

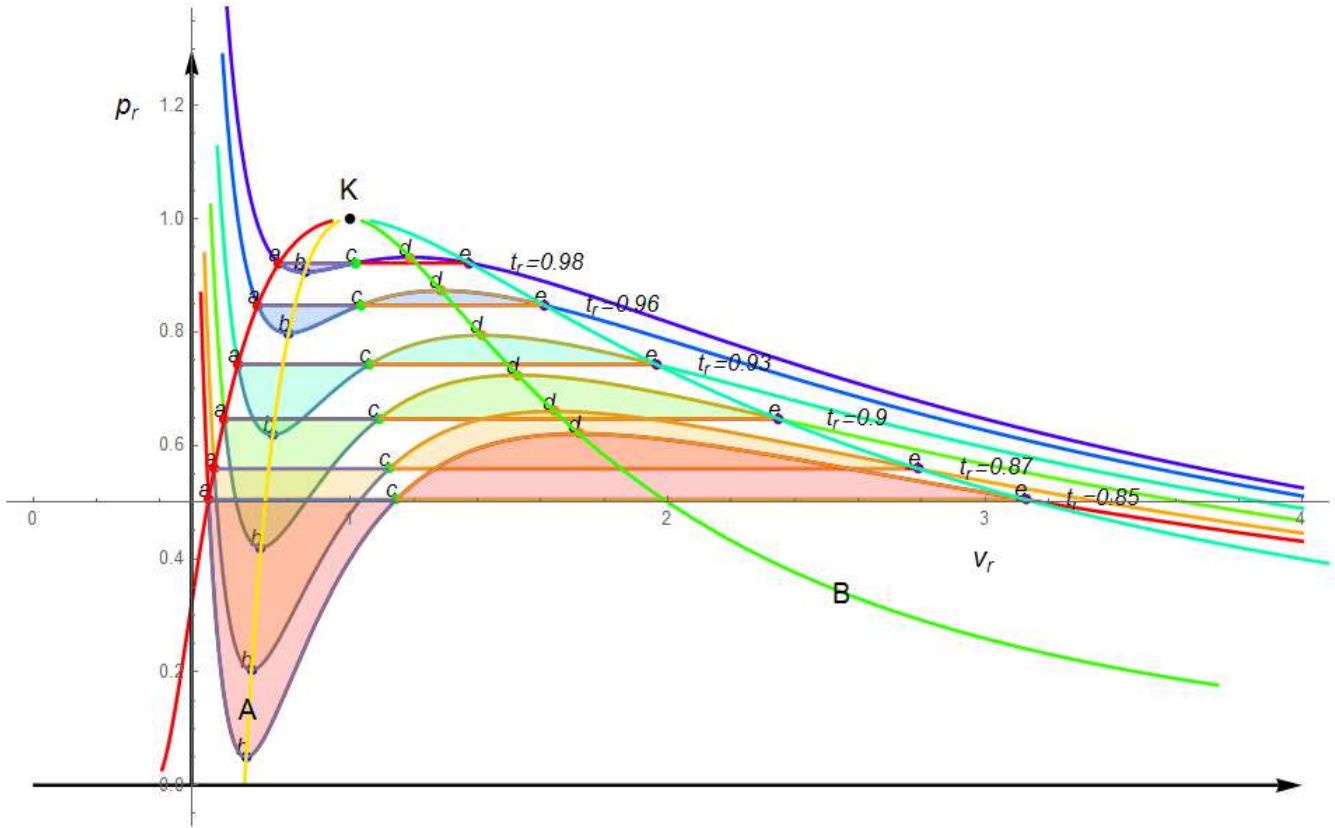
van der Waals gas
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Johannes Diderik van der Waals (November 23, 1837 – March 8, 1923) was a Dutch theoretical physicist and thermodynamicist famous for his work on an equation of state for gases and liquids. His name is primarily associated with the van der Waals equation of state that describes the behavior of gases and their condensation to the liquid phase. His name is also associated with van der Waals forces (forces between stable molecules), with van der Waals molecules (small molecular clusters bound by van der Waals forces), and with van der Waals radii (sizes of molecules).

He became the first physics professor of the University of Amsterdam when it opened in 1877 and won the 1910 Nobel Prize in physics.



http://en.wikipedia.org/wiki/Johannes_Diderik_van_der_Waals



1. Introduction

The **van der Waals equation** is a thermodynamic equation describing gases and liquids under a given set of pressure (P), volume (V), and temperature (T) conditions (i.e., it is a thermodynamic equation of state). It was derived in 1873 by Johannes Diderik van der Waals, who received the Nobel Prize in 1910 for "his work on the equation of state for gases and liquids. The equation is a modification to and improvement of the ideal gas law, taking into account the nonzero size of atoms and molecules and the attraction between them. van der Waals equation of state, when supplemented by the Maxwell construction (equal-area rule), provides in principle a complete description of the gas and its transition to the liquid, including the shape of the coexistence boundary curve.

Here we discuss the physics of the van der Waals equation of state from numerical calculations. We use the Mathematica to determine the detail of the flat portion (the coexistence line of liquid phase and gas phase). We also discuss the critical behavior near the critical point. To this end, it is significant for us to get the appropriate Mathematica program to determine the nature of the flat portion (the coexistence of liquid and gas phase). Before we started to make our own Mathematica program for the van der Waals equation of state, we found three resources for the programs related to this equation (as far as we know). The Maxwell construction was briefly discussed using the Mathematica by Kinzel and Reents (1998). Second is from the book of Nino Boccara, *Essentials of Mathematica* (Springer, 2007). The third is from Paul Abbott, *The Mathematica Journal* vol.8 Issue 1 (2001, Trick of the Trade, Maxwell Construction). Here we use the method with FindRoot, which is used by Abbott for the evaluation of Maxwell's construction. There is no simple analytical solution to equation for the Maxwell construction. Fairly

accurate initial guesses are required. These can be obtained from the plots of the unphysical van der Waals equation. Here we show our Mathematica program to discuss the van der Waals equation of state.

Here we use the Mathematica (ContourPlot, ParametricPlot, Plot3D, ParametricPlot3D, and so on) for the calculations. Because of the nature of the nonlinearity in the van der Waals equation of state, the use of the Mathematica is essential to our understanding on the critical behavior of liquid-gas system around the critical point.

Although we spent many years in understanding the nature of the van der Waals equation of state, unfortunately our understanding was not sufficient. Thanks to the Mathematica, finally we really understand how to calculate the exact values of thermodynamic parameters at fixed temperatures such as p_1 , v_1 , v_2 , v_3 , v_{m1} , p_{m1} , v_{m3} , p_{m3} (see the definitions in the text) using the Mathematica. Using these parameters we will discuss various thermodynamic properties of the van der Waals equation of state. There have been so many books and papers since the appearance of the van der Waals equation. Almost all the universal properties of van der Waals equation have been discussed thoroughly. Although there is nothing new in this article, we present our results of calculations using Mathematica.

2. Historical Background

The proper elucidation of the nature of gas-liquid equilibrium and the so-called critical point was gained by a series of experiments carried out by Thomas Andrews at Queen's College, Belfast, between 1861 and 1869. He chose carbon dioxide (CO_2) for his work. It is gaseous at normal temperatures and the pressure required for studying the whole range where gas and liquid are in equilibrium are relatively low. He determined, at different temperatures, the change in the volume of a given quantity of the substance when the pressure varied. The resultant curves are called isotherms because they each refer to one and the same temperature.

The flat part of the isotherm reveals an important fact. Since the pressure remains constant, while more and more of the gas condenses into liquid, the pressure of the gas in contact with the liquid must be always the same, quite independent of whether a small or a large fraction of the volume is occupied by liquid. It also is apparent from Andrew's diagram that this equilibrium pressure rises as we go to higher isotherms, i.e., as the temperature is increased. Moreover, we also notice that the flat part becomes shorter until a singularly important isotherm is reached which has no true flat portion at all but just one point (the so-called the critical point T_c) at which the direction of the curve changes its sign. The higher isotherms are now all ascending smoothly over the whole range of pressure and volume, and if one goes to still higher temperatures, the isotherms attain more and more the shape of true rectangular hyperbola. This is then the region in which Boyle's law is valid.

- CO₂ -

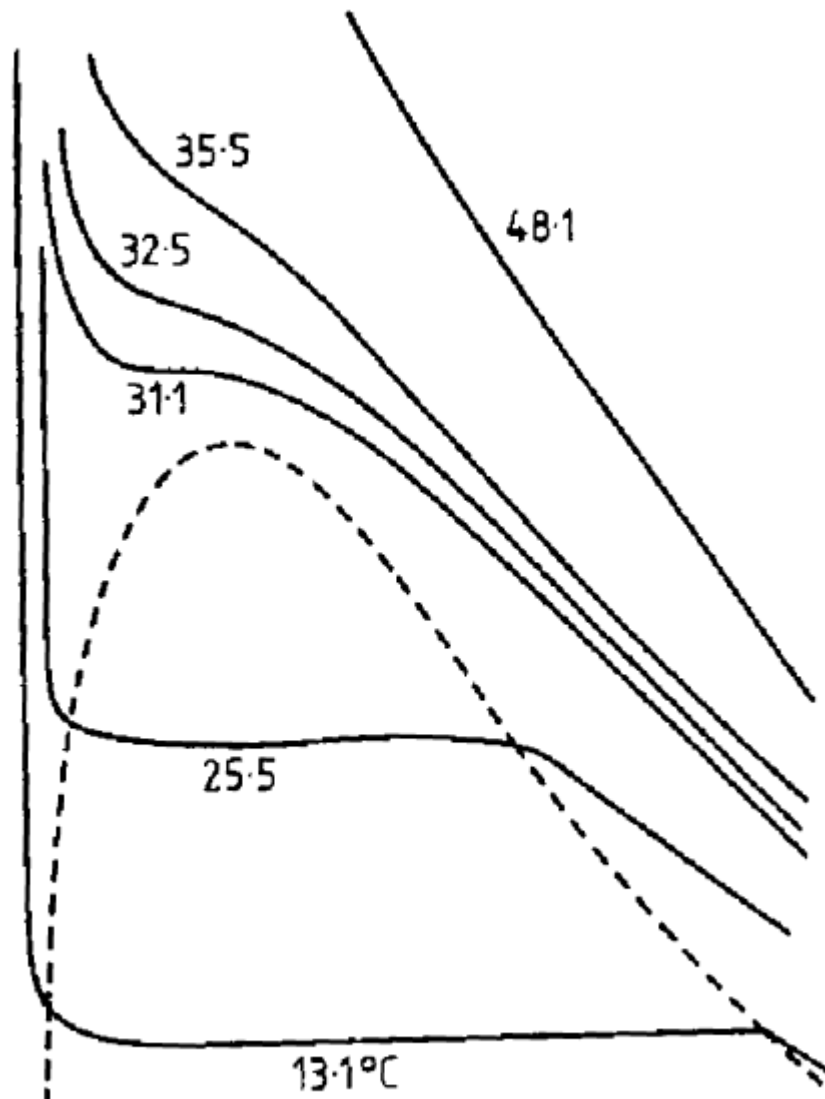


Fig.3 Isotherms of a real gas (CO_2) as measured by **Andrews**. They approximate Boyle's law only at high temperatures. At low temperatures they are more complicated and below the critical point there is a region of liquefaction. The critical temperature of CO_2 is 31 °C.

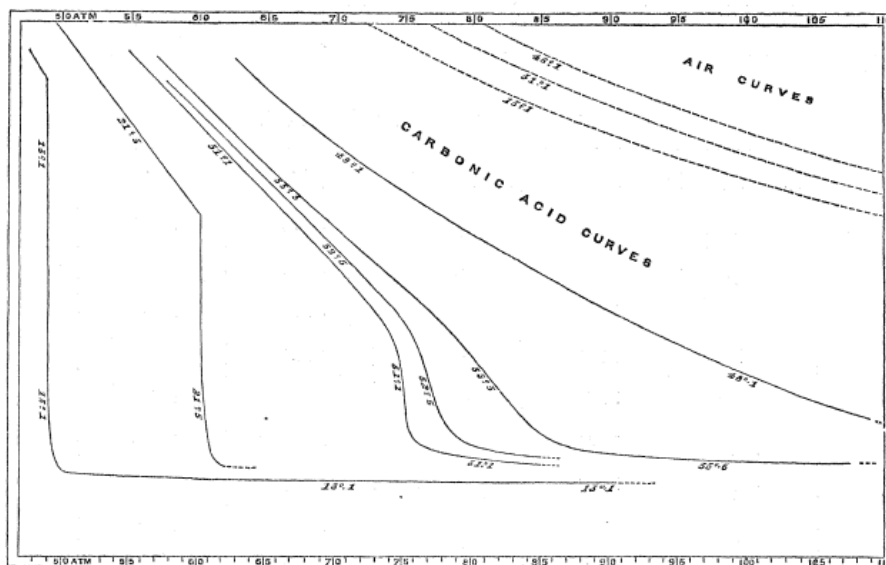


Fig.4 Isotherms of a real gas (H_2CO_3) as measured by **Andrews**.

Andrew's result not only yielded a wealth of new facts but they also presented a beautifully complete and satisfying picture of the relation between the gaseous and liquid states of aggregation. Andrew's careful measurements opened the way to an understanding of the strong forces of cohesion which are vested in each atom but never reach the dimension of ordinary macroscopic observation. It should also be noted that, while Andrew's observations were confined to carbon dioxide, the pattern is quite generally valid.

We have used Andrew's diagram not only for its historical interest but also because it illustrates in a clear and convincing manner the significance and the boundaries of the liquid state. Van der Waals used Andrews's terminology, and even adopted the title of Andrews's Bakerian lecture, without reference, almost verbatim as the title of his doctoral thesis of Van der Waals developed his equation of state independently, but he did compare it with Andrews's results.

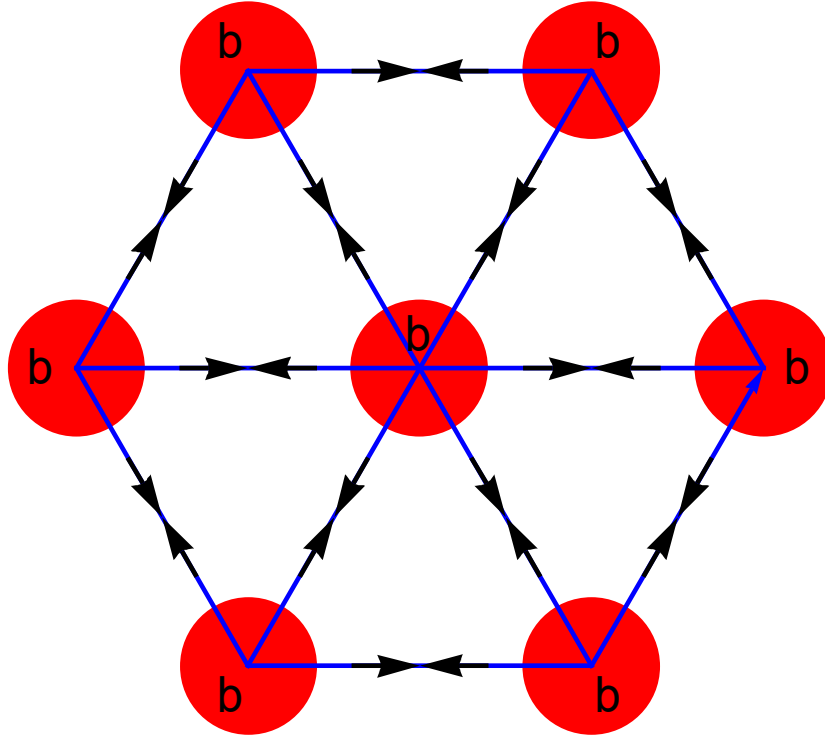


Fig.5 (i) The container of volume V has N molecules, each of volume b . The volume not occupied by molecules is $V - Nb$. Intuition suggests that the free volume should be used in the gas law in place of the container volume V . (ii) Attractive force between molecules. These forces contribute a negative internal pressure N^2a/V^2 near the boundary should be used as the pressure in the gas law.

Only four years elapsed before van der Waals used newly developing ideas on the kinetic theory of gases to give a plausible theoretical explanation of Andrew's experimental data. van der Waals assumed that gas is made up of molecules with a hard core and a long-range mutual attraction. The range of the attractive forces was assumed to be long compared with the mean free path, and they give rise to a negative internal pressure.

$$P_{\text{internal}} = -\frac{a}{v^2},$$

where $v = V/N$ is the volume per molecule. For the hard core he made the simplest assumption that the available volume is reduced from v to $v-b$. Hence the equation he put forward was

$$P = P_{\text{internal}} + \frac{k_B T}{v-b}, \quad \text{or} \quad P + \frac{a}{v^2} = \frac{k_B T}{v-b}.$$

The new equation, which instead of the old $PV/T = \text{constant}$ now has, when plotted, a peculiar wiggly shape. In this wiggly region van der Waal's equation has for any given pressure three solutions for the volume. A straight line, joining any of these three solutions will then result in a curve which very closely resembles the flat portion of the Andrew's isotherms. It is no doubt that in its broad concepts the van der Waals' approach was correct. The importance of this equation was quickly recognized by Maxwell who reviewed the thesis in *Nature* in 1874, and in a lecture to Chemical Society in 1875. It was in this lecture that Maxwell put forward his famous "equal-area construction, which completes the van der Waals treatment of liquid-gas equilibrium. The equal-area rule (Maxwell construction) can be expressed as

$$P_V(V_g - V_l) = \int_{V_l}^{V_g} P dV ,$$

where P_V is the vapor pressure (flat portion of the curve), V_l is the volume of the pure liquid phase on the diagram, and V_g is the volume of the pure gas phase. The sum of these two volumes will equal the total volume V .

Thanks to such pioneering works, we now understand the essential nature of liquid phase and gas phase. A flat portion for the low temperature phase, corresponds to the region where the liquid condenses from the gas. Following any of these isotherms from large to small volume, i.e., starting on the right-hand side, we encounter the rise and then a kink where the level portion starts. Here the very first droplets of liquid appear. When now the volume is further decreased, more and more of the gas turns into liquid until, at the end of the level stretch, there is no gas left at all. From now on any further increase in pressure hardly changes the volume at all, showing that the liquid phase is highly incompressible.

Much more detail of the historical background on the van der Waals equation of state can be learned from the following books.

3. Origin for the van der Waals equation of state

van der Waals realized that two main factors were to be added to the ideal gas equation: the effect of molecular attraction and the effect of molecular size. The intermolecular forces would add a correction to the ideal gas pressure, whereas the molecular size would decrease the effective volume. In the case of the ideal gas there is no intermolecular attraction. The intermolecular attraction decreases the pressure from its ideal value. If P_{real} is the pressure of a real gas and P_{ideal} is the corresponding pressure of the ideal gas, i.e. the pressure in the absence of intermolecular forces, then

$$P_{ideal} = P_{real} + \delta p ,$$

where δp is the correction. Since the pressure is proportional to the number density (N/V) (as can be seen from the ideal gas equation), δp should be proportional to (N/V) . In addition, the total force on each molecule close to the wall of the container is also proportional to the number density (N/V); hence δp should be proportional to two factors of (N/V) so that one may write:

$$\delta p = a\left(\frac{N}{V}\right)^2.$$

The correction to the volume due to the molecular size, i.e., the "excluded volume," is simply proportional to the number of molecules. Hence

$$V_{ideal} = V - Nb,$$

in which b is the correction for one mole. Substituting these values in the ideal gas equation

$$P_{ideal}V_{ideal} = Nk_B T.$$

we obtain the van der Waals equation

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T.$$

since

$$P_{real} = P = P_{ideal} - \delta p = P_{ideal} - a\left(\frac{N}{V}\right)^2, \quad \text{or} \quad P_{ideal} = P + a\left(\frac{N}{V}\right)^2$$

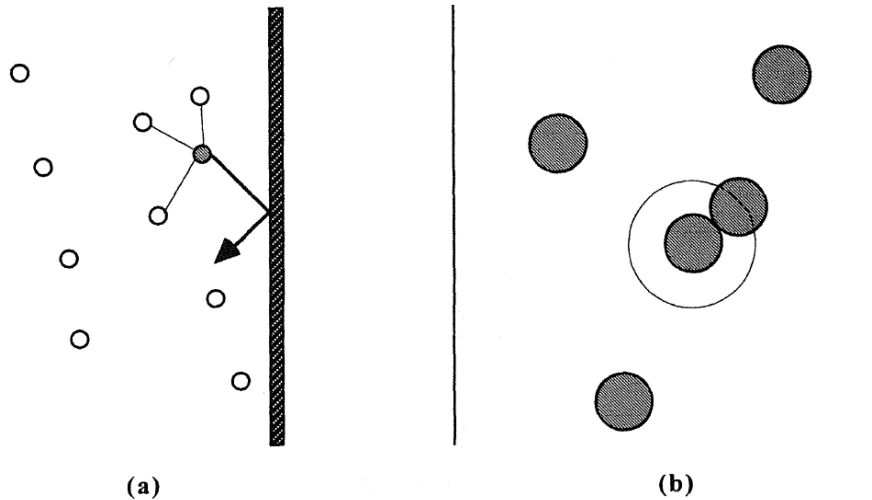


Fig.6

van der Waals considered molecular interaction and molecular size to improve the ideal gas equation. (a) The pressure of a real gas is less than the ideal gas pressure because intermolecular attraction decreases the speed of the molecules approaching the wall. Therefore $P_{real} = P_{ideal} - \delta p$. (b) The volume available to molecules is less than the volume of the container due to the finite size of the molecules. This "excluded" volume depends

on the total number of molecules. Therefore $V_{ideal} = V - Nb$. [D. Kondepudi and I. Prigogine, *Modern Thermodynamics*, p.18 Figure 1.4].

4. Derivation of van der Waals equation: Helmholtz free energy

For ideal gas, the partition function is given by

$$Z_1 = n_Q V$$

so the free energy F is calculated as

$$\begin{aligned} F &= -k_B T \ln \left(\frac{Z_1^N}{N!} \right) \\ &= -k_B T (N \ln Z_1 - \ln N!) \\ &\approx -k_B T (N \ln Z_1 - N \ln N + N) \\ &= -k_B T N \left[\ln \left(\frac{Z_1}{N} \right) + 1 \right] \\ &= -k_B T N \left[\ln \left(\frac{n_Q}{n} \right) + 1 \right] \end{aligned}$$

where $n = \frac{N}{V}$, and n_Q is the quantum concentration;

$$n_Q = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} = \left[\frac{mk_B T}{2\pi \frac{h^2}{4\pi^2}} \right]^{3/2} = \left[\frac{2\pi mk_B T}{h^2} \right]^{3/2} = \frac{(2\pi mk_B T)^{3/2}}{h^3},$$

where m is a mass of atom. Here we replace $n = \frac{N}{V}$ by $\frac{N}{V - Nb} = \frac{1}{v - b}$. We also add a correction for the intermolecular attractive forces, $-N^2 \frac{a}{V} = -N \frac{a}{v}$. Then the Helmholtz free energy is obtained as

$$\begin{aligned} f &= \frac{F}{N} = -k_B T \{ \ln [n_Q (v - b)] + 1 \} - \frac{a}{v} \\ &= -k_B T \ln (v - b) - \frac{a}{v} - k_B T (\ln n_Q + 1) \\ &= -k_B T \ln (v - b) - \frac{a}{v} + \Phi(T) \end{aligned}$$

where

$$\begin{aligned}
\Phi(T) &= -k_B T [\ln n_Q + 1] \\
&= -k_B T \left\{ \ln \left[\frac{(2\pi m k_B T)^{3/2}}{h^3} \right] + 1 \right\} \\
&= -k_B T \left\{ \ln T^{3/2} + \ln \frac{(2\pi m k_B)^{3/2}}{h^3} + 1 \right\} \\
&= -k_B T (\ln T^{3/2} + \ln \alpha + 1) \\
&= -k_B T \left(\frac{3}{2} \ln T + \ln \alpha + 1 \right)
\end{aligned}$$

with the constant α

$$\alpha = \frac{(2\pi m k_B)^{3/2}}{h^3}.$$

In summary the Helmholtz free energy is obtained as

$$f = -\frac{a}{v} - k_B T [\ln(v-b) + \frac{3}{2} \ln T + \ln \alpha + 1].$$

The pressure P is obtained as

$$P = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = -\left(\frac{\partial f}{\partial v} \right)_{T,N} = \frac{k_B T}{v-b} - \frac{a}{v^2},$$

or more simply,

$$(P + \frac{a}{v^2})(v-b) = k_B T,$$

((van der Waals equation of state))

or

$$P = -\frac{a}{v^2} + \frac{k_B T}{v-b}.$$

Since $v = \frac{V}{N}$, the above van der Waals equation can be rewritten as

$$(P + \frac{N^2 a}{V^2})(V - bN) = Nk_B T.$$

((Note))

Helmholtz free energy:

$$F = -Nk_B T \left\{ \ln \left[n_Q \left(\frac{V - Nb}{N} \right) \right] + 1 \right\} - \frac{N^2 a}{V}$$

Entropy:

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = Nk_B \left\{ \ln \left[n_Q \left(\frac{V - Nb}{N} \right) \right] + \frac{5}{2} \right\}$$

Internal energy:

$$U = F + ST = \frac{3}{2} Nk_B T - \frac{N^2 a}{V}$$

Pressure:

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = - \frac{N^2 a}{V^2} + \frac{Nk_B T}{V - bN}$$

Enthalpy:

$$H(T, V) = U + PV = \frac{5}{2} Nk_B T - \frac{2N^2 a}{V} + \frac{N^2 b k_B T}{V}$$

Gibbs free energy:

$$\begin{aligned} G &= F + PV \\ &= -Nk_B T \left\{ \ln \left[n_Q \left(\frac{V - Nb}{N} \right) \right] + 1 \right\} - \frac{2N^2 a}{V} + \frac{Nk_B T}{V - bN} V \end{aligned}$$

REFERENCES

C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman, 1980).

