P^{sat}, v_g, and v_l.

To calculate (1.19) numerically, we present it in the following form:

$$\frac{RT}{v_l - b} - \frac{a}{v_l^2 + 2bv_l - b^2} = \frac{RT}{v_g - b} - \frac{a}{v_g^2 + 2bv_g - b^2}, \tag{1.20a}$$

$$F \equiv (v_g - v_l)P^{\text{sat}} - RT \ln \frac{(v_g - b)}{(v_l - b)} + \frac{a}{2\sqrt{2}b} \ln \frac{(v_g - v_1)(v_l - v_2)}{(v_g - v_2)(v_l - v_1)} = 0$$

(1.20b)

$$\text{where } P^{\text{sat}} = \frac{RT}{v_g - b} - \frac{a}{v_g^2 + 2bv_g - b^2} \tag{1.20c}$$

Two unknown values in (1.20a) and (1.20b) are v_g and v_l. We solve this system as follows:

(1) For a series of values $v_g(k)$, we calculate $v_l(k)$ by solving the nonlinear Equation (1.20a).
(2) We then calculate the function $F(k)$ from (1.20b).
(3) We find the minimum of $|F|$, which should tend to 0; we also determine the value of k that corresponds to this minimum (it is called "ki").
(4) We then calculate explicitly $v_l = v_l(ki)$ and $v_g = v_g(ki)$;
(5) Then we calculate explicitly P^{sat} from (1.20c).

The code Matlab is presented in Appendix F.

The examples of the calculation are presented in Figures1.4 and 1.5.

A maximal temperature exists, above which Equations (1.19) have no nontrivial solutions. For high T, the volume tends to infinity, and the system tends to the ideal gas, so the existence of the two-phase state becomes impossible.

As mentioned, the solution to Equations (1.19) can be obtained graphically using the Maxwell technique: the straight line that corresponds to the two-phase equilibrium should be traced in such a way that the surfaces between the curve $P(v)$ and this straight line under and over it would be equivalent.

1.2.7 Logarithmic Representation for Chemical Potential – Fugacity

For real gases, one uses the form similar to (1.14) while replacing the pressure by a new function called "the fugacity" f (introduced by Lewis in 1901):

$$\mu = RT \ln \frac{f(P,T)}{f(P_*,T)} + \mu(P_*,T) \tag{1.21}$$

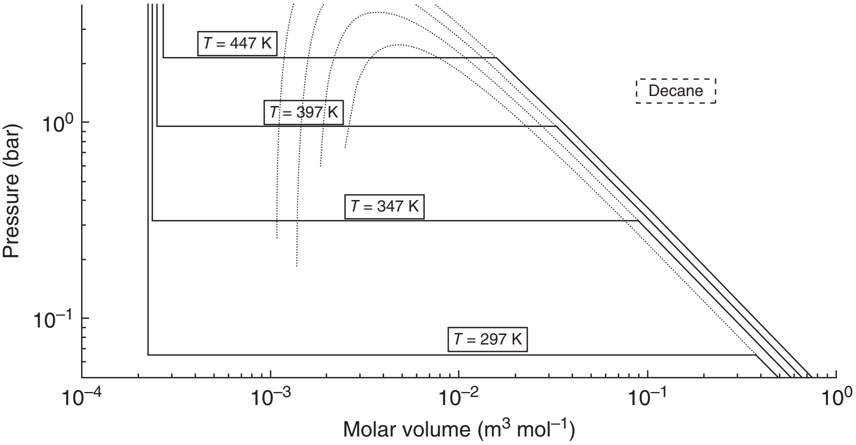

Figure 1.4 Phase diagram computed numerically for decane, for four values of temperature.

In particular, $P_* = P_{at}$.

The two properties of the fugacity result from its definition:

(1) $$f = P \quad \text{for ideal gas} \tag{1.22}$$

(2) $$f \underset{P\to 0}{\to} P, \text{ as any substance tends to the ideal gas when } P \to 0 \tag{1.23}$$

Then the fugacity is a bounded function at $P \to 0$, while the chemical potential tends to $-\infty$, which explains why the use of the fugacity is preferable.

Using the fact that the fugacity at P_{at} is practically equal to the pressure, it is possible to replace f_{at} by pressure P_{at} in (1.21):

$$\mu = RT \ln \frac{f(P,T)}{P_{at}} + \mu_{at}^{\text{ideal}}(T) \tag{1.24}$$

in which the chemical potential μ_{at}^{ideal} (for an ideal gas at P_{at}) is not the same as $\mu(P_{at}, T)$. Frequently, this difference is however neglected. In this case, the equivalence (1.24) becomes approximate.

The expression for the fugacity through volume and/or pressure follows from the general relationship for the chemical potential (1.12):

$$\ln \frac{f}{f_*} = \frac{1}{RT} \int_{P_*}^{P} v(\overline{P}, T) \mathrm{d}\overline{P} \tag{1.25}$$

where P_* is an arbitrary pressure. In particular, if $P_* = P_{at}$, then we obtain

$$\ln \frac{f}{f_{at}} \approx \ln \frac{f}{P_{at}} = \frac{1}{RT} \int_{P_{at}}^{P} v(\overline{P}, T) \mathrm{d}\overline{P}. \tag{1.26}$$

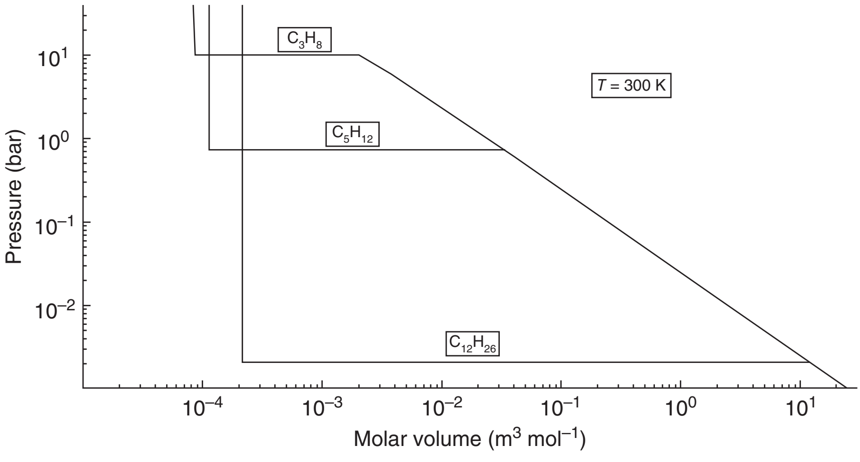

Figure 1.5 Phase diagram computed numerically for three chemical components: propane, pentane, and decane, for $T = 300$ K.