5. Law of the corresponding state

$$\left(\frac{\partial P}{\partial v}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0. \quad (1)$$

From the condition, $\left(\frac{\partial P}{\partial v}\right)_T = 0$, we get

$$\frac{2a}{v^3} - \frac{k_B T}{(v-b)^2} = 0. \quad (2)$$

From the condition, $\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$, we get

$$\frac{-3a}{v^4} + \frac{k_B T}{(v-b)^3} = 0. \quad (3)$$

From Eqs.(1) - (3), we have

$$P_c = \frac{a}{27b^2}, \quad v_c = \frac{V_c}{N} = \frac{1}{\rho_c} = 3b, \quad T_c = \frac{8a}{27k_B b}.$$

Note that

$$P_c v_c = \frac{3}{8} k_B T_c,$$

or

$$P_c (N_A v_c) = \frac{3}{8} k_B N_A T_c = \frac{3}{8} R T_c,$$

$$a = \frac{27 k_B^2 T_c^2}{64 P_c} = \frac{1}{N_A^2} \frac{27 R^2 T_c^2}{64 P_c} \quad b = \frac{k_B T_c}{8 P_c} = \frac{1}{N_A} \frac{R T_c}{8 P_c}$$

$$\frac{a}{b} = \frac{27}{8} k_B T_c \text{ (thus the unit if } a/b \text{ is the energy).}$$

Here we define the dimensionless variables by

$$p_r = \frac{P}{P_c}, \quad v_r = \frac{V}{V_c} = \frac{v}{v_c}, \quad t_r = \frac{T}{T_c},$$

and the dimensionless form of the van der Waals equation,

$$\left(p_r + \frac{3}{v_r^2}\right)\left(v_r - \frac{1}{3}\right) = \frac{8}{3}t_r \quad \Rightarrow \text{Law of corresponding state.}$$

((Universality)) Law of corresponding state

This equation is universal since it contains no parameters characteristic of an individual substance, and so it is equally valid for all. The variables of p_r , v_r , and t_r is called the reduced variables. The thermodynamic properties of substances are the same in corresponding states, that is, states with a pair of equal reduced variables from the complete triplet of variables. In fact, the existence of such an equation implies that if two reduced variables are the same for a set of the systems, then the third reduced variable is also the same throughout the set.

((Visualization of the phase transition of van der Waals system by Mathematica))

The phase diagrams of p_r vs v_r and v_r vs p_r are shown below. It can be obtained by using the Maxwell construction for the van der Waals system (we use the Mathematica to get this. The method will be discussed later).

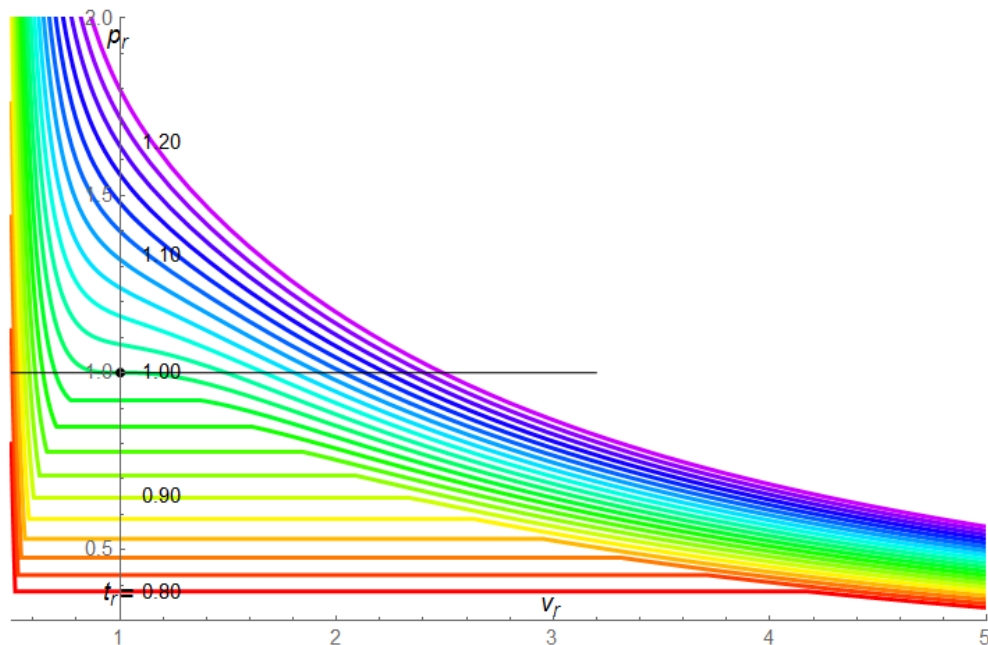
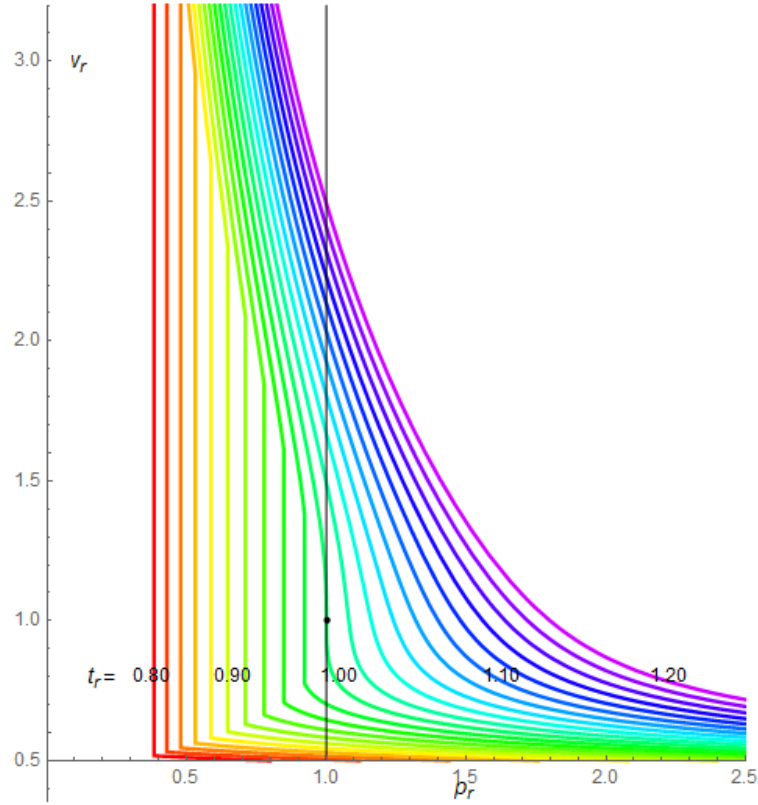


Fig.7

The phase diagrams of p_r vs v_r for $t_r = 0.80 - 1.20$. The horizontal straight line for $t_r < 1$ is the coexistence line between the liquid phase and the gas phase.

**Fig.8**

The v_r vs p_r phase diagram at fixed reduced temperatures ($t_r = 0.80 - 1.20$ with $\Delta t_r = 0.02$). The vertical straight line for $t_r < 1$ is the coexistence line between the liquid phase and gas phase.

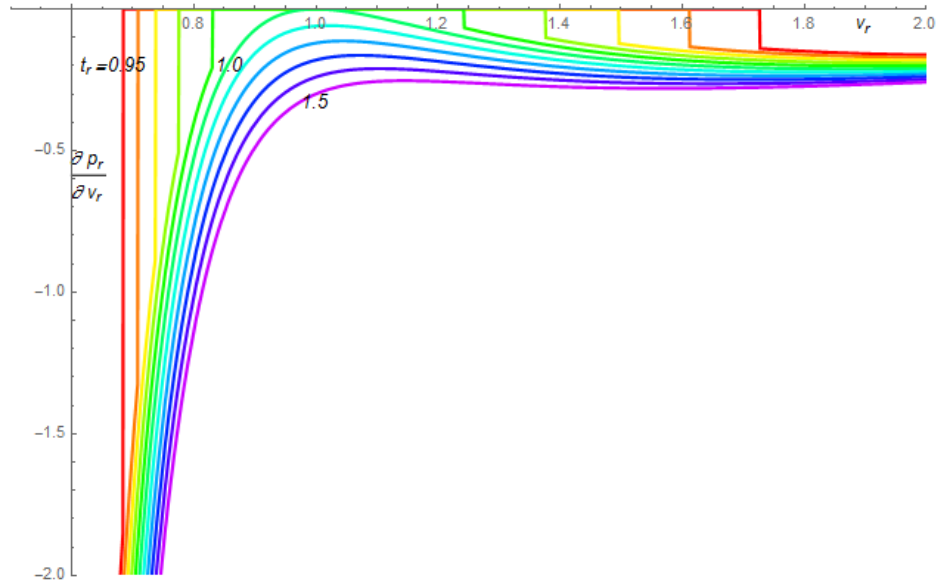
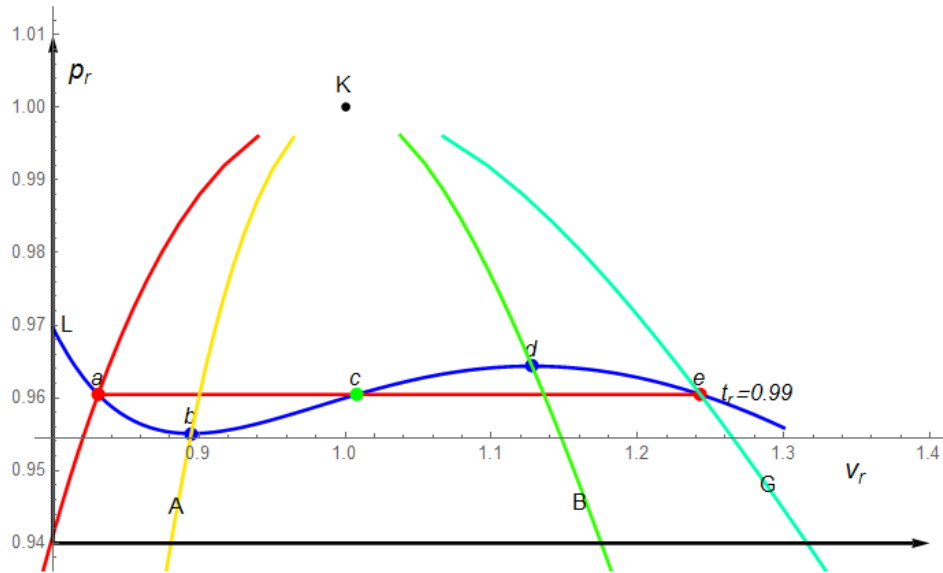


Fig.9 $\partial p_r / \partial v_r$ vs v_r phase diagram at fixed reduced temperatures ($t_r = 0.80 - 1.20$ with $\Delta t_r = 0.02$).
 $\partial p_r / \partial v_r = 0$ for $v_1 \leq v \leq v_3$ ($t_r < 1$).



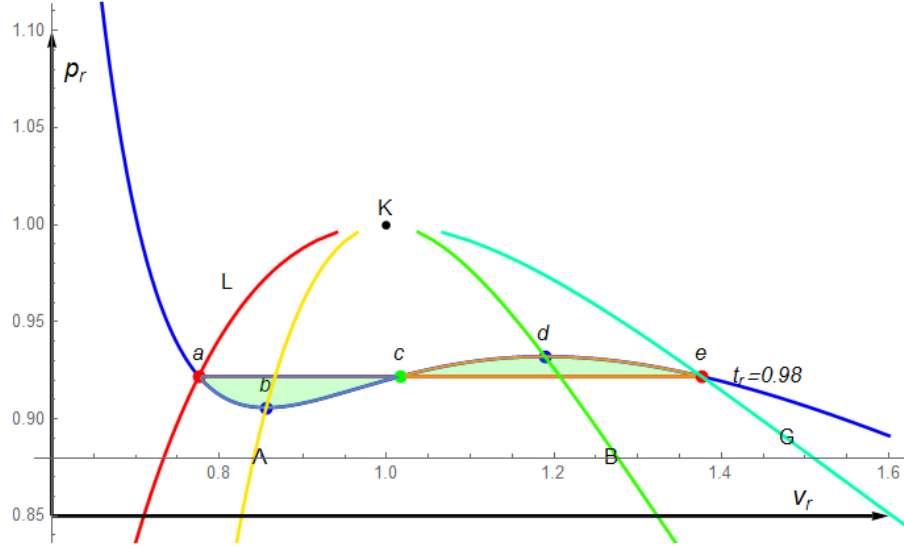


Fig.10 Typical examples for the Maxwell construction. The phase diagrams of p_r vs v_r for $t_r = 0.99$ and 0.98 . The area of closed path $a-c-b-a$ is equal to that of the closed $c-d-e-c$. The path $a-c-e$ is the coexistence line.

6. Critical points and critical exponents

To examine the critical behavior, we write

$$p_r = \frac{P}{P_c} = 1 + \pi,$$

$$v_r = \frac{v}{v_c} = 1 + \omega,$$

$$t_r = \frac{T}{T_c} = 1 + \tau$$

where π , ω , and τ can be regarded as small. We obtain the universal equation

$$p_r = 1 + \pi = -\frac{3}{(1 + \omega)^2} + \frac{8(1 + \tau)}{2 + 3\omega}$$

or expanding

$$\begin{aligned} p_r &= 1 + \pi \\ &= 1 + 4\tau - 6\tau\omega + 9\tau\omega^2 - \left(\frac{3}{2} + \frac{27}{2}\tau\right)\omega^3 + \left(\frac{21}{4} + \frac{81}{4}\tau\right)\omega^4 - \left(\frac{99}{8} + \frac{243}{8}\tau\right)\omega^5 \\ &\quad + \left(\frac{393}{16} + \frac{729}{16}\tau\right)\omega^5 + \dots \\ &= 1 + 4\tau - 6\tau\omega + 9\tau\omega^2 - \frac{3}{2}\omega^3 + O(\tau\omega^2, \omega^4) \end{aligned} \tag{1}$$

The term omitted from this expression are justified post hoc in fact, we can see that $\omega \approx \sqrt{\tau}$, so Eq.(1) is indeed the lowest non-trivial order approximation to the equation of state near the critical point.

((Mathematica))

Critical parameter of the van der Waal's equation
 P_c , v_c , and T_c

```
Clear["Global`*"];
```

$$P = \frac{k_B T}{v - b} - \frac{a}{v^2};$$

```
eq1 = D[P, v] // Simplify
```

$$-\frac{k_B T}{(b - v)^2} + \frac{2 a}{v^3}$$

```
eq2 = D[P, {v, 2}] // FullSimplify
```

$$-\frac{6 a}{v^4} + \frac{2 k_B T}{(-b + v)^3}$$

```
eq3 = Solve[{eq1 == 0, eq2 == 0}, {v, T}] // Simplify
```

$$\left\{ \left\{ v \rightarrow 3 b, T \rightarrow \frac{8 a}{27 b k_B} \right\} \right\}$$

```
{Pc, vc, Tc} = {P, v, T} /. eq3[[1]]
```

$$\left\{ \frac{a}{27 b^2}, 3 b, \frac{8 a}{27 b k_B} \right\}$$

```
eq5 = P / Pc /. {T -> Tc t} // FullSimplify
```

$$b \left(-\frac{27 b}{v^2} + \frac{8 t}{-b + v} \right)$$

```
eq6 = eq5 /. {v -> vc (1 + ω), t -> 1 + τ} // FullSimplify
```

$$-\frac{3}{(1 + \omega)^2} + \frac{8 (1 + \tau)}{2 + 3 \omega}$$

```
Series[eq6, {ω, 0, 8}, {τ, 0, 8}] // Normal
```

$$1 + 4 \tau - 6 \tau \omega + 9 \tau \omega^2 + \left(-\frac{3}{2} - \frac{27 \tau}{2} \right) \omega^3 +$$

$$\left(\frac{21}{4} + \frac{81 \tau}{4} \right) \omega^4 + \left(-\frac{99}{8} - \frac{243 \tau}{8} \right) \omega^5 + \left(\frac{393}{16} + \frac{729 \tau}{16} \right) \omega^6 +$$

$$\left(-\frac{1419}{32} - \frac{2187 \tau}{32} \right) \omega^7 + \left(\frac{4833}{64} + \frac{6561 \tau}{64} \right) \omega^8$$

(a) Critical exponent β

We start with

$$p \approx 1 + 4\tau - 6\tau\omega + 9\tau\omega^2 - \frac{3}{2}\omega^3$$

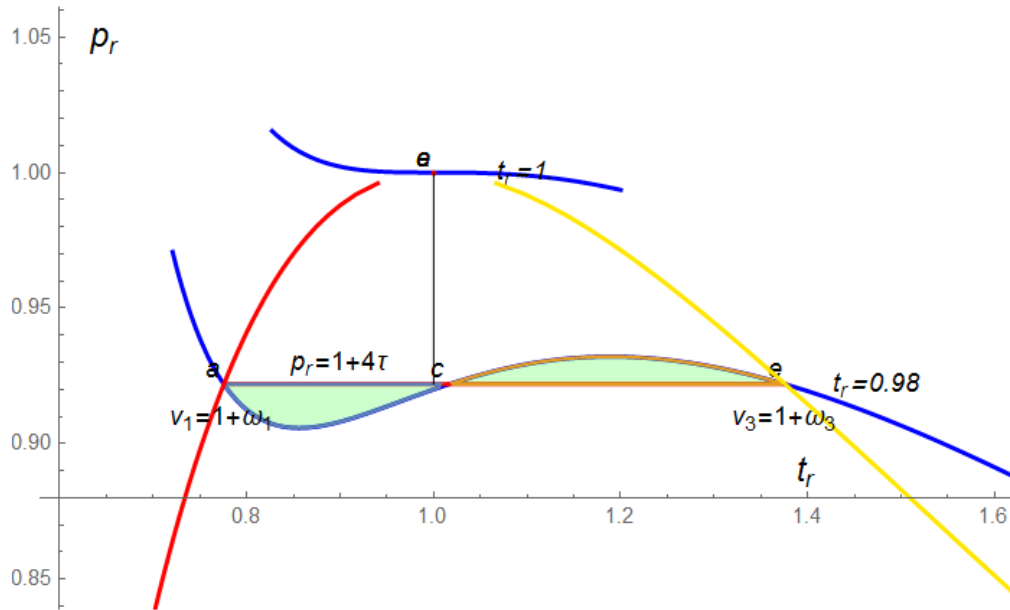


Fig.11 Physical meaning of $p_r = 1 + 4\tau$ at $\omega = 0$.

When $\omega = 0$,

$$p_r = 1 + 4\tau \quad \text{with } \tau < 0.$$

which is nearly equal to the reduced pressure p_1 for the coexistence line (the path a - c - e). Then we have

$$-6\tau\omega - \frac{3}{2}\omega^3 = 0,$$

or

$$\omega = 0, \quad \omega = \pm 2\sqrt{-\tau}.$$

where $\tau < 0$. Then we have

$$\omega_3 = 2\sqrt{-\tau}, \quad \omega_1 = -2\sqrt{-\tau}.$$

The reduced pressures $v_1 (= v_l)$ at the point a and $v_3 (= v_g)$ at the point e , are obtained as

$$v_1 = 1 + \omega_1 = 1 + 2\sqrt{-\tau},$$

$$v_3 - v_1 = v_g - v_l = 4\sqrt{-\tau},$$

$v_g - v_l$ depends on $(-\tau)$. It reduces to zero when $\tau \rightarrow 0_-$. The critical exponent β is equal to $1/2$.

$$\beta = \frac{1}{2} \quad (\text{mean-field exponent}).$$

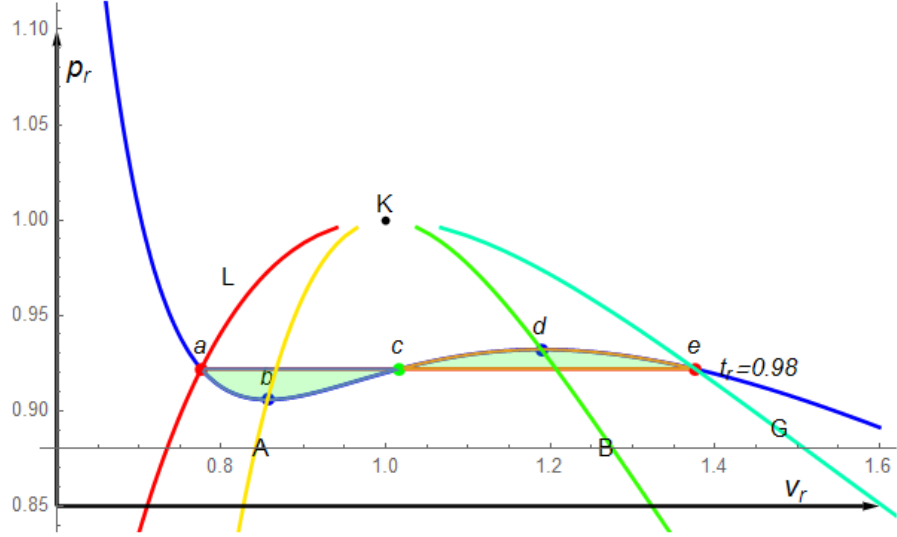


Fig.12 The points $a; (v_1, p_1)$, $c; (v_2, p_1)$, and $e; (v_3, p_1)$, in the p_r - v_r plane. $p_1 = 1 + 4\tau$. $v_1 = 1 + \omega_1 = 1 + 2\sqrt{-\tau}$. $v_3 = 1 + \omega_3 = 1 - 2\sqrt{-\tau}$. τ is negative. $\varepsilon = -\tau = |\tau|$ is very small.

(b) Critical exponent γ and γ'

The isothermal compressibility is defined by

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{P_c v_r} \left(\frac{\partial v_r}{\partial p_r} \right)_\tau \approx -\frac{1}{P_c} \left(\frac{\partial \omega}{\partial \pi} \right)_\tau.$$

Since

$$\pi = 4\tau - 6\tau\omega - \frac{3}{2}\omega^3, \quad \left(\frac{\partial \omega}{\partial \pi} \right)_\tau = -\frac{1}{6\tau + \frac{9}{2}\omega^2},$$

we get

$$K_T = -\frac{1}{P_c} \left(\frac{\partial \omega}{\partial \pi} \right)_\tau = \frac{1}{P_c} (6\tau + \frac{9}{2}\omega^2)^{-1}.$$

For $\tau \geq 0$, $\omega = 0$.

$$K_T = \frac{1}{6P_c} \tau^{-1}.$$

For $\tau < 0$, $\omega^2 = -4\tau$,

$$\kappa_T = \frac{1}{P_c} (6\tau - 18\tau)^{-1} = \frac{1}{12P_c} (-\tau)^{-1},$$

The isothermal compressibility κ_T diverges as $t_r \rightarrow 1 \pm 0$ with a critical exponent

$$\gamma = \gamma' = 1. \quad (\text{mean-field exponent}).$$

In summary, we have

$$K_T = \begin{cases} \frac{1}{6P_c\tau} & T > T_c \\ \frac{1}{12P_c(-\tau)} & T < T_c \end{cases}$$

(c) Critical exponent for specific heat at constant volume

The specific heat predicted by the van der Waals theory is

$$c_V = \begin{cases} k_B \left[\frac{3}{2} + \frac{9}{2} \left(1 - \frac{28}{25} \varepsilon + \dots \right) \right] & t_r < 1 \\ k_B \frac{3}{2} & t_r > 1 \end{cases}$$

where $c_V = 3k_B/2$ is the non-interacting (high-temperature) limit or ideal gas. Thus we have the critical exponent,

$$\alpha = 0.$$

Note that the slope of c_V vs t_r is finite as $t_r \rightarrow 1$ from below, so that we have $\alpha' = 0$.

((Note)) This discussion is repeated later for the critical behavior of the specific heat.

(d) Critical exponent δ (critical isotherm)

$$p_r = -\frac{3}{v_r^2} + \frac{8t_r}{3v_r - 1}$$

at $t_r = 1$. We expand p_r at $t_r=1$ ($T = T_c$) in the vicinity of $v_r = 1$.

$$p_r - 1 = -\frac{3}{2}(v_r - 1)^3 + \frac{21}{4}(v_r - 1)^4 - \frac{99}{8}(v_r - 1)^5 + \dots$$

This is approximated by

$$p_r - 1 \approx -\frac{3}{2}(v_r - 1)^3 \propto (v_r - 1)^\delta,$$

or

$$v_r - 1 \approx (p_r - 1)^{1/\delta}.$$

in the region very close to the critical point, leading to the critical exponent (critical isotherm)

$$\delta = 3 \quad (\text{the mean-field exponent})$$

(e) Thermal expansion coefficient

The thermal expansion coefficient is given by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{T_c v_r} \left(\frac{\partial v_r}{\partial t_r} \right)_P = -\frac{1}{T_c v_r} \frac{\left(\frac{\partial p_r}{\partial t_r} \right)_V}{\left(\frac{\partial p_r}{\partial v_r} \right)_T}$$

Using the expression of K_T ,

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{P_c v_r} \left(\frac{\partial v_r}{\partial p_r} \right)_T$$

we have

$$\begin{aligned}
\alpha &= -\frac{1}{T_c v_r} \left(\frac{\partial v_r}{\partial p_r} \right)_T \left(\frac{\partial p_r}{\partial t_r} \right)_V \\
&= -\frac{1}{T_c v_r} (-P_c v_r K_T) \left(\frac{\partial p_r}{\partial t_r} \right)_V \\
&= \frac{P_c}{T_c} K_T \left(\frac{\partial p_r}{\partial t_r} \right)_V
\end{aligned}$$

Noting that

$$\left(\frac{\partial p_r}{\partial t_r} \right)_V = \left(\frac{\partial p_r}{\partial t_r} \right)_{v_r} = \frac{8}{3v_r - 1}$$

we get

$$\alpha = \frac{P_c}{T_c} K_T \frac{8}{3v_r - 1}$$

Around the critical point, we have

$$\alpha \rightarrow \frac{4P_c}{T_c} K_T = \begin{cases} \frac{2}{3T_c \tau} & T > T_c \\ \frac{1}{3T_c (-\tau)} & T < T_c \end{cases}$$

So that it is strongly divergent like K_T .

(f) Mean-field exponent relation

From the above discussion, we find that the following relation is valid,

$$\alpha + 2\beta + \gamma = 2,$$

which is the same as that predicted from the mean-field theory. We also have the relation predicted from the mean field theory of phase transition,

$$\beta = \frac{2 - \alpha}{1 + \delta} = \frac{1}{2}, \quad \gamma = \frac{(\alpha - 2)(1 - \delta)}{1 + \delta} = 1$$

These results imply that the van der Waals theory is one of the mean field theories. Well above the critical temperature there exists the short-range order due to the attractive interaction between particles. On approaching the critical temperature, short range grows gradually. At the critical temperature, a part of short range order changes into the long-range order. Well below the critical temperature, the long-range order extends over the entire system.

7. Scaled thermodynamic potential

(a) Scaled Helmholtz free energy f

Using the reduced variables, the Helmholtz free energy is given by

$$\begin{aligned} f &= -\frac{a}{v} - k_B T \left[\ln(v-b) + \frac{3}{2} \ln T + \ln \alpha + 1 \right] \\ &= \frac{a}{b} \left\{ -\frac{1}{3v_r} - \frac{8}{27} t_r \left[\ln(v_r - \frac{1}{3}) + \frac{3}{2} \ln t_r + C_1 \right] \right\} \end{aligned}$$

where C_1 is constant

$$C_1 = \frac{3}{2} \ln(T_c) + \ln \alpha + \ln(3b) + 1 = \frac{s_0}{k_B} - \frac{3}{2}.$$

$$\frac{a}{b} = \frac{27}{8} k_B T_c.$$

(b) The law of the corresponding states

The pressure is given by

$$\begin{aligned} P &= - \left(\frac{\partial f}{\partial v} \right)_{T,N} = -\frac{a}{v^2} + \frac{k_B T}{v-b} \\ &= -\frac{a}{9b^2 v_r^2} + \frac{k_B T_c t_r}{3b v_r - b} \\ &= -\frac{a}{9b^2 v_r^2} + \frac{8a}{27b^2} \frac{t_r}{3v_r - 1} \\ &= \frac{a}{b^2} \left(-\frac{1}{9v_r^2} + \frac{8}{27} \frac{t_r}{3v_r - 1} \right) \end{aligned}$$

The reduced pressure p_r is given by

$$p_r = \frac{P}{P_c} = \frac{1}{\frac{a}{27b^2}} \frac{a}{b^2} \left(-\frac{1}{9v_r^2} + \frac{8}{27} \frac{t_r}{3v_r - 1} \right) = -\frac{3}{v_r^2} + \frac{8t_r}{3v_r - 1}$$

or

$$p_r = -\frac{3}{v_r^2} + \frac{8t_r}{3v_r - 1}.$$

(c) Scaled internal energy u

The internal energy is determined by standard thermodynamics,

$$\begin{aligned} u &= \frac{U}{N} \\ &= -T^2 \frac{\partial}{\partial T} \left(\frac{f}{T} \right)_v \\ &= -\frac{a}{v} + \frac{3}{2} k_B T \quad . \\ &= -\frac{a}{3bv_r} + \frac{3}{2} k_B T_c t_r \\ &= \frac{a}{b} \left(-\frac{1}{3v_r} + \frac{4t_r}{9} \right) \end{aligned}$$

or

$$u = \frac{a}{b} \left(-\frac{1}{3v_r} + \frac{4t_r}{9} \right)$$

with

$$\frac{a}{b} = \frac{27}{8} k_B T_c .$$

(d) Scaled entropy s

The entropy S can be similarly determined by standard thermodynamics

$$s = \frac{S}{N}$$

where

$$\begin{aligned}
 s &= -\left(\frac{\partial f}{\partial T}\right)_v = k_B \ln(v-b) + k_B \left[\ln \frac{(2\pi m k_B T)^{3/2}}{h^3} + \frac{5}{2} \right] \\
 &= k_B \ln(v-b) + \frac{3}{2} k_B \ln T + k_B \left(\ln \alpha + \frac{5}{2} \right) \\
 &= k_B \ln(3b v_r - b) + \frac{3}{2} k_B \ln(t_r T_c) + k_B \left(\ln \alpha + \frac{5}{2} \right)
 \end{aligned}$$

or

$$\begin{aligned}
 s &= k_B \left\{ \ln\left(v_r - \frac{1}{3}\right) + \frac{3}{2} \ln t_r + \frac{3}{2} \ln T_c + \ln \alpha + \ln(3b) + \frac{5}{2} \right\} \\
 &= k_B \left[\ln\left(v_r - \frac{1}{3}\right) + \frac{3}{2} \ln t_r \right] + s_0
 \end{aligned}$$

where

$$s_0 = k_B \left[\ln \alpha + \ln(3b) + \frac{3}{2} \ln T_c + \frac{5}{2} \right]$$

In the adiabatic process ($s = \text{constant}$, isentropic process), we have

$$\ln\left[\left(v_r - \frac{1}{3}\right) t_r^{3/2}\right] = \text{const.}$$

or

$$\left(v_r - \frac{1}{3}\right) t_r^{3/2} = \text{constant}$$

Note that for the ideal monatomic gas,

$$v_r t_r^{3/2} = \text{constant.}$$

(e) Scaled Gibbs free energy g

The Gibbs free energy G is given by

$$\begin{aligned}
g(T, P) &= \frac{G(T, P)}{N} \\
&= f + Pv \\
&= -\frac{2a}{v} + \frac{k_B T v}{v-b} - k_B T [\ln(v-b) + \frac{3}{2} \ln T + \ln \alpha + 1]
\end{aligned}$$

$g(T, P)$ can be rewritten as

$$\begin{aligned}
g(T, P) &= -\frac{2a}{3b(v_r)} + \frac{k_B t_r T_c 3b(v_r)}{3b(v_r) - b} - k_B t_r T_c \{ \ln[3b(v_r) - b] \\
&\quad + \frac{3}{2} \ln(t_r T_c) + \ln \alpha + 1 \} \\
&= -\frac{2a}{3b(v_r)} + \frac{8a}{27b} \frac{t_r v_r}{v_r - \frac{1}{3}} - \frac{8a}{27b} t_r [\ln(v_r - \frac{1}{3}) \\
&\quad + \frac{3}{2} \ln t_r + \frac{3}{2} \ln(T_c) + \ln \alpha + \ln(3b) + 1] \\
&= \frac{a}{b} \left\{ -\frac{2}{3v_r} + \frac{8}{27} \left(\frac{t_r v_r}{v_r - \frac{1}{3}} \right) - \frac{8}{27} t_r [\ln(v_r - \frac{1}{3}) \right. \\
&\quad \left. + \frac{3}{2} \ln t_r + \frac{3}{2} \ln(T_c) + \ln \alpha + \ln(3b) + 1] \right\} \\
&= \frac{a}{b} \left\{ -\frac{2}{3v_r} + \frac{8}{27} \left(\frac{t_r v_r}{v_r - \frac{1}{3}} \right) - \frac{8}{27} t_r [\ln(v_r - \frac{1}{3}) + \frac{3}{2} \ln t_r + C_1] \right\}
\end{aligned}$$

Here we have

$$C_1 = \frac{3}{2} \ln(T_c) + \ln \alpha + \ln(3b) + 1 = \frac{s_0}{k_B} - \frac{3}{2}.$$

where s_0 is the constant entropy. Note that the above equation gives g as a function of v and T . The natural variables for g are P and T ,

$$(p_r + \frac{3}{v_r^2})(v_r - \frac{1}{3}) = \frac{8}{3} t_r.$$

We note that the Gibbs free energy can also be obtained by the following approach.

$$\begin{aligned}
g &= \frac{G}{N} \\
&= u - Ts + Pv \\
&= \frac{a}{b} \left(-\frac{1}{3v_r} + \frac{4t_r}{9} \right) - T_c t_r k_B \left[\ln(v_r - \frac{1}{3}) + \frac{3}{2} \ln t_r + \frac{s_0}{k_B} \right] - \frac{a}{3bv_r} + \frac{k_B T_c t_r 3bv_r}{3bv_r - b} \\
&= \frac{a}{b} \left(-\frac{1}{3v_r} + \frac{4t_r}{9} \right) - \frac{8a}{27b} t_r \left[\ln(v_r - \frac{1}{3}) + \frac{3}{2} \ln t_r + \frac{s_0}{k_B} \right] - \frac{a}{3bv_r} + \frac{8a}{27b} \frac{t_r v_r}{v_r - \frac{1}{3}} \\
&= \frac{a}{b} \left\{ -\frac{2}{3v_r} + \frac{8}{27} \frac{t_r v_r}{v_r - \frac{1}{3}} - \frac{8}{27} t_r \left[\ln(v_r - \frac{1}{3}) + \frac{3}{2} \ln t_r - \frac{3}{2} + \frac{s_0}{k_B} \right] \right\} \\
&= \frac{a}{b} \left\{ -\frac{2}{3v_r} + \frac{8}{27} \frac{t_r v_r}{v_r - \frac{1}{3}} - \frac{8}{27} t_r \left[\ln(v_r - \frac{1}{3}) + \frac{3}{2} \ln t_r + C_1 \right] \right\}
\end{aligned}$$

(f) Thermodynamics surface

From the expression of u , the temperature T is calculated as

$$k_B T = \frac{2}{3} \left(\frac{a}{v} + u \right).$$

The thermodynamics surface $u(s, v)$ is obtained by eliminating T , as

$$s - k_B \ln(v - b) - s_1 = \frac{3}{2} k_B \ln T = \frac{3}{2} k_B \ln \frac{2(\frac{a}{v} + u)}{3k_B}$$

or

$$s = k_B \left[\ln(v - b) + \frac{3}{2} \ln T \right] + s_1$$

with

$$s_1 = k_B \left(\ln \alpha + \frac{5}{2} \right)$$

Then we get

$$\begin{aligned}
\frac{2(\frac{a}{v} + u)}{3k_B} &= \exp\left\{\frac{2}{3k_B}[s - s_1 - k_B \ln(v - b)]\right\} \\
&= \exp\left[\frac{2}{3k_B}(s - s_1)\right] \exp\left[-\frac{2}{3} \ln(v - b)\right] \\
&= (v - b)^{-2/3} \exp\left[\frac{2}{3k_B}(s - s_1)\right]
\end{aligned}$$

Thus u depends on v and s ,

$$\begin{aligned}
u &= -\frac{a}{v} + \frac{3k_B}{2} (v - b)^{-2/3} \exp\left[\frac{2(s - s_1)}{3k_B}\right] \\
&= -\frac{a}{v} + c_0 (v - b)^{-2/3}
\end{aligned}$$

with

$$c_0 = \frac{3k_B}{2} \exp\left[\frac{2(s - s_1)}{3k_B}\right]$$

8. Maxwell construction using the Gibbs free energy

(a) Maxwell construction for the v_r - p_r phase diagram

Unfortunately we cannot conveniently put G into an analytic form as a function of P instead of V . We need

$$G(T, P, N) = N\mu(T, P).$$

It is μ that determines the phase co-existence relation; $\mu_l = \mu_g$. At any T , the lowest branch represents the stable phase. The point a ($v_r = v_l = v_l$) and the point e ($v_r = v_3 = v_g$) are on the coexistence line denoted by the path a - c - e .

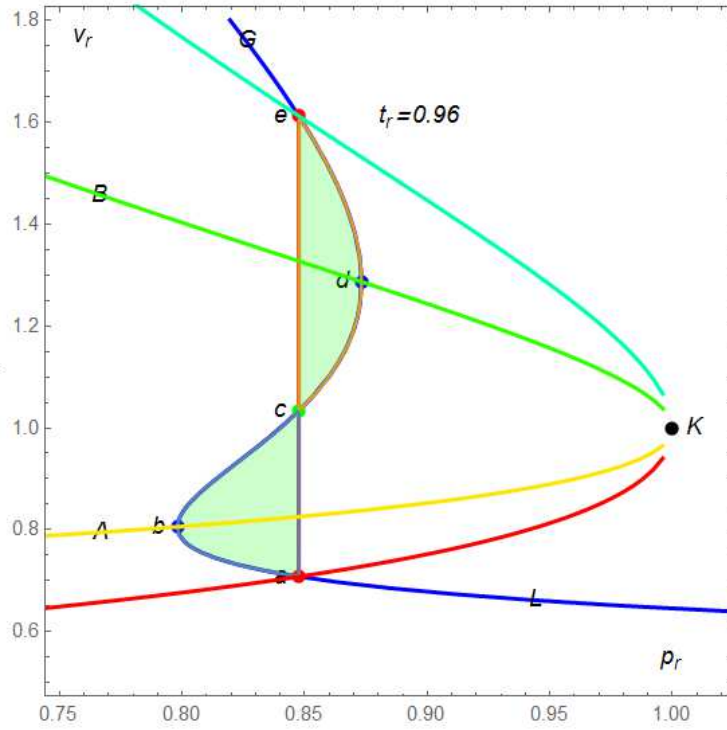


Fig.13 The v_r vs p_r phase diagram with a fixed reduced temperature t_r (in this case $t_r = 0.96$). The area $a-b-c-a$ is equal to the area $e-d-c-e$. (Maxwell construction)

The reduced volumes v_1 and v_3 are determined by the condition that

$$\mu_l(t_r, p_r) = \mu_g(t_r, p_r),$$

along the horizontal line between v_1 and v_3 . This will occur if the shaded area below the line is equal to the shaded area above the line.

$$dG = -SdT + VdP + \mu dN.$$

For $N = \text{constant}$ and $T = \text{constant}$,

$$dg = v_r dp_r,$$

for the scaled Gibbs free energy, and

$$g_g - g_l = \int v_r dp_r.$$

The integral is just the sum of the shaded area (Maxwell construction).

(b) Maxwell construction for the p_r vs v_r phase diagram

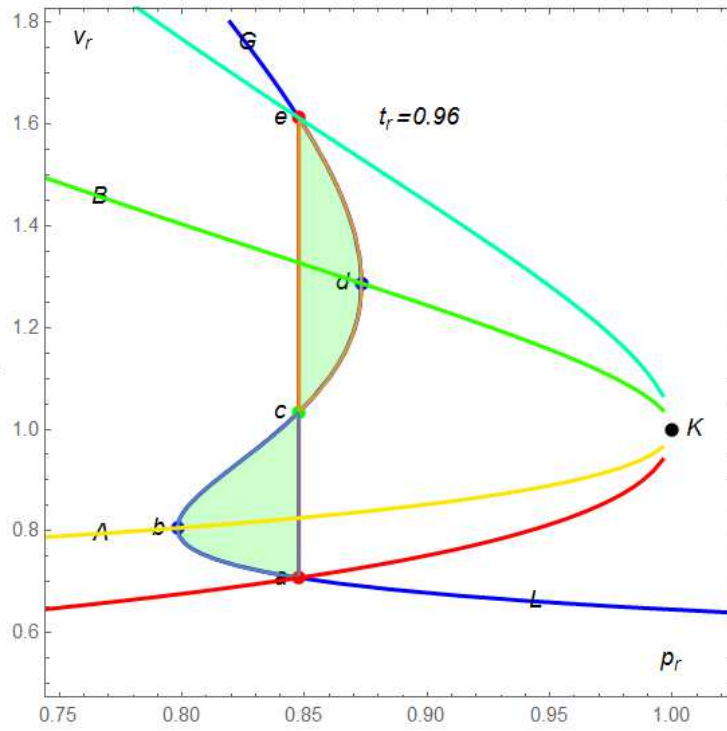


Fig.14 The phase diagram of v_r vs p_r at $t_r = 0.96$.

At $t_r = t_1$,

$$g(t_r = t_1, p_r) = g(t_1, p_a) + \int_{p_a}^p v_r(p_r, t_1) dp_r ,$$

We assume that $p_0 = p_e$ (the pressure at the point e). Then we have

$$g(t_r = t_1, p_e) = g(t_1, p_a) + \int_{abc} v_r(p_r, t_1) dp_r + \int_{cde} v_r(p_r, t_1) dp_r ,$$

Since $g(t_1, p_a) = g(t_1, p_e)$, we have

$$\int_{abc} v_r(p_r, t_1) dp_r + \int_{cde} v_r(p_r, t_1) dp_r = 0 ,$$

or

$$\int_{ed} v_r(p_r, t_1) dp_r + \int_{dc} v_r(p_r, t_1) dp_r = \int_{ab} v_r(p_r, t_1) dp_r + \int_{bc} v_r(p_r, t_1) dp_r .$$

We note that

$$\int_{ed} v_r(p_r, t_1) dp_r > 0 , \quad \int_{dc} v_r(p_r, t_1) dp_r = - \int_{cd} v_r(p_r, t_1) dp_r$$

and

$$\int_{bc} v_r(p_r, t_1) dp_r > 0 , \quad \int_{ab} v_r(p_r, t_1) dp_r = - \int_{ba} v_r(p_r, t_1) dp_r .$$

Then we have

$$\int_{ed} v_r(p_r, t_1) dp_r - \int_{cd} v_r(p_r, t_1) dp_r = \int_{bc} v_r(p_r, t_1) dp_r - \int_{ba} v_r(p_r, t_1) dp_r ,$$

which means that the area of the region $e-d-c$ is the same as that of the region $a-b-c$. Note that

$$p_a = p_c = p_e = p_1 .$$

It is only after the nominal (non-monotonic) isotherm has been truncated by this equal area construction that it represents a true physical isotherm.

In summary, in the p_r vs v_r phase diagram,

- (i) The a-c-e- is the coexistence line ($p_r = p_1$ and $t_r = t_1$) of the liquid phase and the gas phase.
- (ii) The area ($a-b-c-a$) is the same as the area ($c-d-e-c$) [Maxwell construction].
- (iii) K is the critical point ($p_r = v_r = t_r = 1$).
- (iv) The line KA and the line AB are the spinodal lines.

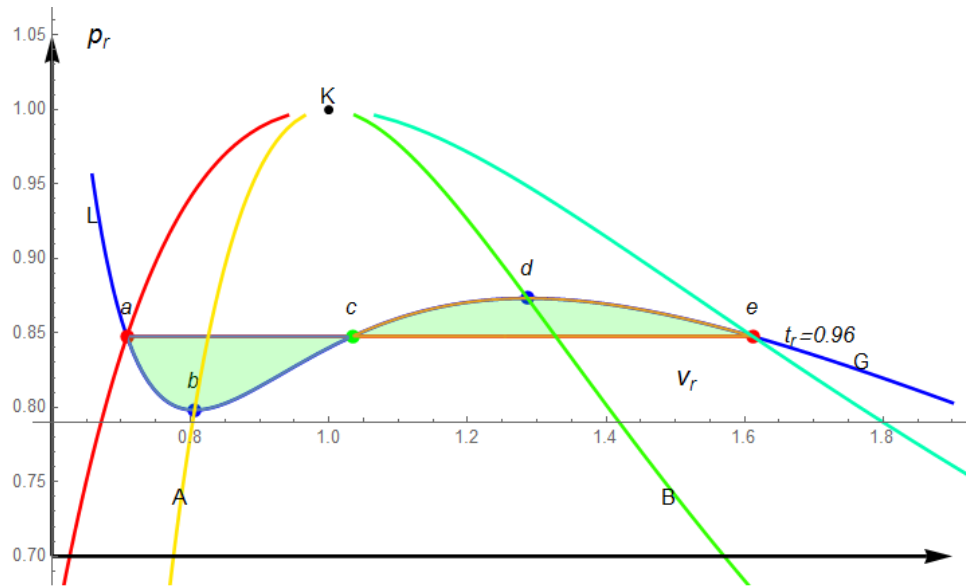
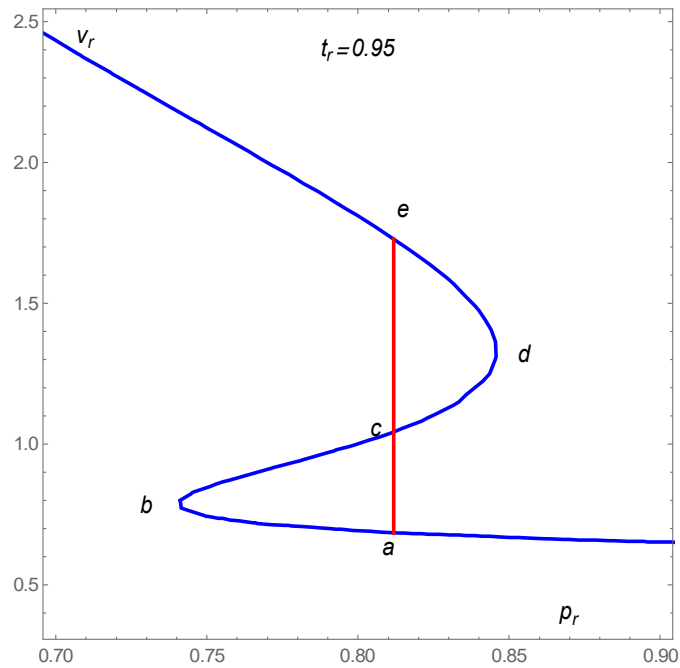


Fig.15 The phase diagram of p_r vs v_r at $t_r = 0.96$.

(c) Example: the area for the v_r vs p_r and the area for the p_r vs v_r for $t_r = 0.95$



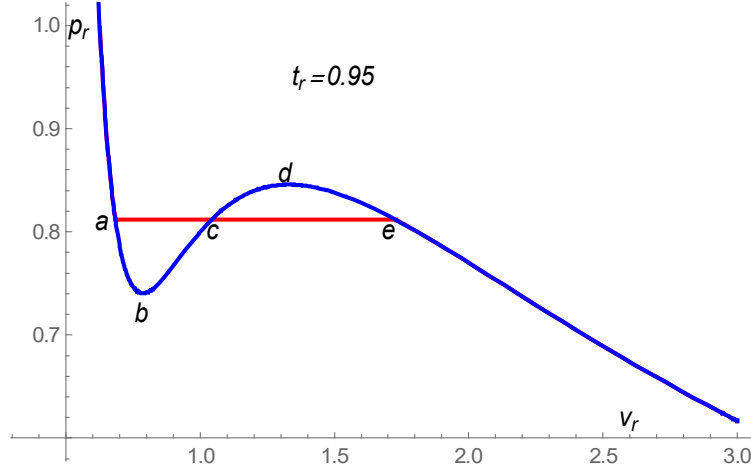


Fig.16 p_r vs v_r curve at $t_r = 0.95$. a : (v_1, p_1) ; b (v_{1m}, p_{1m}) , c (v_2, p_1) , d (v_{3m}, p_{3m}) , e (v_3, p_1) . Maxwell (equal-area) construction. The pressure p where two phase coexistence begins for $t_r = 0.95$ is determined so that the areas above($c-e-d$) and below the horizontal line ($a-b-c$) are equal. In this case, $p = 0.811879$ (the pressures at a and e).

$$\begin{aligned}
 t_r = 0.95 \quad & p_1 = 0.811879, \\
 & v_1 = 0.684122, \quad v_2 = 1.04247 \quad v_3 = 1.72707 \\
 & v_{3m} = 1.33004, \quad p_{3m} = 0.845837 \quad (\text{local maximum point}) \\
 & v_{1m} = 0.786967, \quad p_{1m} = 0.74049 \quad (\text{local minimum point}) \\
 & g(t_r, v_1) = 0.313223. \quad g(t_r, v_{3m}) = 0.319189 \\
 & g(t_r, v_{1m}) = 0.307563
 \end{aligned}$$

(d) The Gibbs energy at the critical point (K)

Let us plot the p_r - v_r plane an isotherm of the liquid and gas. According to the thermodynamic inequality we have

$$\left(\frac{\partial p_r}{\partial v_r} \right)_{t_r} < 0,$$

which implies that p_r is a decreasing function of v_r . The segments $a-b$ and $d-e$ of the isotherms correspond to metastable super-heated liquid state and super-cooled vapor state, in which the thermodynamic inequality is still satisfied.

A complete-equilibrium isothermal change of state between the points a and e corresponds to the horizontal segment $a-c-e$, on which separation into two phases occur. If we use the fact that the points a

and e have the same ordinate $p_r = p_1$, it is clear that the two parts of the isotherm cannot pass continuously into each other: there must be a discontinuity between them.

The isotherms terminates at b and e , where

$$\left(\frac{\partial p_r}{\partial v_r} \right)_{t_r} = 0 .$$

Curve A-K-B on which the thermodynamic inequality is violated for a homogeneous body; boundary of a region in which the body can never exist in a homogeneous state.

Near the critical point, the specific volumes of the liquid and gas are almost the same, denoting them by v_r and $v_r + \delta v_r$, we can write the condition for equal pressure of the two phases

$$p_r(v_r, t_r) = p_r(v_r + \delta v_r, t_r),$$

or

$$\left(\frac{\partial p_r}{\partial v_r} \right)_{t_r} + \frac{1}{2} \delta v_r \left(\frac{\partial^2 p_r}{\partial v_r^2} \right)_{t_r} + \dots = 0 .$$

Hence we see that, when $\delta v_r \rightarrow 0$ (at the critical point),

$$\left(\frac{\partial p_r}{\partial v_r} \right)_{t_r} = 0 .$$

(e) Properties of the Gibbs free energy in the metastable state and unstable state

To see the qualitative behavior of the Gibbs function $g(t_r, p_r)$ as a function of p_r , we use the relation

$$v_r = \left(\frac{\partial g}{\partial p_r} \right)_{t_r} ,$$

or

$$g(t_r, p_r) = g(t_r, p_0) + \int_{p_0}^p v_r dp_r .$$

On the $g(t_r, p_r)$ curve as a function of p_r , v_r represents the slope, $(\frac{\partial g}{\partial p_r})_{t_r}$:

$$v_r = \left(\frac{\partial g}{\partial p_r}\right)_{t_r}.$$

We take the van der Waals isotherm $a-b-c-d-e$ in the p_r - v_r diagram. We make a plot of the corresponding $g(t_r, p_r)$ curve as function of p_r at $t_r = t_1$ (in this case, $t_r = 0.95$).

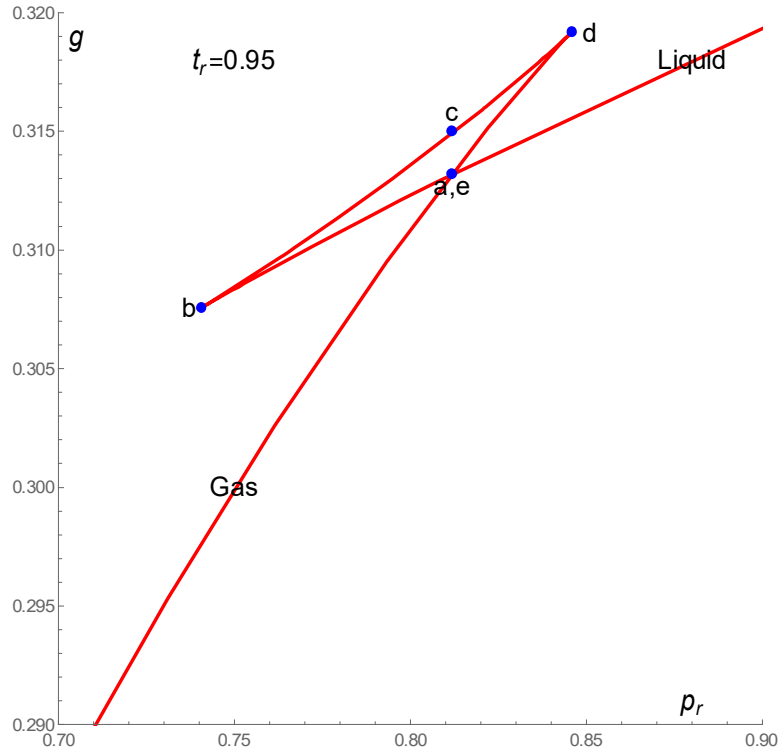


Fig.17 Gibbs free energy as a function of p_r at $t_r = 0.95$.

- (i) Around the point d (on the path $d-e-g$) where $(\frac{\partial p_r}{\partial v_r})_{t_1} = 0$, and $\xi_{m3} = -(\frac{\partial^2 p_r}{\partial v_r^2})_{t_1} > 0$, p_r can be expressed by using the Taylor expansion, as

$$p_r - p_{m3} \approx \left(\frac{\partial p_r}{\partial v_r}\right)_{t_1} (v_r - v_{m3}) + \frac{1}{2} \left(\frac{\partial^2 p_r}{\partial v_r^2}\right)_{t_1} (v_r - v_{m3})^2,$$

or

$$p_r - p_{m3} \approx -\frac{\xi_{m3}}{2}(v_r - v_{m3})^2,$$

or

$$v_r - v_{m3} = \sqrt{2\xi_{m3}}^{1/2}(p_{m3} - p_r)^{1/2}.$$

Then we have

$$\left(\frac{\partial v_r}{\partial p_r}\right)_{t_1} = -\frac{\xi_{m3}^{1/2}}{\sqrt{2}}(p_{m3} - p_r)^{-1/2}.$$

So that $\left(\frac{\partial v_r}{\partial p_r}\right)_{t_1}$ become infinite at the point d . Then $g(t_1, p_r)$ curve has a cusp.

(ii) From b to d (on the path b - c - d). $v_r = \left(\frac{\partial g}{\partial p_r}\right)_{t_1}$ increases as p_r increases. $\left(\frac{\partial v_r}{\partial p_r}\right)_{t_1}$ is positive (this portion is unstable).

(iii) Around the point b (on the path l - a - b) where $\left(\frac{\partial p_r}{\partial v_r}\right)_{t_1} = 0$ and, $\xi_{m1} = \left(\frac{\partial^2 p_r}{\partial v_r^2}\right)_{t_1} > 0$, p_r can be expressed by using the Taylor expansion, as

$$p_r - p_{m1} \approx \left(\frac{\partial p_r}{\partial v_r}\right)_{t_1}(v_r - v_{m1}) + \frac{1}{2}\left(\frac{\partial^2 p_r}{\partial v_r^2}\right)_{t_1}(v_r - v_{m1})^2,$$

or

$$p_r - p_{m1} \approx \frac{1}{2}\xi_{m1}(v_r - v_{m1})^2$$

or

$$v_r - v_{m1} = \sqrt{2\xi_{m1}}^{1/2}(p_r - p_{m1})^{1/2}.$$

Then we have

$$\left(\frac{\partial v_r}{\partial p_r}\right)_{t_1} = \frac{\xi_{m1}^{1/2}}{\sqrt{2}}(p_r - p_{m1})^{-1/2}.$$

So that $\left(\frac{\partial v_r}{\partial p_r}\right)_{t_1}$ become infinite at the point b and $g(t_1, p_r)$ curve has another cusp.

(iv) From l to b (on the path $l-a-b$). $v_r = \left(\frac{\partial g}{\partial p_r}\right)_{t_r}$ decreases as p_r increases. $\left(\frac{\partial v_r}{\partial p_r}\right)_{t_r}$ is negative, but becomes small as the point l is approached.

In summary, the path $d-c-b$ corresponds to unstable region and the paths $e-d$ and $b-a$ are metastable.

(f) Numerical calculation

We can make a plot of g vs p_r where t_r is fixed, using the ParametricPlot of the Mathematica. The scaled Gibbs free energy g and the reduced pressure p_r are given by

$$g = -\frac{2}{3v_r} + \frac{8}{27} \left(\frac{t_r v_r}{v_r - \frac{1}{3}} \right) - \frac{8}{27} t_r \left[\ln(v_r - \frac{1}{3}) + \frac{3}{2} \ln t_r - \frac{3}{2} \right],$$

and

$$p_r = -\frac{3}{v_r^2} + \frac{8t_r}{3v_r - 1}.$$

So we make a ParametricPlot of the co-ordinate (p_r, g) when t_r is given as a fixed parameter and v_r is continuously changed as a variable. The Mathematica which we use is as follows.

((Mathematica))


```

Clear["Global`*"];
gl[tr_, vr_] :=
  
$$\frac{-2}{3 vr} + \frac{8}{27} \frac{tr vr}{vr - \frac{1}{3}} - \frac{8}{27} tr \left( \text{Log}\left[vr - \frac{1}{3}\right] + \frac{3}{2} \text{Log}[tr] - \frac{3}{2} \right);$$

pr[tr_, vr_] := 
$$\frac{-3}{vr^2} + \frac{\frac{8}{3}}{vr - \frac{1}{3}} tr;$$

tr = 0.95;

sl = ParametricPlot[Evaluate[{pr[tr, vr], gl[tr, vr]}],
  {vr, 0.5, 10}, PlotStyle -> {Red, Thick},
  PlotRange -> {{0.70, 0.9}, {0.29, 0.32}},
  AspectRatio -> Full];

```

(i) $t_r = 0.99$

The p_r dependence of the scaled Gibbs energy is shown below. We note that the scaled Gibbs energy is the same at the points *a* and *e*. The Gibbs energy along the path *a-b* (the metastable state), along the path *b-c-d* (the unstable state), and along the path *d-e* is higher than that along the path *l* (liquid)-*a* and along the path *e-g* (gas). This means that the coexistence line (*a-c-e*) is the equilibrium state. It is seen that the Gibbs free energy vs p_r shows a thermodynamically invisible bow tie.

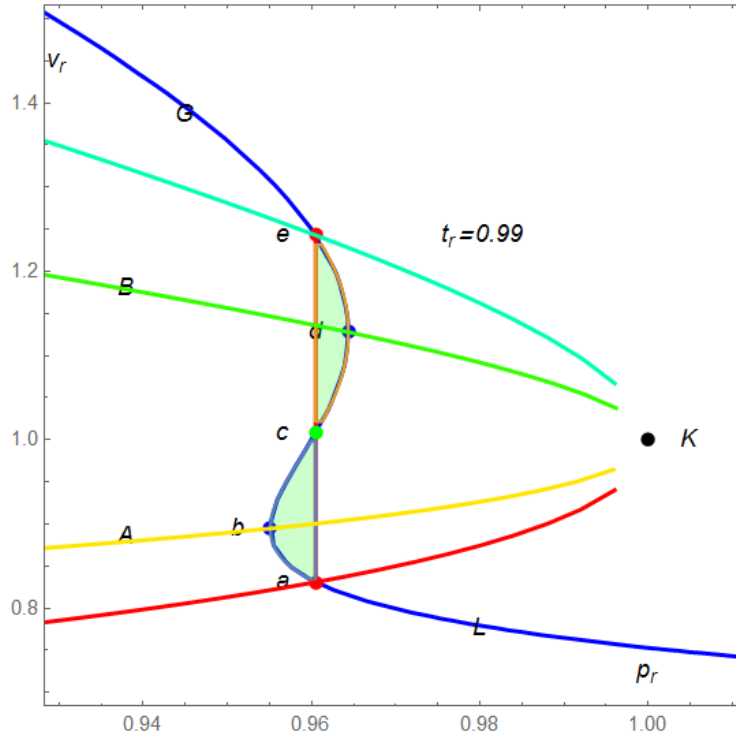


Fig.18

v_r vs p_r for $t_r = 0.99$. The line $a-c-e$ is the co-existence line between the gas and liquid phases. K: critical point. The lines A-K and B-K are spinodal lines. The path $a-c-e$ is the co-existence line of the liquid and gas phases.

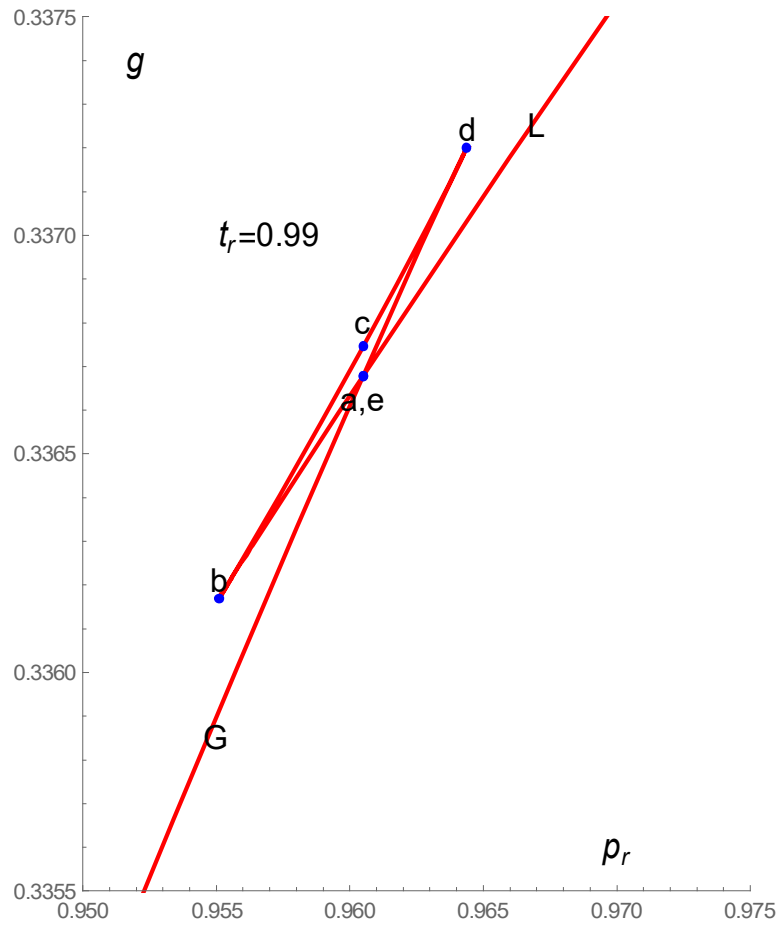


Fig.19

Scaled Gibbs free energy g vs p_r for $t_r = 0.99$. g is in the units of (a/b) . The path b - c - d is unstable. $p_1 = 0.960479$. $p_{m1} = 0.955095$ (point b). $p_{m3} = 0.964369$ (point d)

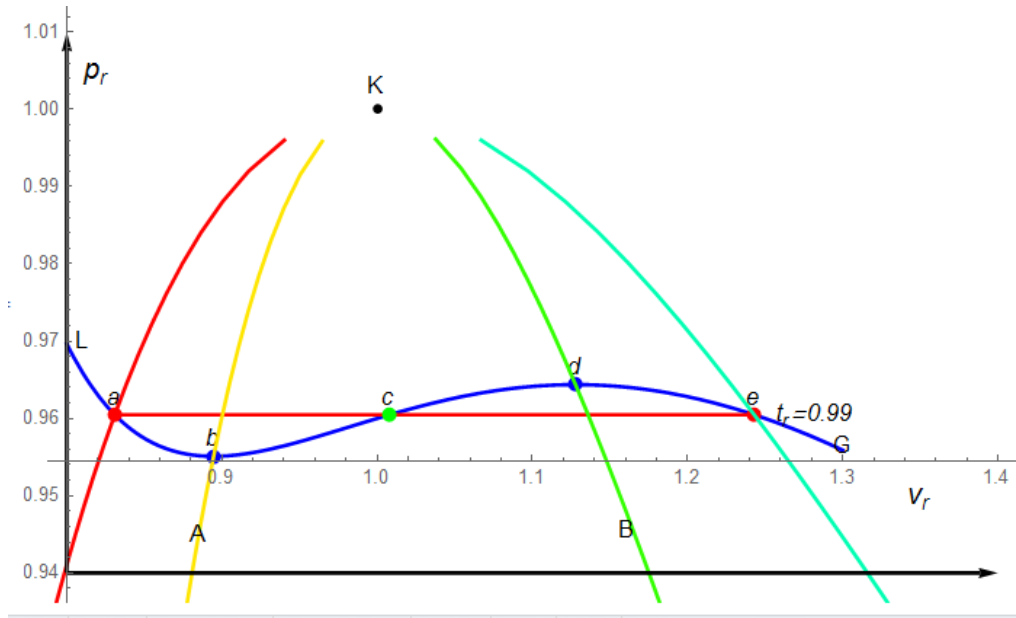


Fig.20 The phase diagram of p_r vs v_r for $t_r = 0.99$. $v_1 = 0.830914$ (point a). $v_3 = 1.24295$ (point e). $p_1 = 0.960479$.

(ii) $t_r = 0.98$

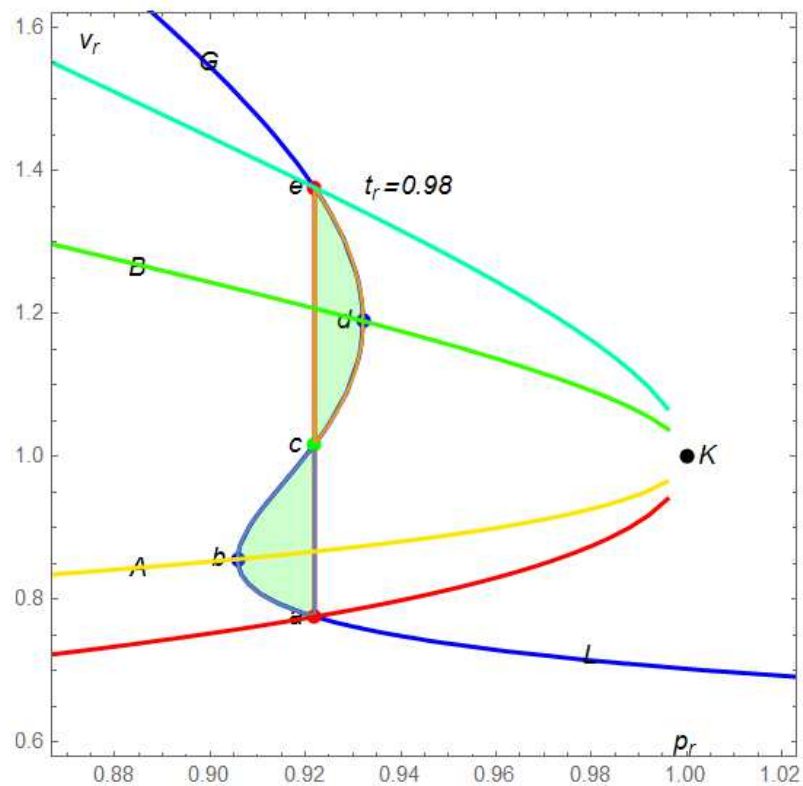


Fig.21

v_r vs p_r for $t_r = 0.98$. The line $a-c-e$ is the coexistence line. The path $b-c-d$ is unstable. The path $a-b$ and the path $d-e$ is unstable. The area enclosed by $a-b-c$ is the same as that by $c-d-e$ (Maxwell construction). $p_1 = 0.921912$. $v_1 = 0.775539$. $v_3 = 1.3761$.

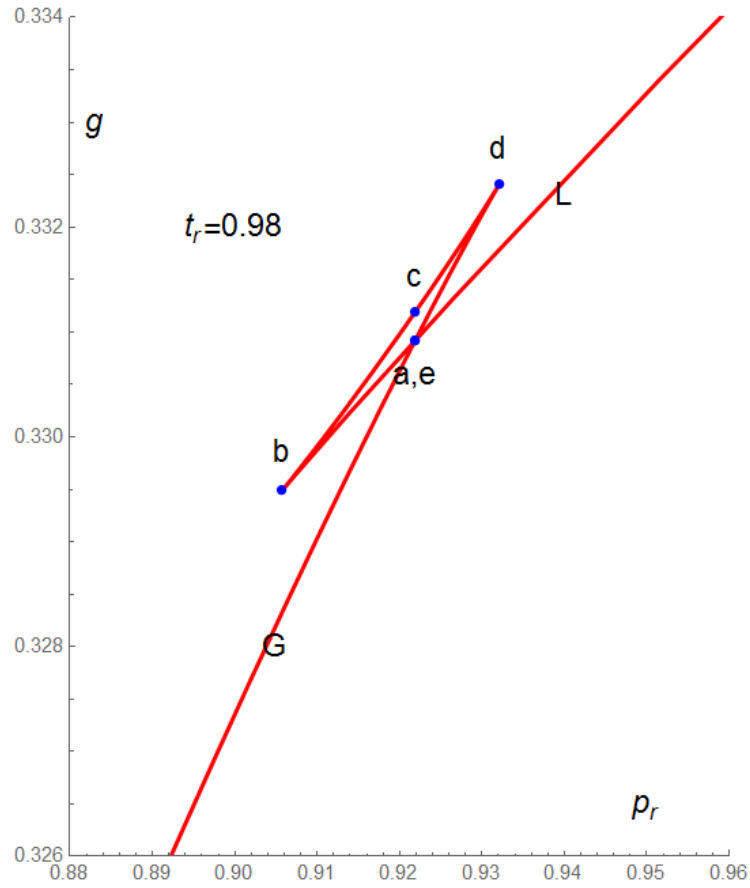


Fig.22

Scaled Gibbs energy g (in the units of a/b) vs p_r for $t_r = 0.98$. The path $b-c-d$ is unstable. The shape of the $b-c-d$ is similar to spine (the spinodal decomposition). The path $a-b$ and the path $d-e$ are unstable. $p_1 = 0.921912$. $p_{m1} = 0.905756$ (point b). $p_{m3} = 0.932089$ (point d).

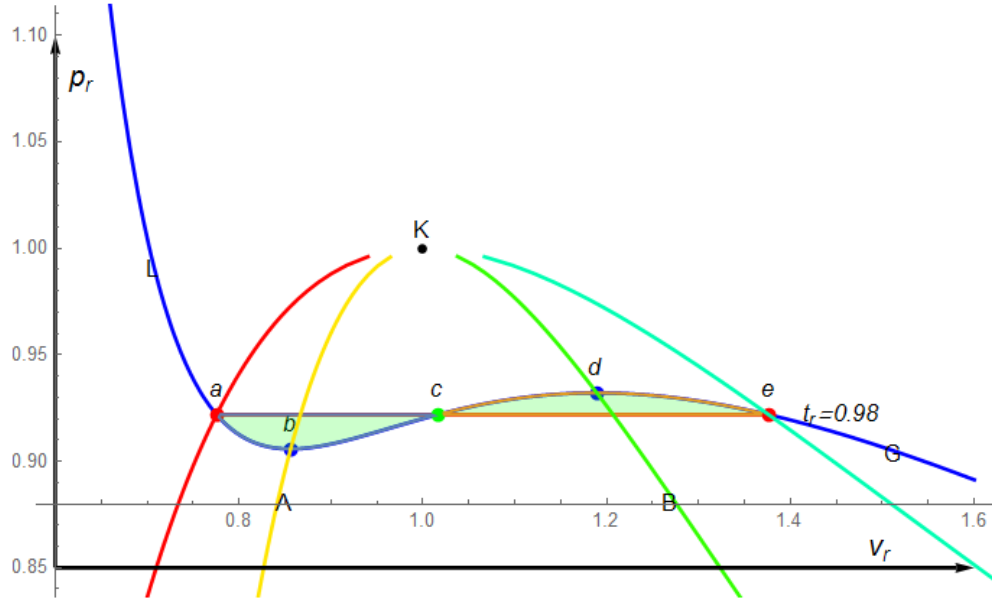


Fig.23 p_r vs v_r for $t_r = 0.98$. The line $a-c-e$ is the coexistence line. The path $b-c-d$ is unstable. The path $a-b$ and the path $d-e$ are metastable. The area enclosed by $a-b-c-a$ is the same as that by $c-d-e-c$ (Maxwell's construction). $p_1 = 0.921912$. $v_1 = 0.775539$. $v_3 = 1.3761$.

(iii) $t_r = 0.97$

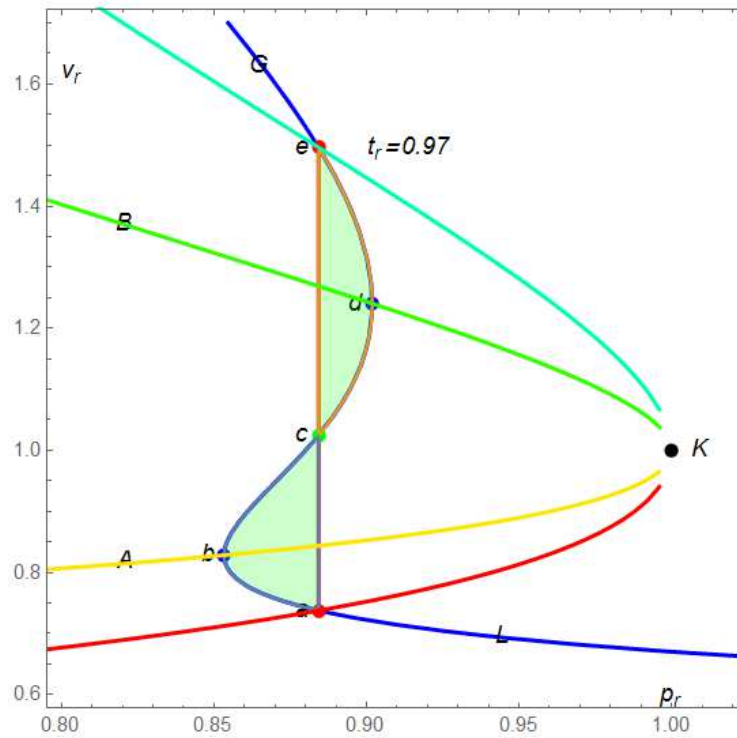
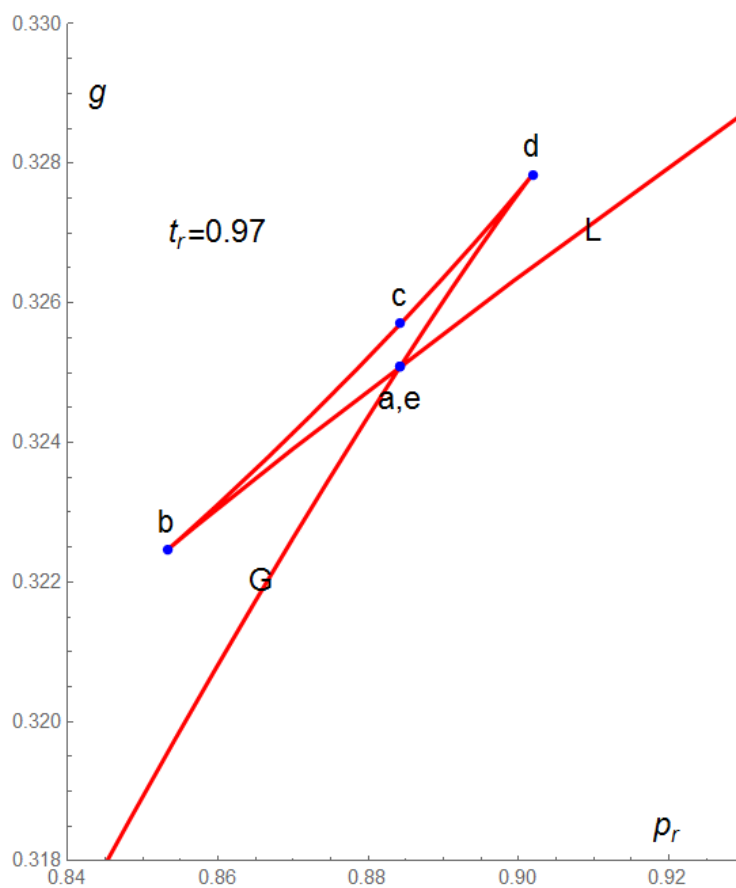


Fig.24Phase diagram of v_r vs p_r at $t_r = 0.97$.**Fig.25**Gibbs free energy as a function of p_r at $t_r = 0.97$. $p_1 = 0.884294$. $p_{m1} = 0.853279$. $p_{m3} = 0.901849$.

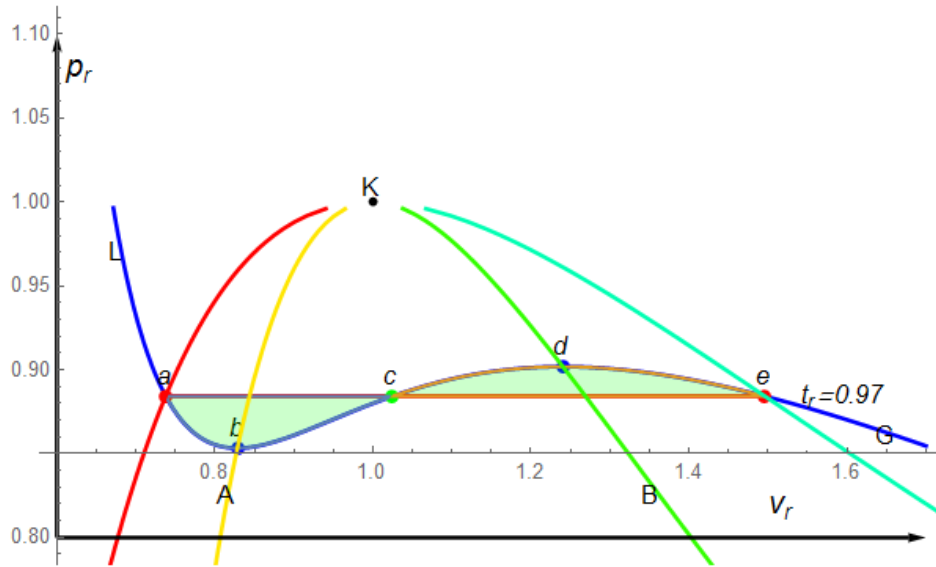


Fig.26 Phase diagram of p_r vs v_r at $t_r = 0.97$.

(iv) $t_r = 0.96$

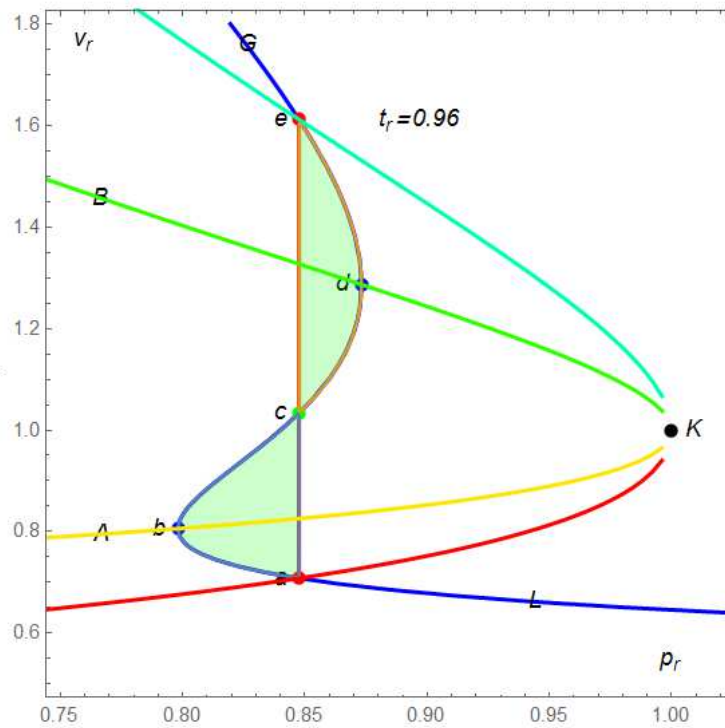


Fig.27 Phase diagram of v_r vs p_r at $t_r = 0.96$.

10. Double-tangent construction based on Helmholtz free energy

Maxwell construction based on the Gibbs free energy is equivalent to the double-tangent construction based on the Helmholtz free energy. Here we discuss the double-tangent construction using the concept of the Helmholtz free energy.

(a) Double-tangent line (coexistence line)

Using the relation

$$p_r = -\frac{\partial f(v_r, t_r)}{\partial v_r},$$

the Helmholtz free energy can be obtained as

$$f(t_r, v_r) = f(t_r, v_{r0}) - \int_{v_{r0}}^{v_r} p_r(v_r, t_r) dv_r.$$

The Helmholtz free energy is related to the Gibbs free energy as

$$g(t_r, p_r) = f(t_r, v_r) + p_r v_r.$$

According to the Maxwell construction from the Gibbs free energy, we have

$$g_1 = g_3,$$

at the point a ($p_r = p_1$, $v_r = v_1$) and point e ($p_r = p_1$, $v_r = v_3$), where

$$g_1 = f_1 + p_1 v_1, \quad \text{at the point } a,$$

$$g_3 = f_3 + p_1 v_3, \quad \text{at the point } e.$$

In the diagram of f vs v_r the point a is located at the co-ordinate (v_1, f_1) , while the point e is located at the co-ordinate (v_3, f_3) . Note that the point a and point b are on the coexistence line in the p_r vs v_r diagram for $t_r < 1$. The straight line (double-tangent line) connecting the points a and e can be given by

$$f_{DT} = f_1 + \left(\frac{f_3 - f_1}{v_3 - v_1} \right) (v - v_1).$$

We note that

$$\frac{\partial f_{DT}}{\partial v} = \left(\frac{f_3 - f_1}{v_3 - v_1} \right) = -p_1.$$

The reduced pressure p_1 corresponds to a negative of the slope of the straight line (the double-tangent line) connecting the point a and the point e . We note that

$$\frac{\partial^2 f_{DT}}{\partial v^2} = 0.$$

We make a plot of the reduced Helmholtz free energy as a function of the reduced volume v_r at fixed temperature (in this case $t_r = 0.85$). The double-tangent line is denoted by the straight line connecting the points a and e . The tangential line at the point a coincides with that at the point e . Note that the Helmholtz free energy at fixed t_r is higher than the corresponding double-tangent line between v_1 and v_3 . This means that this double tangent line is the coexistence line between the points a and e .

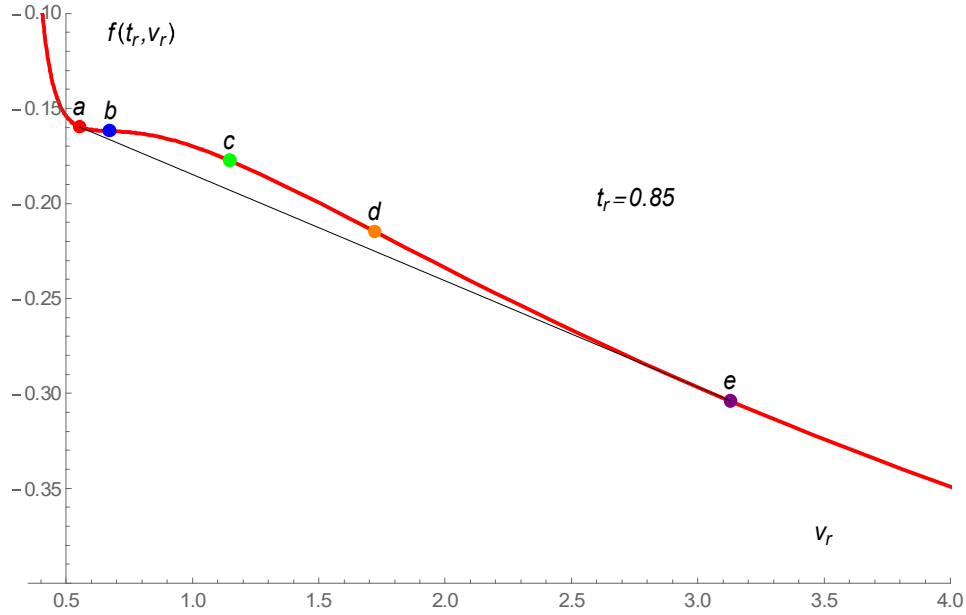
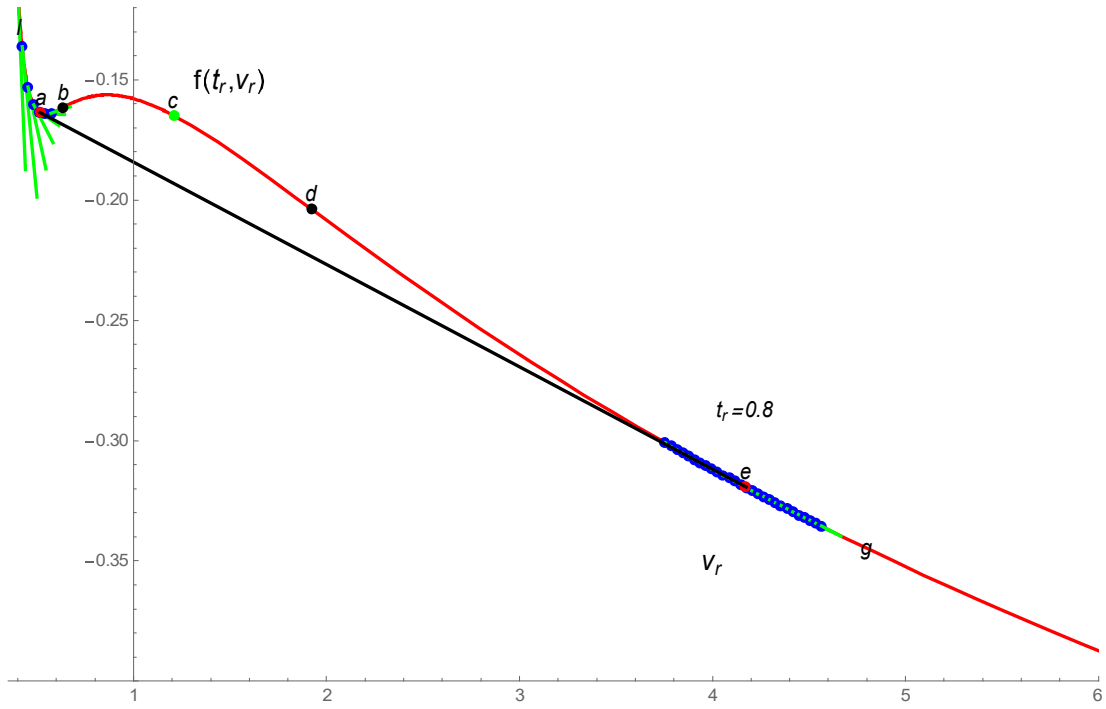
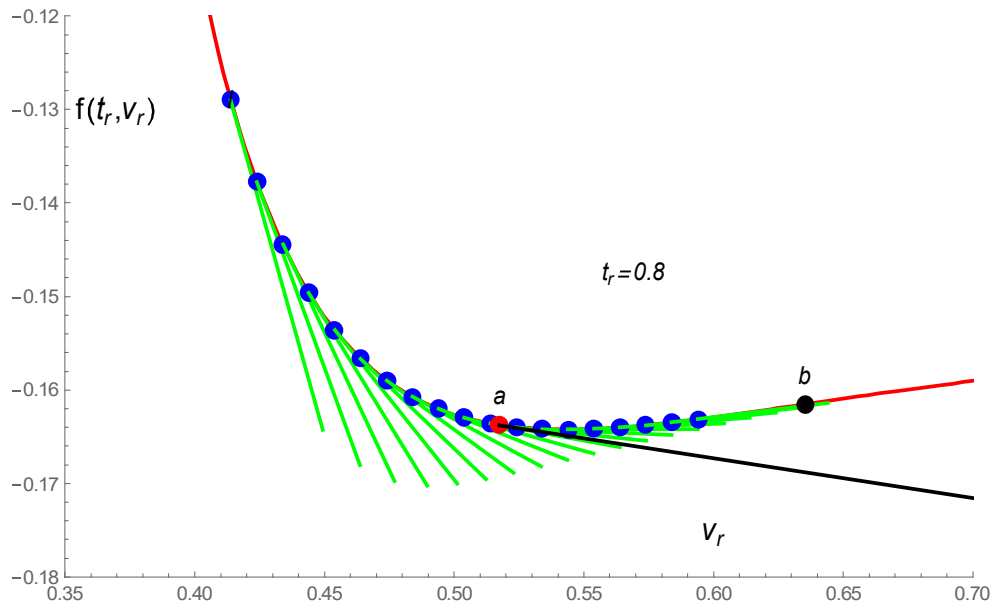


Fig.30

The isothermal Helmholtz energy f as a function of the reduced volume. $t_r = 0.85$. The Helmholtz free energy has two inflection points at the point b and the point d below the critical point. The double-tangent line (the straight line $a-e$) represents coexisting vapor and liquid phases. The Helmholtz free energy with double-tangent line (the path $a-e$) is lower than the metastable (the path $a-b$ and the path $d-e$) and unstable part (the path $b-c-d$) between v_1 (the point a) and v_3 (the point e); double-tangent construction. $v_1 = 0.55336$. $v_3 = 3.12764$. $p_1 = 0.504492$.



(a)



(b)

Fig.31 (a) and (b)

Tangential line (green line) of the Helmholtz free energy vs v_r , corresponding to $-p_r$ at fixed reduced temperature $t_r (= 0.8, \text{ in this case})$. The double-tangent line (black line) is the co-existence

curve with $p_r = p_1$ between $v_r = v_1$ (the state a) and v_3 (the state e). The tangential line at the point a , coincides with that at the point e . $v_1 = 0.517409$. $v_2 = 1.20827$. $v_3 = 4.17246$.

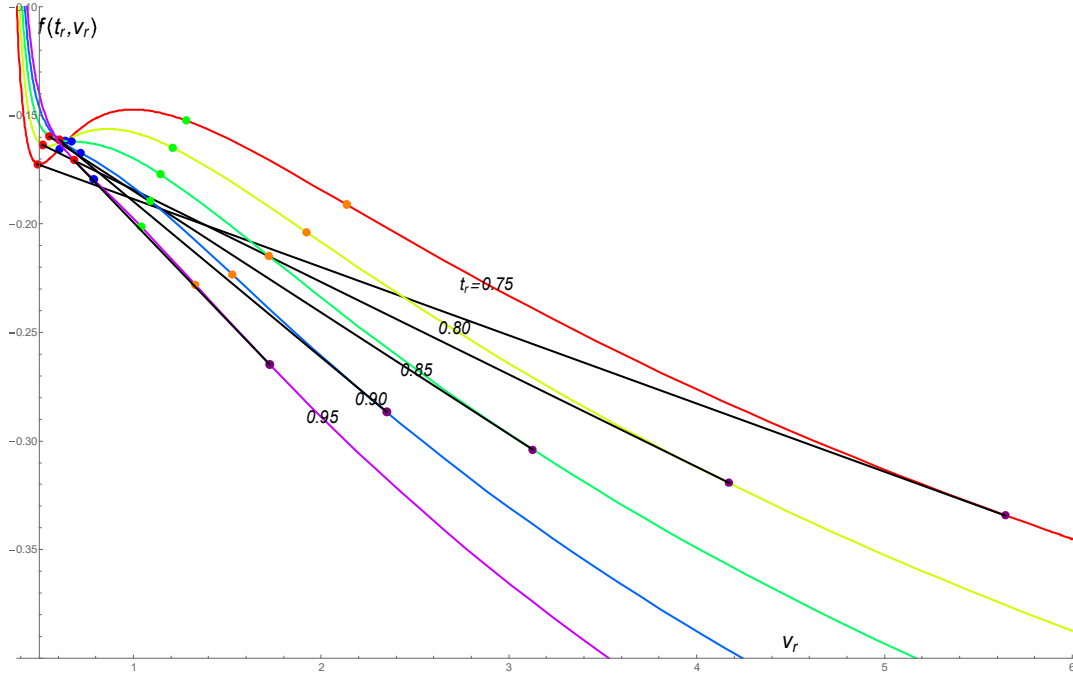


Fig.32 $f(t_r, v_r)$ vs v_r at each fixed reduced temperature t_r ($t_r = 0.75, 0.80, 0.85, 0.90$, and 0.95). The double-tangent lines are also denoted by the black straight lines connecting between the point a and the point e .

(b) Pressure as a function of the reduced volume

The reduced pressure is given by

$$p_r = - \left(\frac{\partial f}{\partial v_r} \right)_{t_r},$$

using the Helmholtz free energy. The reduced pressure p_r is plotted as a function of the reduced volume ($t_r = 0.85$). Above the critical point, as v_r increases, the Helmholtz free energy decreases, corresponding to the monotonic decrease in p_r vs v_r . This is a typical of any temperature above the critical point. Below the critical point, we see that the path l (liquid)- a and the path e - g (gas) in which the reduced pressure decreases monotonically as v_r increases. These are joined by a straight line. The path a - e touching the path l - a at the point a and touching the path e - g at the point e . The three portions correspond to the liquid phase, to the gas phase, and to a two-phase liquid-gas system. This typically happens when $t_r < 1$. Note that the path a - b represents superheated liquid. The path d - e represent super-cooled vapor. We see that all states represented by these portions of curves are *metastable*.

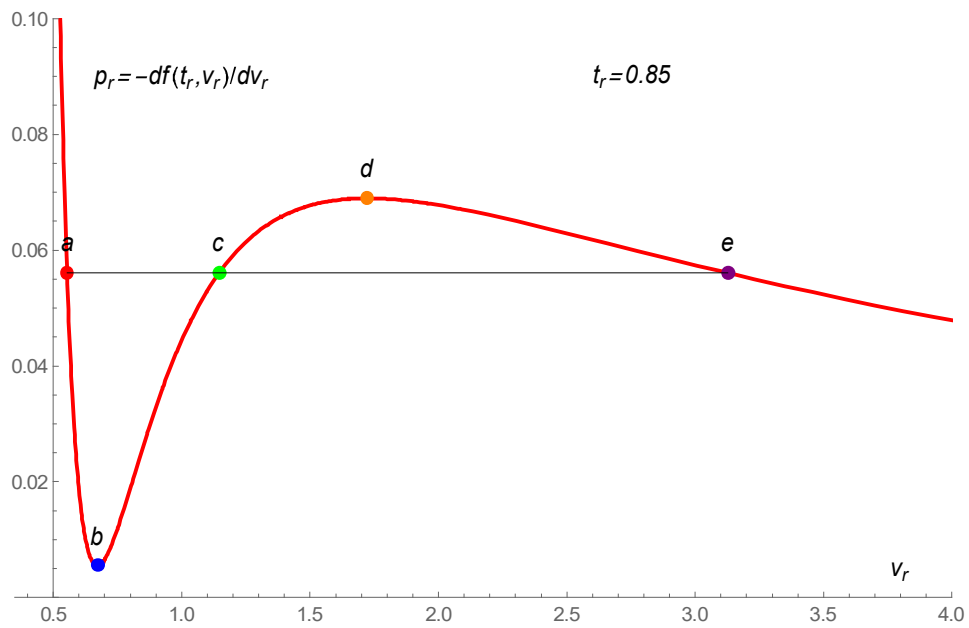


Fig.33 $p_r = -(\partial f / \partial v_r)_{t_r}$ as a function of v_r . $t_r = 0.85$. The path a - c - e is the coexistence boundary.

(c) Metastable state and unstable state

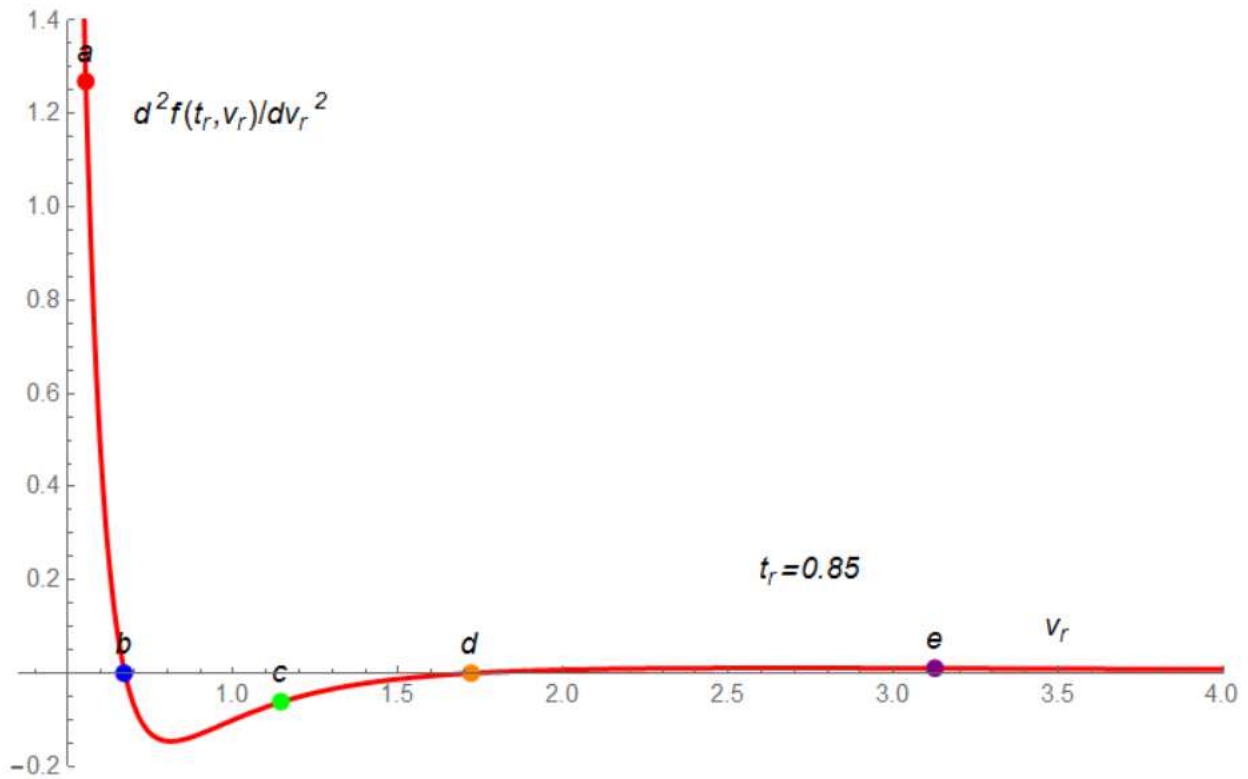


Fig.34 $\left(\partial^2 f / \partial v_r^2\right)_{t_r}$ as a function of v_r . $t_r = 0.85$. $\left(\partial^2 f / \partial v_r^2\right)_{t_r} < 0$ for the path $b-c-d$, indicating that the curve f vs v_r is concave upwards (unstable). $\left(\partial^2 f / \partial v_r^2\right)_{t_r} > 0$ for the path $a-b$ and path $d-e$, indicating that the curve is concave downwards (metastable).

The Helmholtz free energy of the superheated liquid (the path $a-b$) or the supersaturated vapor (the path $d-e$) is greater than that for the double-tangent line. The portions curve $a-b$ and $d-e$ are in the metastable state. They have curvature *concave upwards* so that

$$\frac{\partial p_r}{\partial v_r} = -\left(\frac{\partial^2 f}{\partial v_r^2}\right) < 0,$$

because of the definition of mathematics,

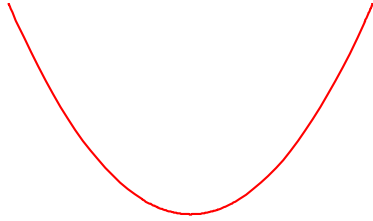


Fig.35 $\left(\frac{\partial^2 f}{\partial v_r^2}\right) > 0$, (concave downwards, or convex upwards),

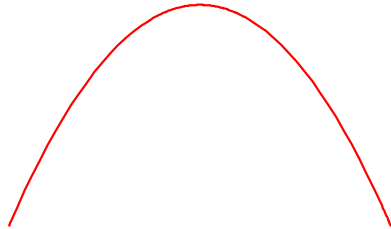


Fig.36 $\left(\frac{\partial^2 f}{\partial v_r^2}\right) < 0$, (concave upwards, or convex downwards).

We note that the path $b-c-d$ has a curvature concave downwards. This would correspond to a positive value of

$$\frac{\partial p_r}{\partial v_r} = -\left(\frac{\partial^2 f}{\partial v_r^2}\right) > 0,$$

leading to unstable states. Such states are not realized.

Since the tangent line $f(v_r)$ maintains the same slope between v_1 and v_3 , the pressure remains constant between v_1 and v_3 :

$$\left(\frac{\partial f(t_r, v_r)}{\partial v_r}\right)_\tau = -p_1.$$

In other words, the line connecting points on the $p_r - v_r$ plot is horizontal and the two coexistence phases are in thermal equilibrium. For each temperature below $t_r = 1$, the phase transformation occurs at a well-defined pressure p_1 , the so-called vapor pressure. Two stable branches g (gas)- $e-d$ and $b-a-l$ (liquid) correspond to different phases: the branch $g-e-d$ (gas phase) and the branch $b-a-l$ (liquid phase). The branch $e-c-a$ is the co-existence line between the gas phase and liquid phase. The branch $e-d$ is a metastable gas phase, while the branch $b-a$ is a metastable liquid phase.

(d) Difference $\Delta f = f - f_{DT}$

Here we define as

$$\Delta f = \Delta f(t_r, v_r) = f(t_r, v_r) - f_{DT}(t_r, v_r),$$

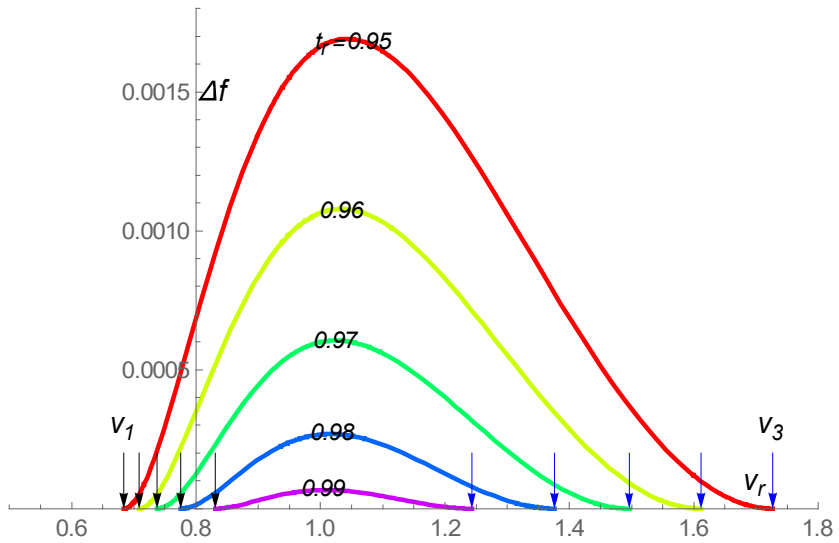
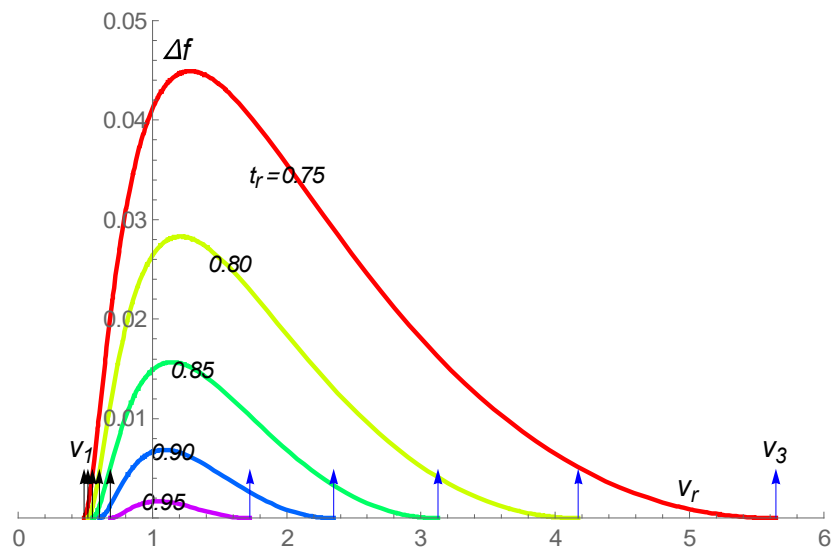
where f_{DT} is given by

$$f_{DT}(t_r, v_r) = f_1 + \frac{f_3 - f_1}{v_3 - v_1}(v_r - v_1),$$

for the double-tangent line. Since $\partial^2 f_{DT}(t_r, v_r) / \partial v_r^2 = 0$, it follows that

$$\partial^2 \Delta f(t_r, v_r) / \partial v_r^2 = \partial^2 f(t_r, v_r) / \partial v_r^2.$$

The plots of Δf vs v_r is shown for the range $(v_1 < v_r < v_3)$, where t_r is changed as a parameter. We note that the difference Δf is equal to zero at $v_r = v_1$ and v_3 . It shows a peak at $v_r = v_2$. We show the deviation Δf vs v_r between v_1 and v_3 at $t_r = 0.95$. The points a ($v_r = v_1$), b , c ($v_r = v_2$), d , and e ($v_r = v_3$), are shown in this figure. $\partial^2 \Delta f / \partial v_r^2 > 0$ for the path $a-b$ (the superheated state) and the path $d-e$ (the super-cooled state). $\partial^2 \Delta f / \partial v_r^2 < 0$ for the path $b-c-d$ (unstable state).



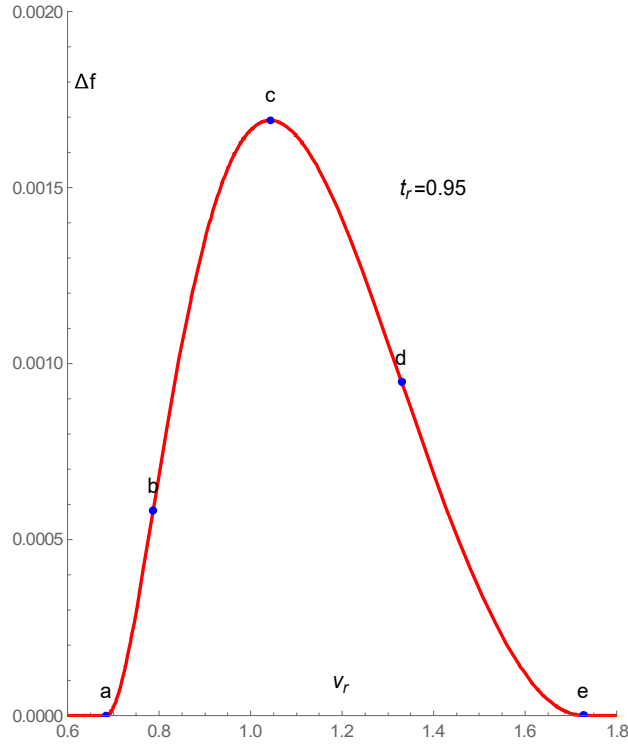


Fig.37

(a), (b), and (c) The deviation Δf vs v_r between v_1 and v_3 at $t_r = 0.95$. The points a ($v_r = v_1$), b , c ($v_r = v_2$), d , and e ($v_r = v_3$), are shown in this figure. $\partial^2 \Delta f / \partial v_r^2 > 0$ for the path a - b (the superheated state) and the path d - e (the super-cooled state). $\partial^2 \Delta f / \partial v_r^2 < 0$ for the path b - c - d (unstable state).

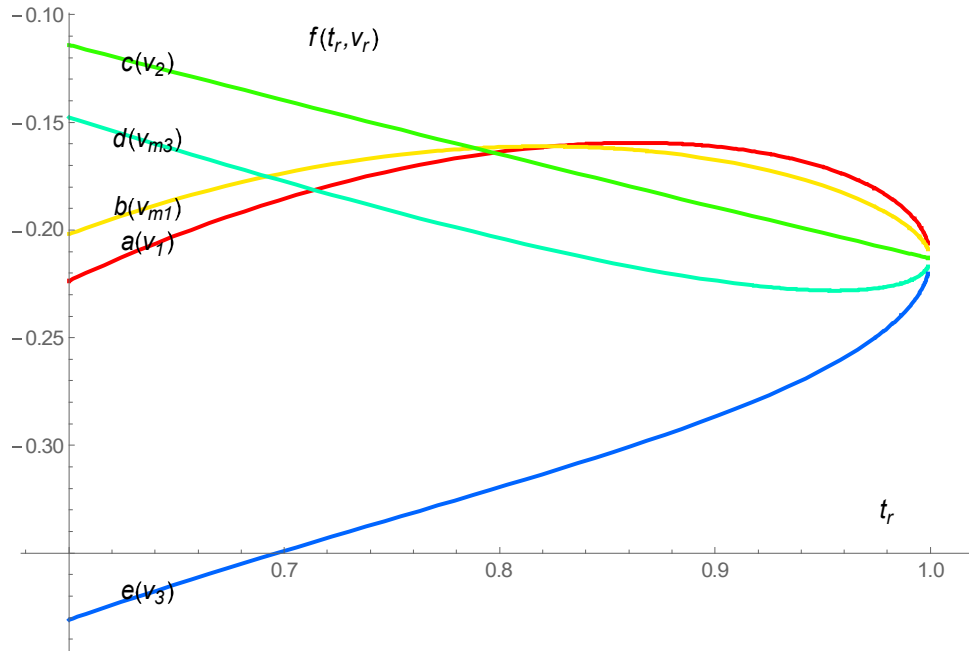


Fig.38 $f(t_r, v_1)$, $f(t_r, v_{m1})$, $f(t_r, v_2)$, $f(t_r, v_{m3})$, and $f(t_r, v_3)$ as a function of t_r . Note that v_1 , v_{m1} , v_2 , v_{m3} , and v_3 are dependent on t_r according to Maxwell construction or double-tangent construction.

(e) The lever rule for the Helmholtz free energy

The straight line connecting the point a and the point e is given by

$$f = f_1 + \left(\frac{f_3 - f_1}{v_3 - v_1} \right) (v - v_1),$$

where $v_1 \leq v \leq v_3$. This can be written as

$$\begin{aligned} f &= f_1 - \left(\frac{f_3 - f_1}{v_3 - v_1} \right) v_1 + \left(\frac{f_3 - f_1}{v_3 - v_1} \right) v \\ &= f_1 \left(\frac{v_3 - v}{v_3 - v_1} \right) + f_3 \left(\frac{v - v_1}{v_3 - v_1} \right) \end{aligned}$$

or

$$f = \theta_1 f_1 + \theta_3 f_3,$$

corresponding to the lever rule for the reduce volume, where

$$\theta_1 = \frac{v_3 - v}{v_3 - v_1}, \quad \theta_3 = \frac{v - v_1}{v_3 - v_1},$$

f can be written as

$$f = \left(\frac{v_3 - v}{v_3 - v_1} \right) f_1 + \left(\frac{v - v_1}{v_3 - v_1} \right) f_3 = \frac{1}{v_3 - v_1} [f_1(v_3 - v) + (v - v_1)f_3],$$

which is the straight line passing through the two points (v_1, f_1) and (v_3, f_3) . We recognize this as the common tangent line.

$$\left(\frac{\partial f}{\partial v} \right)_\tau = \frac{f_3 - f_1}{v_3 - v_1} = -p_1,$$

and

$$\left(\frac{\partial^n f}{\partial v^n} \right)_\tau = 0.$$

(f) Summary

According to the Maxwell relation

$$p_r = - \left(\frac{\partial f(t_r, v_r)}{\partial v_r} \right)_{t_r},$$

the Helmholtz free energy can be obtained as the area under the isotherm:

$$f(t_r, v_r) = - \int_{\text{isotherm}} p_r dv_r.$$

Note that v_1 and v_3 are defined by the double-tangent construction. At any point along the tangent, the Helmholtz free energy is a linear combination of those at a and e , and thus represent a mixture of the liquid and gas phases. Note that the value of $f(t_r, v_r)$ for $v_1 < v_r < v_3$ is larger than that on the double tangent line, as is obvious from the graphical construction. Thus the phase-separated state is the equilibrium state. The states a and e are defined by the condition

$$p_1 = - \frac{\partial f}{\partial v_1} = - \frac{\partial f}{\partial v_3}, \quad (\text{equal pressure})$$

$$\frac{\partial f}{\partial v_1} = \frac{\partial f}{\partial v_3} = \frac{f_3 - f_1}{v_3 - v_1}, \quad (\text{common tangent})$$

$$\int_{v_1}^{v_3} p_r dv_r = p_1(v_3 - v_1), \quad (\text{Maxwell construction})$$

or

$$\int_{v_1}^{v_3} [p_r - p_1] dv_r = 0.$$

For local stability at any point the curve $f(T, v)$ must always lie above its tangent, and for global stability this tangent must not cut the primitive $f(T, v)$ curve at any other point. If it does, the substance will split into a mixture of two phases with values of volume v_1, v_2 corresponding to the two points of contact of the tangent. The double-contact tangent corresponds to the co-existence of two phases in equilibrium.

11. Critical behavior of v_1 and v_3 around the critical point

We make a plot of the values of characteristic reduced volumes (v_1, v_{m1}, v_{m3} , and v_3) as a function of t_r for $t_r \leq 1$.

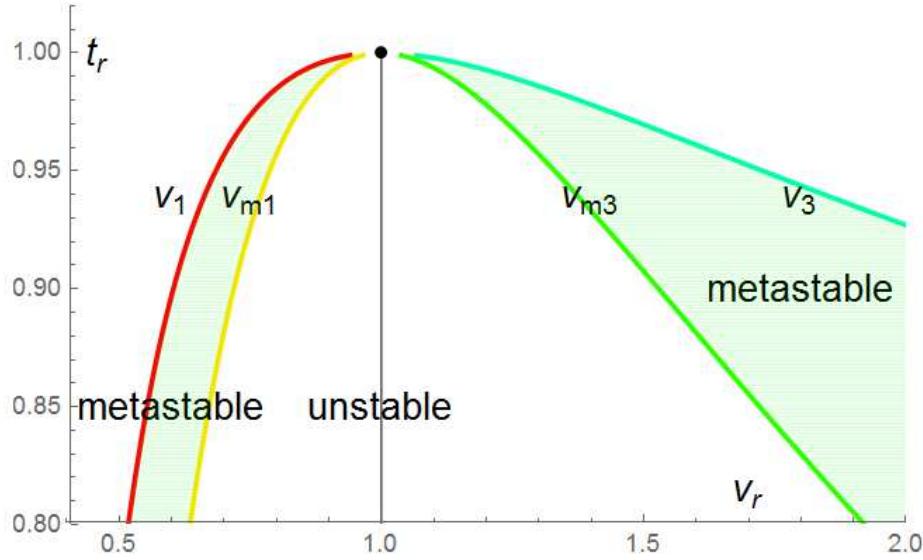


Fig.39 t_r vs v_1 , t_r vs v_{m1} , t_r vs v_{m3} , and t_r vs v_3 with v_1 and v_3 lines (bimodal lines) and v_{m1} and v_{m3} lines (spinodal lines).

12. Lever rule for the reduced volume in the coexistence line

At the point e the substance is entirely in the gas phase with volume v_3 ; at the point a , it is entirely in the liquid phase with volume v_1 . At any point on the line $a-c-e$ (the coexistence line), the reduced volume can be described by

$$v = \theta_1 v_1 + \theta_3 v_3,$$

using the lever rule, where θ_1 is the fraction of the liquid phase and θ_3 is the fraction of the gas phase,

$$\theta_1 + \theta_3 = 1.$$

Then we have

$$\theta_1 = \frac{v_3 - v}{v_3 - v_1},$$

$$\theta_3 = \frac{v - v_1}{v_3 - v_1}.$$

For $v = v_1$, $\theta_1 = 1$ and $\theta_3 = 0$ (the pure liquid phase).

For $v = v_3$, $\theta_1 = 0$ and $\theta_3 = 1$. (the pure gas phase).

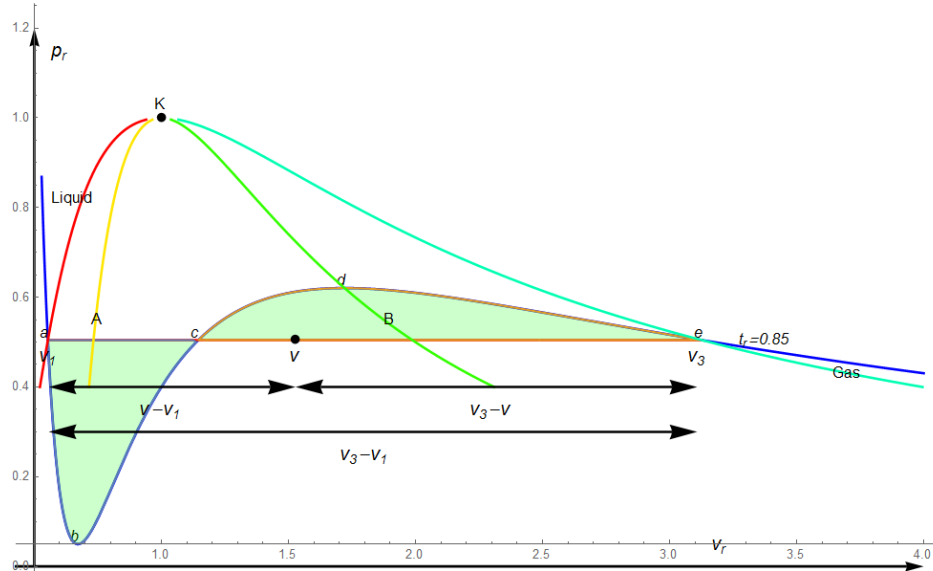


Fig.40 Lever rule ($t_r = 0.85$ in this case). The reduced volume v on the coexistence line between v_1 and v_3 , $v = \theta_1 v_1 + \theta_3 v_3$. θ_1 is the fraction of the liquid phase and θ_3 is the fraction of the gas phase.

13. van der Waals equation with reduced density

(a) Law of the corresponding states

We consider the law of the corresponding states with the reduced density defined by

$$v = \frac{1}{\rho} = \frac{V}{N}.$$

We start with the law of corresponding state,

$$p_r = -\frac{3}{v_r^2} + \frac{8}{3} t_r \frac{1}{v_r - \frac{1}{3}}.$$

We introduce a reduced density variable defined by

$$\rho_r = \frac{1}{v_r}.$$

Then we have

$$p_r = -3\rho_r^2 + \frac{8t_r\rho_r}{3 - \rho_r}.$$

(b) Maxwell construction

On the co-existence curve, we have

$$p_r = p_1 = p_3 \quad \text{at} \quad t_r = t = 1 + \tau,$$

where

$$\rho_1 = \frac{1}{v_1}, \quad \rho_3 = \frac{1}{v_3},$$

with

$$\rho_1 > 1 > \rho_3.$$

From the condition $p_1 = p_1 = p_3$, or,

$$p_r = -3\rho_1^2 + \frac{8t\rho_1}{3 - \rho_1} = -3\rho_3^2 + \frac{8t\rho_3}{3 - \rho_3},$$

we get the expression of t as

$$t = 1 + \tau = \frac{1}{8}(3 - \rho_1)(3 - \rho_3)(\rho_1 + \rho_3).$$

Using this t , we get

$$p_1 = \rho_1\rho_3(3 - \rho_1 - \rho_3).$$

The Maxwell's construction can be expressed by

$$I_1 = I_2,$$

where I_1 and I_2 are the area of the region ($a-b-c-d-e$) and the area of the region ($a-c-e$) of the co-existence line,

$$I_1 = \int_{\rho_3}^{\rho_1} \frac{p_r}{\rho_r^2} d\rho_r = -3(\rho_1 - \rho_3) - \frac{1}{3}(3 - \rho_1)(3 - \rho_3)(\rho_1 + \rho_3) \ln\left[\frac{\rho_3(3 - \rho_1)}{\rho_1(3 - \rho_3)}\right]$$

$$I_2 = p_1 \left(\frac{\rho_1 - \rho_3}{\rho_1 \rho_3} \right) = \rho_1 \rho_3 (3 - \rho_1 - \rho_3) \left(\frac{\rho_1 - \rho_3}{\rho_1 \rho_3} \right) = (3 - \rho_1 - \rho_3)(\rho_1 - \rho_3).$$

Then we have

$$-3(\rho_1 - \rho_3) - \frac{1}{3}(3 - \rho_1)(3 - \rho_3)(\rho_1 + \rho_3) \ln\left[\frac{\rho_3(3 - \rho_1)}{\rho_1(3 - \rho_3)}\right] = (3 - \rho_1 - \rho_3)(\rho_1 - \rho_3)$$

or

$$(6 - \rho_1 - \rho_3)(\rho_1 - \rho_3) - \frac{1}{3}(3 - \rho_1)(3 - \rho_3)(\rho_1 + \rho_3) \ln\left[\frac{\rho_1(3 - \rho_3)}{\rho_3(3 - \rho_1)}\right] = 0$$

Suppose that

$$\rho_1 = 1 + \Delta_1, \quad \rho_3 = 1 - \Delta_3$$

where $0 < \Delta_1 \ll 1$ and $0 < \Delta_3 \ll 1$. We substitute these forms into the Maxwell's construction, and expand each side in powers of Δ_1 and Δ_3 . The coefficients up to the third-order in the left-hand side is zero. The coefficient of the fourth order in the left-hand side is given by

$$-\frac{3}{4}\Delta_1\Delta_3^3 + \frac{3}{4}\Delta_3\Delta_1^3,$$

which is equal to zero. Thus we have

$$\Delta_3 = \Delta_1 = \Delta,$$

leading to the symmetry of the van der Waals coexistence line near the critical point.

(c) **Critical behavior for the difference $(\rho_1 - \rho_3)$ as $t_r \rightarrow 1$ along the coexistence curve.**

$$\begin{aligned}
 1-t &= 1 - \frac{1}{8}(3-\rho_1)(3-\rho_3)(\rho_1+\rho_3) \\
 &= 1 - \frac{1}{8}(2-\Delta_1)(2+\Delta_3)(2+\Delta_1+\Delta_3) \\
 &\approx \frac{1}{4}(\Delta_1^2 + \Delta_3^2 - \Delta_1\Delta_3)
 \end{aligned}$$

We then let $\Delta_1 = \Delta_3 = \Delta$. We get

$$1-t = -\tau \approx \frac{1}{4}\Delta^2$$

or

$$\Delta = 2(-\tau)^{1/2} = 2\varepsilon^{1/2}$$

We define the quantity $(\rho_1 - \rho_3) = \Delta_1 + \Delta_3 = 2\Delta$ as the order parameter of the gas-liquid critical point. The critical exponent is $\beta = \frac{1}{2}$, a manifestation of the mean-field nature of the van der Waals theory.

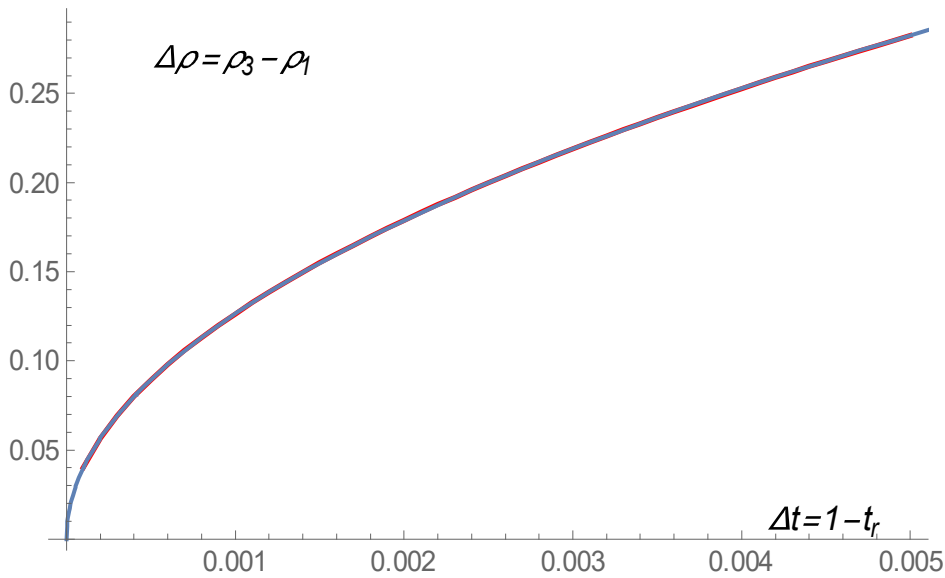


Fig.50 $(\rho_1 - \rho_3) = \Delta_1 + \Delta_3 = 2\Delta$ as a function of $\Delta t = 1 - t_r$.

The result of the least squares fitting:

$$\rho_1 - \rho_3 = \rho_{liquid} - \rho_{gas} = A(-\tau)^\beta = A\varepsilon^\beta,$$

for $t_r = 0.995 - 1$. The least squares fit of the data yields

$$A = 3.983 \text{ and } \beta = 0.4994,$$

which is in good agreement with the mean field exponent ($\beta = 1/2$).

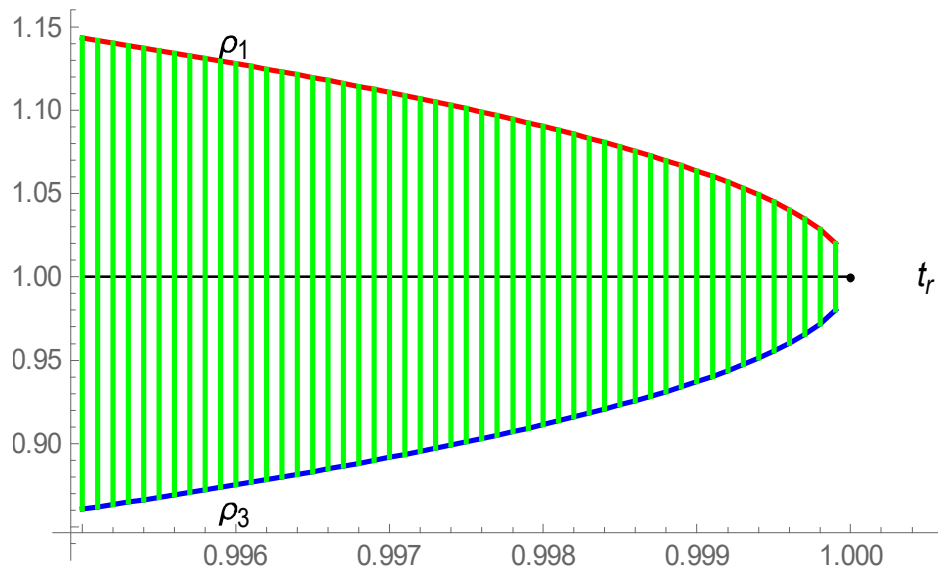


Fig.41 ρ_1 (liquid) vs t_r and ρ_3 (gas) vs t_r for $t_r \leq 1$. The shaded portion represents a coexistence region.

((Mathematica))

```

Clear["Global`*"]; p0 =  $\frac{8 t x}{3 - x} - 3 x^2$ ; p01 = p0 /. x → x1;
p03 = p0 /. x → x3;
seq1 = Solve[p01 == p03, t]

 $\left\{ \left\{ t \rightarrow \frac{1}{8} (-3 + x1) (-3 + x3) (x1 + x3) \right\} \right\}$ 

p011 = p01 /. seq1[[1]] // FullSimplify

 $-x1 x3 (-3 + x1 + x3)$ 

eq1 =
Integrate[ $\frac{p0}{x^2}$ , {x, x3, x1}, GenerateConditions → False] //
Simplify; eq11 = eq1 /. seq1[[1]];

eq2 =  $\left( \frac{p011}{x1 x3} (x1 - x3) \right) - eq11$  // FullSimplify
rule1 = {x1 → 1 + d1, x3 → 1 - d3};
eq3 = eq2 /. rule1 // Series[#, {d1, 0, 3}, {d3, 0, 3}] & //
FullSimplify


$$O[d3]^4 + \left( -\frac{3 d3^3}{4} + O[d3]^4 \right) d1 + \left( \frac{3 d3^3}{8} + O[d3]^4 \right) d1^2 +$$


$$\left( \frac{3 d3}{4} + \frac{3 d3^2}{8} + O[d3]^4 \right) d1^3 + O[d1]^4$$


Coefficient[eq3, {d3^3 d1, d1^3 d3}]

 $\left\{ -\frac{3}{4}, \frac{3}{4} \right\}$ 

```

(d) Phase diagram of p_r vs reduced density

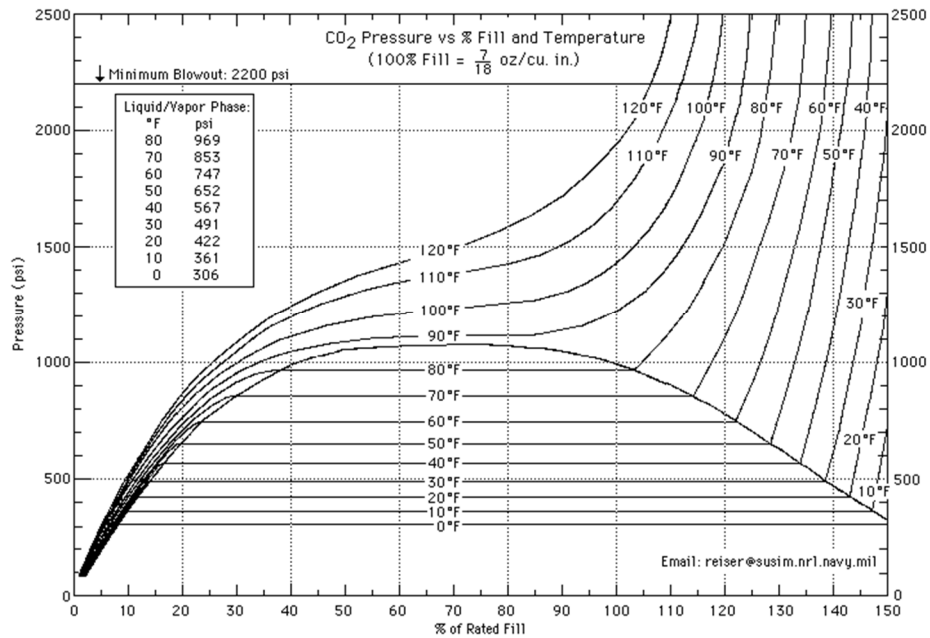


Fig.52

Pressure vs density at fixed temperature for carbon dioxide (CO₂).

<http://www.warpig.com/paintball/technical/gasses/co2pv.gif>

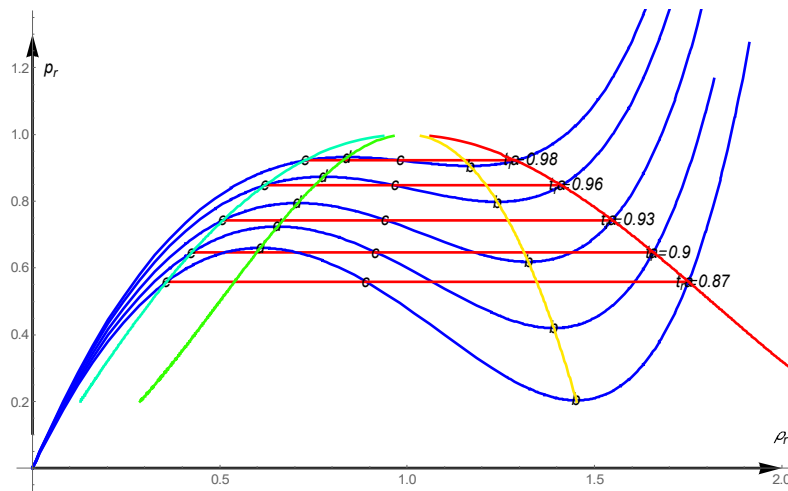


Fig.42

p_r vs $\rho_r = 1/v_r$ phase diagram where t_r is fixed as $t_r = 0.87, 0.90, 0.93, 0.96$, and 0.98 .

In the co-ordinates $(t_r - v_r)$, when there is a critical point, the equilibrium diagram appears as shown in this Fig. As the reduced temperature t_r approaches its critical value $t_r = 1$, the reduced volumes of the liquid phase and gas phase in equilibrium becomes closer, and at the critical point, these phases coincide.

For the liquid-vapor transition, as the critical temperature was approached from below ($T < T_c$), the theory predicted that the order parameter is expressed by

$$\rho_1 - \rho_3 \propto (1 - t_r)^\beta,$$

with $\beta = 1/2$. The average $\frac{1}{2}(\rho_1 + \rho_3)$ is denoted by the blue line (so called the rectilinear diameter: locus of the mid-point). It is seen to trace the straight line.

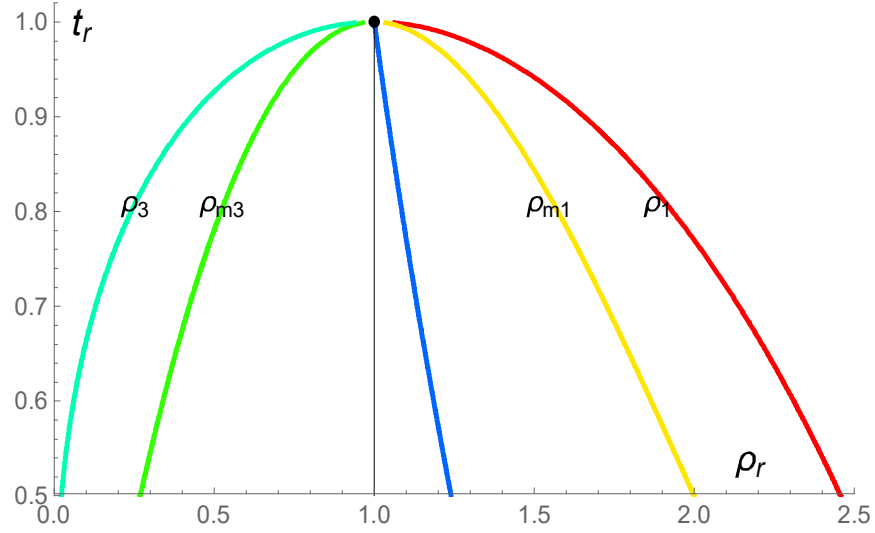


Fig.43

t_r vs ρ_1 , t_r vs ρ_{m1} , t_r vs ρ_{m3} , and t_r vs ρ_3 . The average $(\rho_1 + \rho_3)/2$ is denoted by the blue line (so called the *rectilinear diameter*).

((Note)) Definition. $\rho_3 = \frac{1}{v_3}$. $\rho_{m2} = \frac{1}{v_{m3}}$, $\rho_{m1} = \frac{1}{v_{m1}}$. $\rho_1 = \frac{1}{v_1}$,

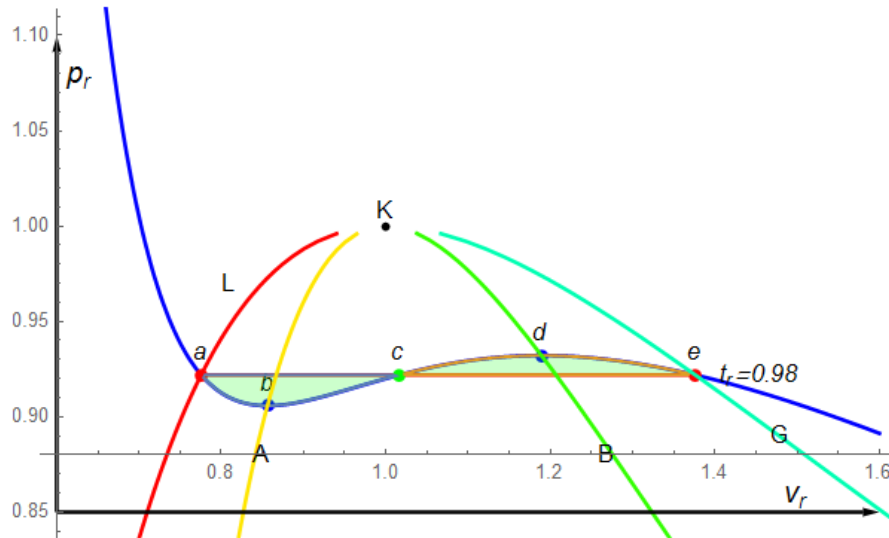
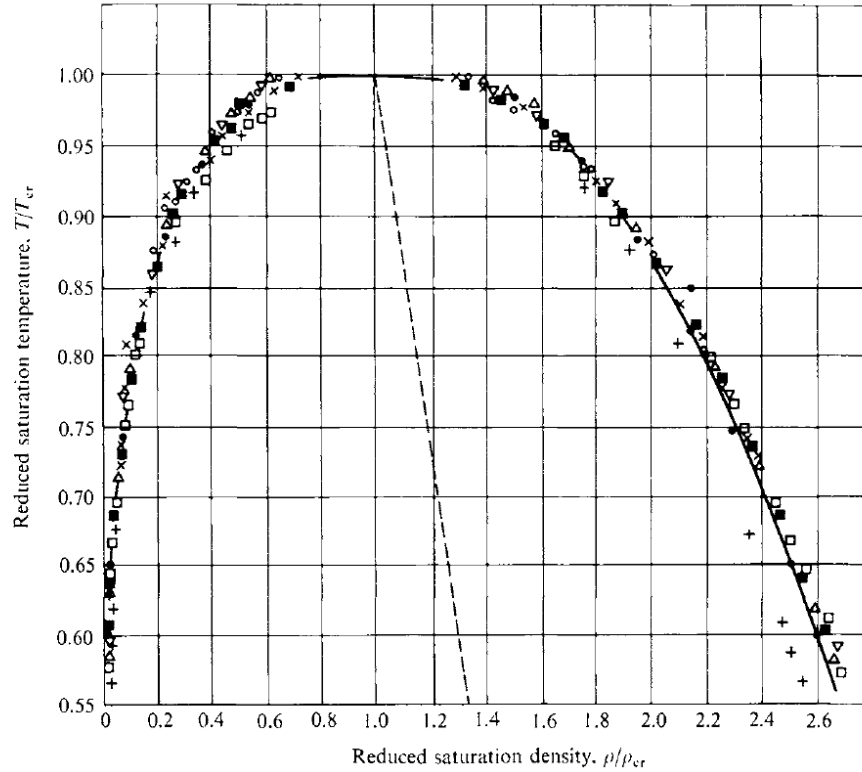


Fig.44

The points $a; (v_1, p_1)$, $b (v_{m1}, p_{m1})$, $c; (v_2, p_1)$, $d (v_{m3}, p_{m3})$, and $e; (v_3, p_1)$, in the p_r - v_r plane. $t_r = 0.98$.

**Fig.45**

Reduced densities of co-existing liquid and gas phases. (E.A. Guggenheim, Thermodynamics). The mean reduced density $(\rho_1 + \rho_3)/2$ is seen to trace the straight line shown in dotted in this diagram.

14. Super-heated state and super-cooled state

Here we show the phase diagram of v_r vs t_r and t_r vs v_r , where t_r is fixed. In the diagram of v_r vs t_r , the vertical line (the path a - c - e) is the coexistence line in thermal equilibrium

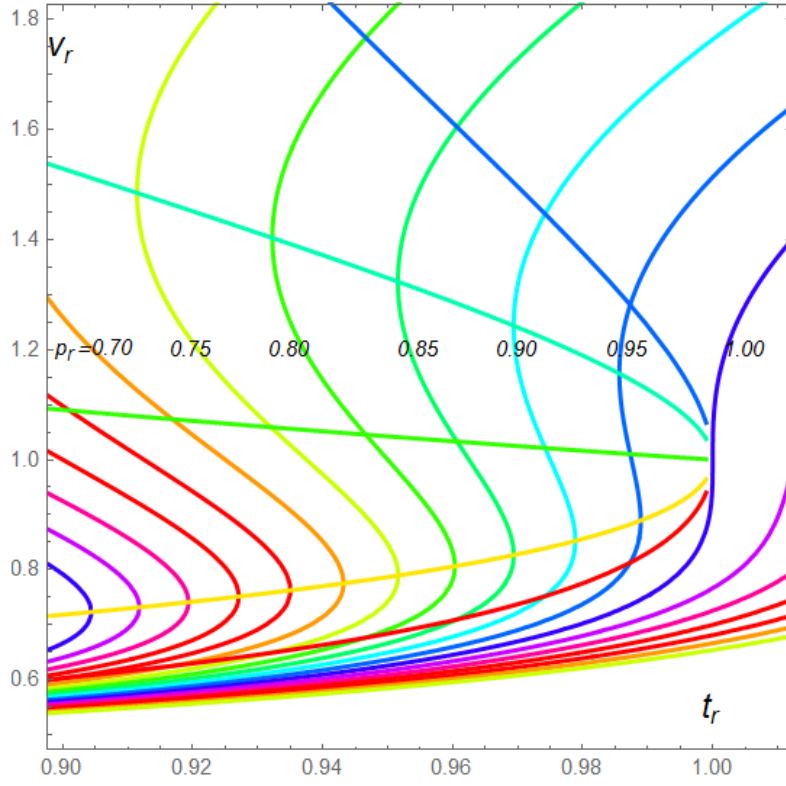


Fig.46

Phase diagram of v_r vs t_r where p_r is changed as a parameter. The bimodal lines are denoted by red and blue lines. The spinodal lines are denoted by yellow and light blue lines.

path Liquid- l - a - b on the rapid increase of temperature. On further heating above the temperature of the state b , there occurs the transition from the state b (metastable state) to the bulk gas phase (the state g).

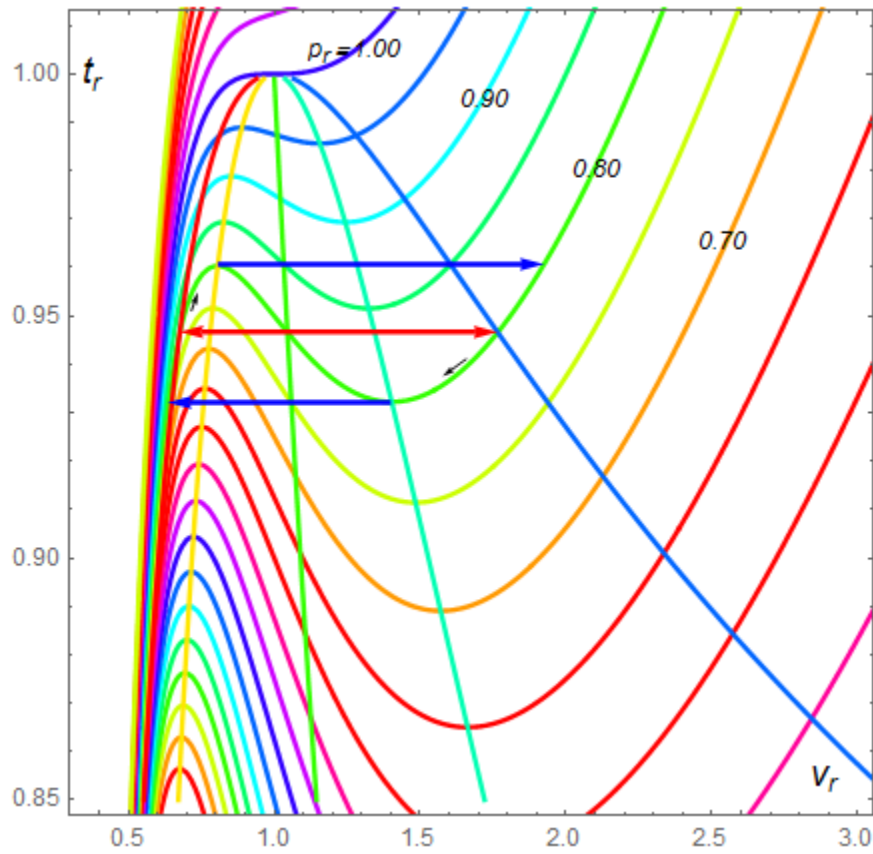


Fig.48 Phase diagram of t_r vs v_r where p_r is changed as a parameter. The super-heated state and the super-cooled state, and the coexistence line are shown for $p_r = 0.80$.

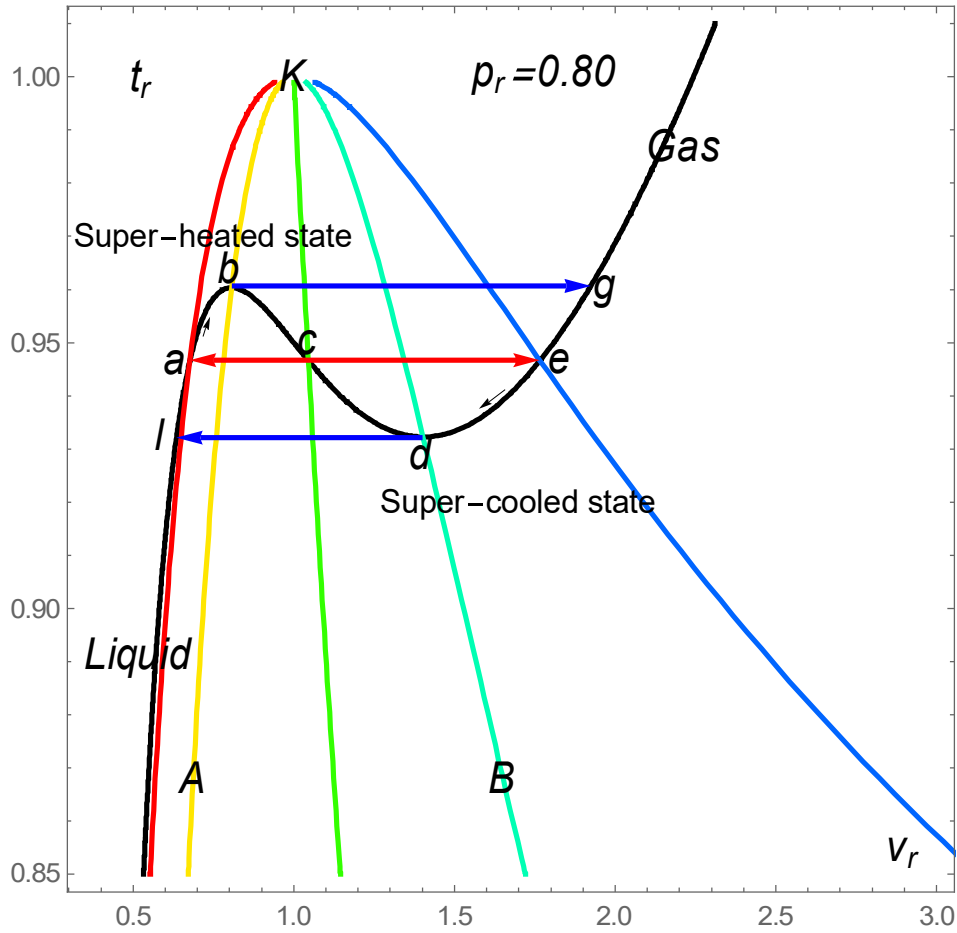


Fig.49 Phase diagram of t_r vs v_r with $p_r = 0.80$. The super-heated state and the super-cooled state, and the coexistence line are shown for $p_r = 0.80$. The binodal lines are denoted by the red line and blue line. The spinodal lines are denoted by yellow (K-A) and light blue lines (K-B). The coexistence line (equilibrium liquid and gas phases) is denoted by the horizontal red line (path $a-c-e$).

((Note)) Dynamics of First order phase transition (by Koch)
nucleation in the metastable state, and spinodal decomposition in the unstable state

The supersaturated vapor of a van der Waals system is a typical example of a metastable state. It may decay because of localized density fluctuations. These fluctuations must have a large amplitude and exceed a certain spatial extension. They are commonly called the critical droplets. The spontaneous formation of critical droplets is a typical example of a hetero-phase fluctuation. Localized liquid regions appear within the supersaturated vapor phase. These hetero-phase fluctuations are the origin of the finite lifetime of metastable states in equilibrium and non-equilibrium systems.

On the other hand, even very small fluctuations are sufficient to initiate the decay of unstable states. A spatially homogeneous system within the spinodal region of its phase diagram decomposes because of infinitesimally small density fluctuations. This is the process of spinodal decomposition. Even though they

may be of infinitesimally small amplitude, these density fluctuations can initiate spinodal decomposition, provided they exceed a critical wavelength. This condition is connected with the increasing surface energy by forming a spatially inhomogeneous distribution. The surface energy has to be compensated by the energy gained by approaching the new equilibrium. The critical wavelength gives rise to the appearance of a characteristic precipitation pattern in the early stages of spinodal decomposition.

15. Clapeyron equation (or Clausius-Clapeyron equation)

We make a plot of the reduced pressure p_1 as a function of reduced temperature t_1 . The values of t_1 and p_1 are listed in the APPENDIX. The critical point is at $t_c = 1$ and $p_c = 1$. The red line denotes the co-existence boundary between the gas phase (lower p_1) and the liquid phase (higher p_1).

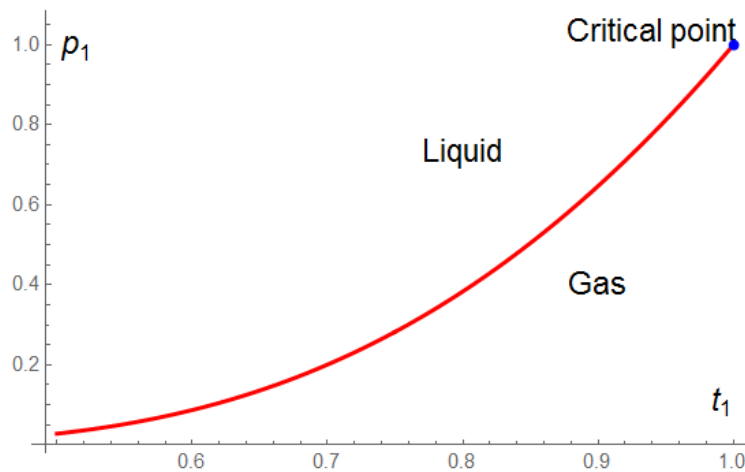


Fig.50 Phase diagram of p_1 vs t_1 , where p_1 for each t_1 is determined from the Maxwell construction. The values of p_1 for each reduced temperature t_1 are listed in the APPENDIX.

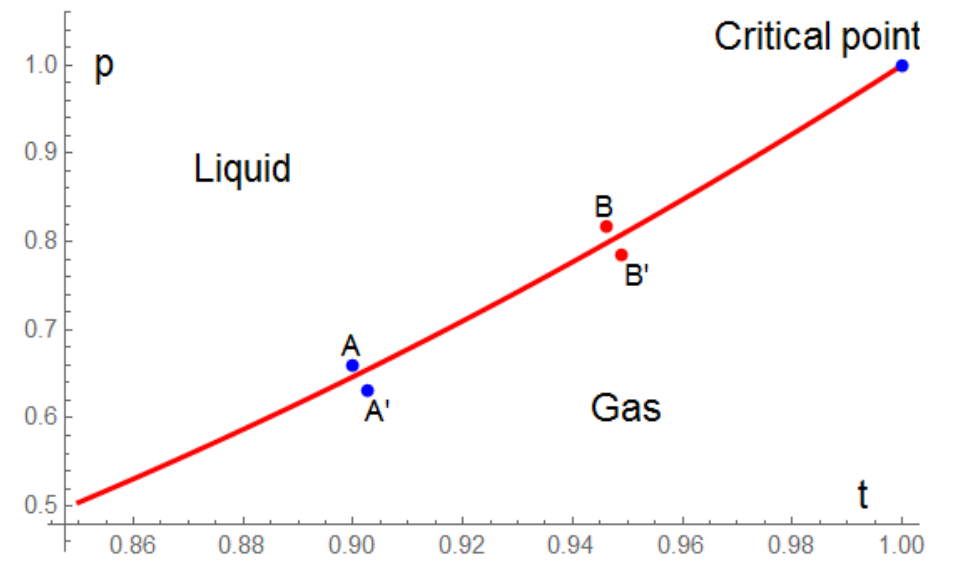


Fig.51 Phase diagram of p_1 vs t_1 . The point A and the point B are in the liquid phase, while the point A' and point B' are in the gas phase. The critical line is denoted by the red line.

Here we discuss the Clapeyron equation (or Clausius-Clapeyron) equation. The change of entropy between the liquid phase and the gas phase can be determined from this equation. To this end, we consider the four states; states A and A' are coincident but corresponds to different phases, and states B and B' are similar.

$$dP = P_B - P_A = P_{B'} - P_{A'}, \quad dT = T_B - T_A = T_{B'} - T_{A'}.$$

The slope of the curve is $\frac{dP}{dT}$. The phase equilibrium requires that

$$G_A = G_{A'}, \quad G_B = G_{B'}.$$

Thus we get

$$G_A - G_B = G_{A'} - G_{B'}.$$

But

$$G_A - G_B = -SdT + VdP,$$

$$G_{A'} - G_{B'} = -S'dT + V'dP.$$

Then we have

$$-SdT + VdP = -S'dT + V'dP,$$

or

$$\frac{dP}{dT} = \frac{S' - S}{V' - V} = \frac{\Delta S}{\Delta V}.$$

The latent heat is given by $L = T\Delta S$. Then we have

$$\frac{dP}{dT} = \frac{L}{T\Delta V}. \quad (\text{Clapeyron equation}).$$

16. The discontinuity of entropy on the coexistence line (the latent heat)

Here we discuss the entropy of the system on the co-existence line between the gas phase and liquid phase in the P - V phase diagram with fixed temperature. The original discussions were given by A.B. Pippard (Elements of Classical Thermodynamics, p.53 Fig.10) and by H.B. Callen (Thermodynamics, p.157, Fig.9.8)

We consider the Carnot cycle, consisting of the two isothermal processes and two adiabatic processes in the P - V phase diagram. W is the total work done on the system during the process. For convenience use W_s instead of W ($= -W_s$). W is the work done on the system, while W_s is the work done by the system.

$$W_s = Q_H - Q_L$$

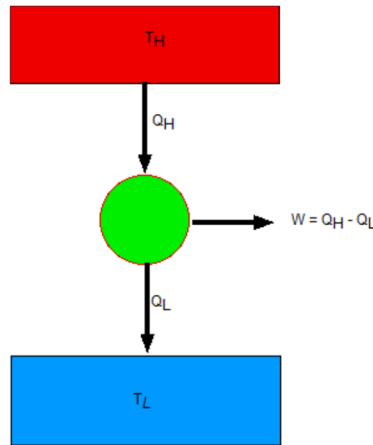


Fig.52 Carnot cycle.

We have the relation

$$\frac{Q_L}{T_L} = \frac{Q_H}{T_H} \quad (\text{Carnot cycle})$$

The efficiency ε_R is defined as

$$\varepsilon_R = \frac{W_s}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

It is dependent only on the temperatures T_H and T_L . The work W_s is equal to the area of the Carnot cycle. Then we have

$$\frac{W_s}{Q_H} = \frac{\delta A}{Q} = \frac{\delta T}{T}$$

where

$$T_H - T_L = \delta T, \quad T_H = T,$$

$$W_s = \delta A, \quad Q_H = Q$$

In the T vs S diagram, the Carnot cycle is formed of the rectangle, consisting of the two isothermal processes and two adiabatic processes;

$$W_s = \delta A = \delta T \delta S, \quad Q_H = T_H \delta S \quad (Q = T \delta S)$$

Then we have

$$\frac{\delta A}{Q} = \frac{\delta T}{T}$$

The entropy is given by

$$\delta S = \frac{\delta A}{\delta T}.$$

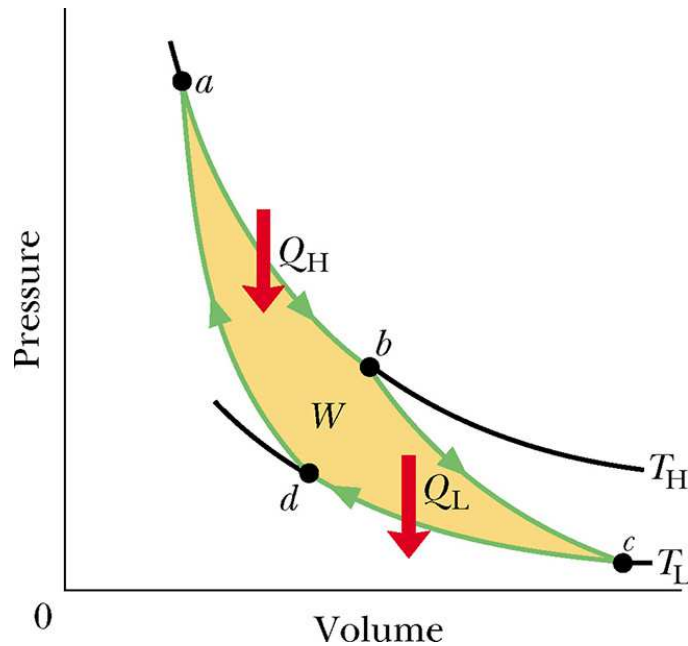


Fig.53 Carnot cycle (P - V phase diagram), which consists of two isothermal processes and two adiabatic processes.

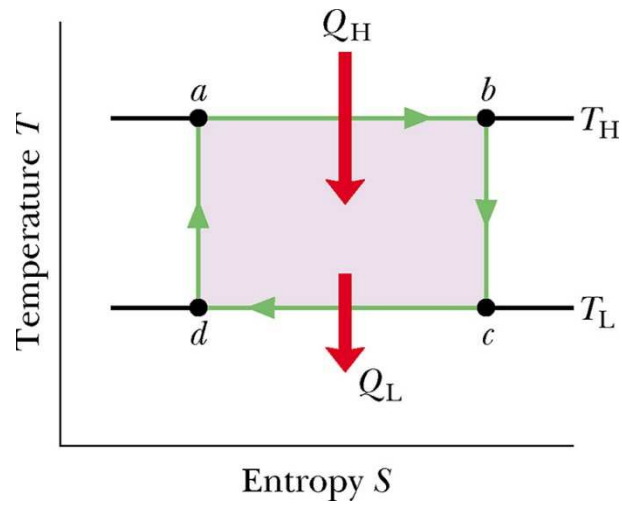
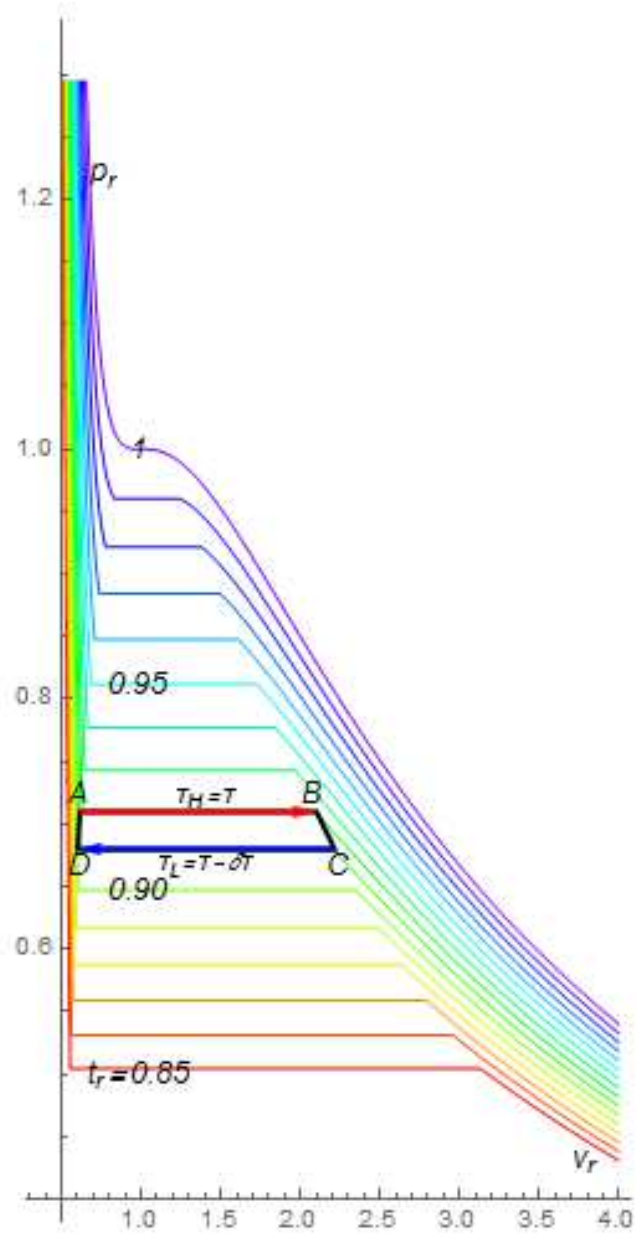


Fig.54 Carnot cycle in the T - S plane, consisting of two isothermal processes and two adiabatic processes.



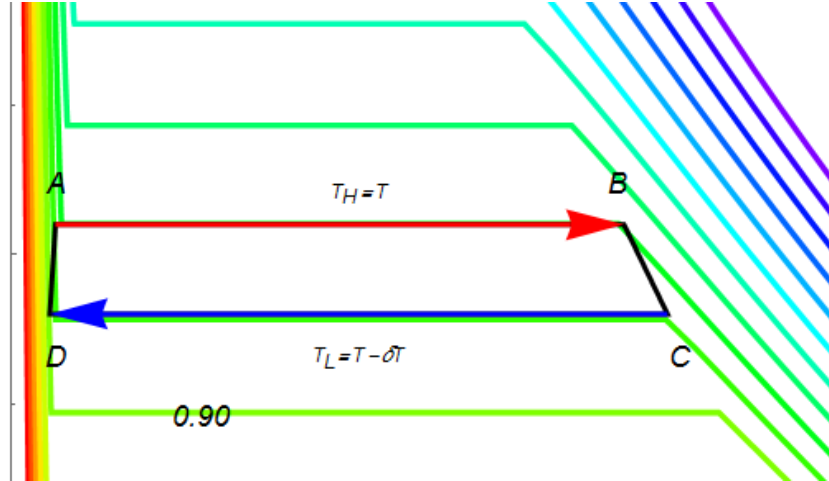


Fig.55 (a) (b) Carnot cycle for the van der Waals gas. The two neighboring isotherms of a liquid-gas co-existence. The path AD and path BC may not be the adiabatic path. This effect can be negligible since the temperature difference is very small.

((A.B. Pippard)) The following discussion is made by Pippard *Elements of Classical Thermodynamics*.

We shall now examine briefly a graphical method which is sometimes used to solve elementary thermodynamic problems. The substance (van der Waals gas) considered is imagined taken around a Carnot cycle between two neighboring temperatures T and $T - \delta T$. If the area of the cycle in the indicator diagram is δA and the heat absorbed at $T_H = T$ along the path $A-B$ (isothermal process) is Q_H , then the heat given out at $T_L = T - \delta T$ along the path $C-D$ (isothermal process) is Q_L . This process is a sort of Carnot cycle.

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}.$$

The work done by the system is

$$W_s = Q_H - Q_L = \delta A$$

which corresponds to the area (δA) enclosed by the closed path (A-B-C-D-A). Then we have

$$\frac{Q}{T} = \frac{Q - \delta A}{T - \delta T}, \quad \text{or} \quad \frac{\delta A}{Q} = \frac{\delta T}{T},$$

where $Q_H = Q$, $Q_L = Q - \delta A$, $T_H = T$, and $T_L = T - \delta T$.

The Carnot cycle consists of two long isotherms AB and CD and two short adiabatic processes $B-C$ and $D-A$. We suppose the variation from A to B to correspond to the evaporation at constant pressure P of unit mass of liquid, necessitating the absorption of heat equal to the latent heat per unit mass l . To find the area of the cycle we note that the length AB is $V_3 - V_1 = V_g - V_l$ the difference in volume between vapor and liquid, while the vertical width of the Carnot cycle is

$$\delta P = \left(\frac{dP}{dT} \right) \delta T ,$$

where P is the equilibrium vapor pressure. Thus we have

$$\delta A = (V_g - V_l) \delta P = (V_g - V_l) \left(\frac{dP}{dT} \right) \delta T .$$

Any difference in slope of AD and BC becomes negligible as $\delta T \rightarrow 0$. Finally we get

$$\delta A = \frac{\delta T}{T} Q = (V_g - V_l) \left(\frac{dP}{dT} \right) \delta T$$

or

$$\frac{dP}{dT} = \frac{Q}{T(V_g - V_l)} \quad (1)$$

which is the Clapeyron equation.

In the phase diagram (T vs S plane), we have

$$Q_H = T_H \Delta S , \quad Q_L = T_L \Delta S \quad (2)$$

where $T_H = T$, $T_L = T - \delta T$, and $Q_H = Q$. The work done by the system is

$$\delta A = W_s = \oint P dV = \oint T dS = \delta T \Delta S$$

since

$$\oint dE = \oint T dS - \oint P dV = 0$$

From Eqs.(1) and (2) we have

$$\Delta S = \frac{Q}{T} = (V_g - V_l) \frac{dP}{dT} = N(v_3 - v_1) \frac{P_c v_c}{T_c} \left(\frac{dp_r}{dt_r} \right)$$

or

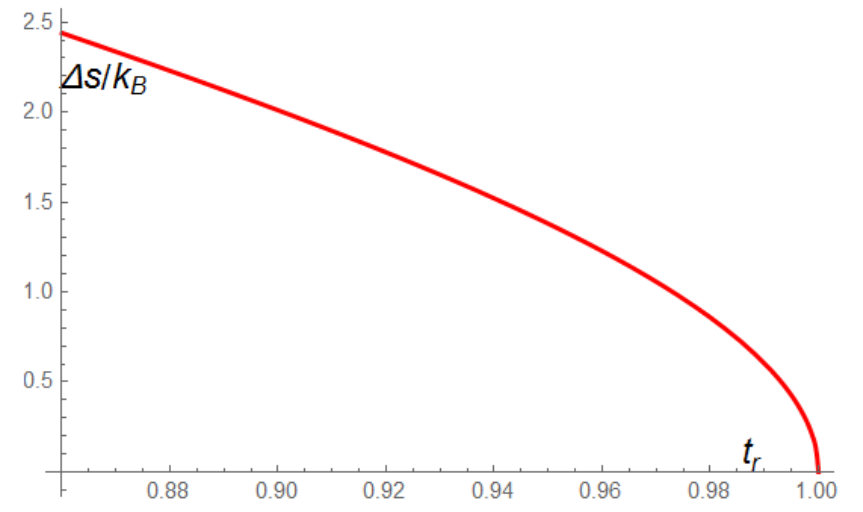
$$\Delta s = \frac{\Delta S}{N} = (v_3 - v_1) \frac{P_c v_c}{T_c} \left(\frac{dp_r}{dt_r} \right) = \frac{3}{8} k_B (v_3 - v_1) \left(\frac{dp_r}{dt_r} \right)$$

We make a plot of $\Delta s / k_B$ as a function of t_r ,

$$\frac{\Delta s}{k_B} = \frac{3}{8} [v_3(t_r) - v_1(t_r)] \frac{dp_r(t_r)}{dt_r}$$

Note that we have the tables for the values of v_1 , v_3 , and p_1 for various t_r below the critical temperatures. We can evaluate the derivative $\frac{dp_r(t_r)}{dt_r}$ using the derivative of the continuous function $p_r(t_r)$ which is constructed by using the interpolation of the pressure $p_r(t_r)$ at the discrete values. Using the Mathematica, we calculate

$$\frac{\Delta s}{k_B} = \frac{3}{8} [v_3 - v_1] \frac{dp_1(t_r)}{dt_r}.$$



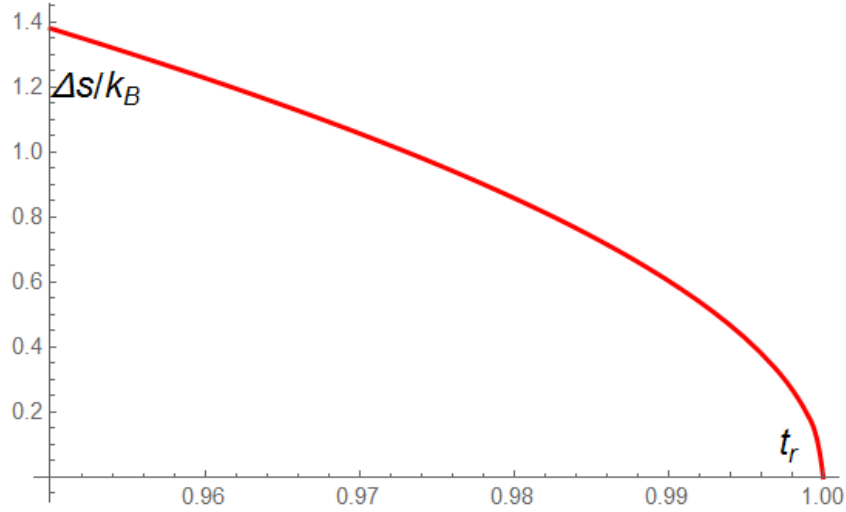


Fig.56 (a), (b) $\frac{\Delta s}{k_B}$ as a function of t_r . The entropy decreases with increasing t_r and reduces to zero at the critical temperature.

As we approach $T \rightarrow T_c$, the discontinuity diminishes and $S_{liquid} \rightarrow S_{gas}$. At the critical point we have a second order phase transition. Above the critical point, there is no sharp distinction between the gas phase and the liquid phase.

Note that $\left(\frac{\partial p_r}{\partial t_r}\right)_v$ is proportional to t_r for $t_r \leq 1$ as shown below in the Mathematica. So the critical

behavior of $\Delta s/k_B$ is the same as that of the difference $(v_3 - v_1)$.

Here we note that

$$\left(\frac{\partial p_r}{\partial t_r}\right)_{v_r} = \frac{8}{3v_r - 1} \approx 4 \quad \text{around } t_r \approx 1.$$

Then we have

$$\frac{\Delta s}{k_B} = \frac{3}{8}[v_3(t_r) - v_1(t_r)] \frac{dp_r(t_r)}{dt_r} \approx \frac{3}{2}[v_3(t_r) - v_1(t_r)] \approx 6\sqrt{-\tau} = 6\varepsilon^{1/2}.$$

In fact the entropy corresponds to the order parameter with the critical exponent ($\beta = 1/2$).

((Callen H.B.)) The following discussion was made by **Callen (Thermodynamics)**.

The change of entropy can be also obtained as follows. From the definition, the change of entropy is given by

$$\Delta S = \int \left(\frac{\partial S}{\partial V} \right)_T dV .$$

Using the Maxwell's relation: $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$, we get

$$\Delta S = \int \left(\frac{\partial P}{\partial T} \right)_V dV \approx \left(\frac{\partial P}{\partial T} \right)_V (V_g - V_l),$$

along the isotherm path (*a-c-b*), which is the same as the result derived by Pippard. The latent heat is

$$\begin{aligned} T\Delta S &= T \left(\frac{\partial P}{\partial T} \right)_V (V_g - V_l) \\ &= P_c t_r \left(\frac{\partial p_r}{\partial t_r} \right)_v N v_c (v_3 - v_1) \\ &= N P_c v_c t_r \left(\frac{\partial p_r}{\partial t_r} \right)_v (v_3 - v_1) \end{aligned}$$

The latent heat is obtained as

$$T\Delta S = P_c v_c t_r \left(\frac{\partial p_r}{\partial t_r} \right)_v (v_3 - v_1) = \frac{3}{8} k_B T_c t_r \left(\frac{\partial p_r}{\partial t_r} \right)_v (v_3 - v_1) .$$

((**Mathematica**))

```

Clear["Global`*"]; p[t_, v_] :=  $\frac{-3}{v^2} + \frac{\frac{8}{3} t}{v - \frac{1}{3}}$ ;

Eq1[t_, v1_, v3_] := p[t, v1] == p[t, v3];
Eq2[t_, v1_, v3_] =
  - $\frac{3}{v1} + \frac{3}{v3} + \frac{8}{3} t$  (-Log[-1 + 3 v1] + Log[-1 + 3 v3]) ==
  p[t, v1] (v3 - v1);
initial[t_ /; t ≤ 1] :=
Module[{v1m, v2m, v3m, v1, v2, v3, v, vi, eq11, eq12,
  eq21, eq22, t1}, t1 = t;
eq11 = D[p[t1, v], v] // Simplify;
eq12 = NSolve[eq11 == 0, v];
v1m = v /. eq12[[1]]; v3m = v /. eq12[[2]];
eq21 = NSolve[p[t1, v] == p[t1,  $\frac{v1m + v3m}{2}$ ], v];
eq22 = Sort[{v /. eq21[[1]], v /. eq21[[2]], v /. eq21[[3]]},
  #1 < #2 &];
vi = {eq22[[1]], eq22[[3]]}]

LG[t_ /; t ≤ 1] := Module[{t1, eq1, v1, v3, v11, v13, p11},
  t1 = t;
  {v11, v13} = initial[t1];
  eq1 = FindRoot[Evaluate[{Eq1[t, v1, v3], Eq2[t, v1, v3]}],
    {v1, v11}, {v3, v13}];
  v11 = v1 /. eq1[[1]];
  v13 = v3 /. eq1[[2]];
  p11 = p[t1, v11];
  {t1, p11, v11, v13}]

```

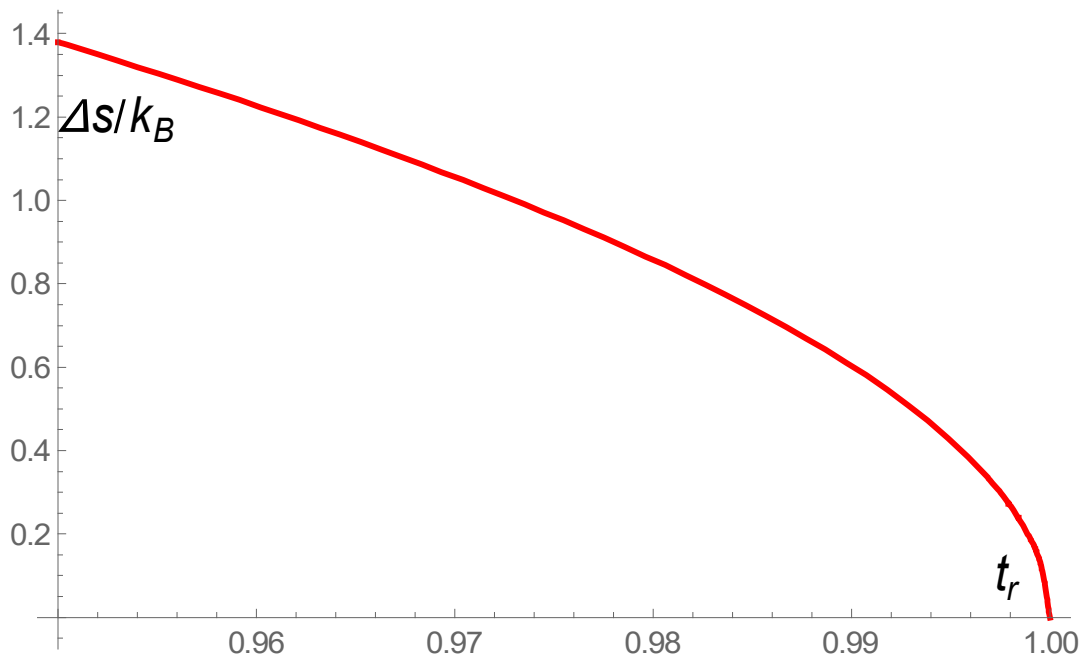
```

h1 = Table[LG[t], {t, 0.85, 1, 0.0005}];
h1 //
TableForm[#, TableHeadings →
  {None, {"tr", "p1", "v1", "v3"}}] &;

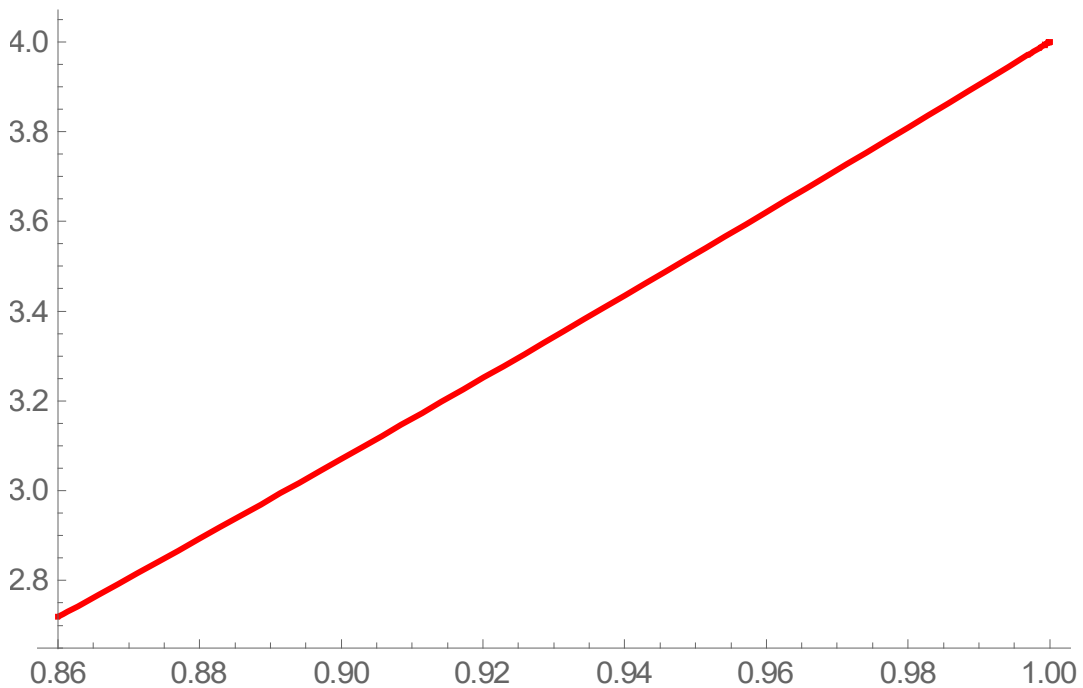
h1 = Table[{LG[t][[1]], LG[t][[2]]}, {t, 0.85, 1, 0.0005}];
g1 = Table[{LG[t][[1]], LG[t][[3]]}, {t, 0.85, 1, 0.0005}];
g2 = Table[{LG[t][[1]], LG[t][[4]]}, {t, 0.85, 1, 0.0005}];
f1 = Interpolation[h1]; f1D = D[f1[x], x];
g11 = Interpolation[g1];
g12 = Interpolation[g2];

k11 = Plot[ $\frac{3}{8}$  f1'[x] (g12[x] - g11[x]), {x, 0.95, 1},
  PlotStyle → {Red, Thick}];
k12 =
Graphics[
  {Text[Style["tr", Black, Italic, 15], {0.998, 0.1}],
   Text[Style["Δs/kB", Black, Italic, 15], {0.953, 1.2}]}];
Show[k11, k12]

```

```
k13 = Plot[ f1 '[x] , {x, 0.86, 1}, PlotStyle -> {Red, Thick}]
```



23. Summary

Since the discovery of the van der Waals equation of state (1873), there have been so many excellent articles on the thermodynamic properties of van der Waals systems. Nevertheless, in our opinion, the essential points of the phase diagram of p_r vs v_r at various temperatures have not been systematically and extensively reported, partly because of restricted spaces in putting results of numerical calculations. It is well known that the van der Waals theory is one of the best examples of the mean field theory. The nature of the attractive interaction between particles changes drastically from short-range order to long range order below the critical temperature. The critical exponents satisfies the relation; $\alpha + 2\beta + \gamma = 2$ predicted from the mean-field theory. The van der Waals systems provides one of typical examples for the phase transition and the critical behavior of the second order phase transition at the critical point as well as the first order phase transition on the coexistence boundary. The coexistence line can be determined from Maxwell construction and the double-tangent construction. Because of the strong-nonlinear nature in the van der Waals equation of state below the critical point, nevertheless, it is sometimes hard for students and even researchers to understand the essential properties of the coexistence line, critical behaviors, and so on.

In spite of very interesting systems for us, our understanding is not sufficient on the nature of the coexistence line, partly because of nonlinearity in the van der Waals equation of state. We do not have a Mathematica program available for the evaluation of Maxwell construction. Recently we have found the Mathematica program (by P. Abbot) for solving the van der Waals equation of state below the critical point, which uses the FindRoot program with appropriate boundary (initial) conditions. Here we have revised the program, which is more convenient to our use, although the essential points are the same. Thanks to this program, it is much easier for one to understand the nonlinear effect of the van der Waals equation of state.

During this work, we also noticed the article of Johnston on the thermodynamic properties of the van der Waals fluids in Los Alamos archive. This article is very useful to our understanding on the physics of van der Waals system. Here we have undertaken systematic numerical calculations on the critical behaviors and phase transitions of the van der Waals system near the critical point. Using the Mathematica, program (which we show), we have no difficulty in evaluating the Maxwell construction based on the Gibbs free energy and the double-tangent construction based on the Helmholtz free energy. So we succeed in getting the visualization of the over-all phase diagram of the van der Waals equation of state. For convenience, here we show our Mathematica programs how to determine the numerical values of v_1 , v_3 , p_1 , and so on for each reduced temperature. We also show the Mathematica programs using the ParametricPlot, Plot3D, and ContourPlot to get the thermodynamic potentials of the Gibbs free energy and Helmholtz. It is our hope that that this article may be useful for students and researchers studying the thermodynamic properties of these systems, although there is nothing new from a view point of research.

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((Nomenclature))

Adiabatic ($\omega = -\pi$)

Adiabatic compressibility

Adiabatic expansion

Binodal line

Bubble point: v_l

Carnot circle

Clapeyron equation (or Clausius-Clapeyron equation)

Coexistence boundary

Coexistence curve

Compressibility

Concave downwards (concave upwards)

Concave bump

Corresponding state

Critical isobar ($\pi = 0$)

Critical isochore ($\omega = 0$)

Critical isotherm ($\tau = 0$)

Critical point

Critical pressure

Critical volume

Cusp

Double-tangent line (Helmholtz free energy)

Double-tangent construction

Entropy

First-order phase transition
 Gibbs free energy
 Helmholtz free energy
 Internal energy
 Isentropic
 Isotherm
 Isothermal compressibility
 Latent heat
 Law of corresponding state
 Legendre transformation
 Lever rule volume, Helmholtz free energy
 Maxwell construction
 Maxwell relation
 Mean-field exponent
 Metastable gas
 Metastable liquid
 Metastable state
 Order parameter
 Primitive curve
 Rectilinear diameter: locus of the mid-point
 Reduced pressure p_r
 Reduced temperature t_r
 Reduced volume v_r
 Saturation point: v_3
 Scaling
 Scaling hypothesis
 Second-order transition
 Specific heat at constant pressure
 Specific heat at constant volume
 Spinodal decomposition
 Spinodal line (AK, BK lines)
 Super-heated liquid
 Super-cooled vapor
 Thermal expansion
 Thermodynamically invisible bow tie (Gibbs free energy)
 Unstable state
 Universality
 van der Waals gas
 van der Waals fluid
 van der Waals system

(a) Scaled van der Waals equation

$$v_r = \frac{v}{v_c} = 1 + \omega, \quad v = \frac{V}{N}, \quad v_c = 3b$$

$$t_r = \frac{T}{T_c} = 1 + \tau, \quad T_c = \frac{8a}{27k_B b}$$

$$p_r = \frac{P}{P_c} = 1 + \pi, \quad P_c = \frac{a}{27b^2}$$

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8}$$

$$\frac{a}{b} = \frac{27}{8} k_B T_c$$

$$p_r = -\frac{3}{v_r^2} + \frac{8t_r}{3v_r - 1}$$

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{P_c v_r} \left(\frac{\partial v_r}{\partial p_r} \right)_T$$

(b) Coexistence line (approximation)

$$v_1 = 1 - 2|\tau|^{1/2} + \frac{18}{5}|\tau| - \frac{147}{25}|\tau|^{3/2} + \dots$$

$$v_3 = 1 + 2|\tau|^{1/2} + \frac{18}{5}|\tau| + \frac{147}{25}|\tau|^{3/2} + \dots$$

$$\frac{1}{2}(v_1 + v_3) = 1 + \frac{18}{5}|\tau| + \dots$$

$$\frac{1}{2}(v_3 - v_1) = 2|\tau|^{1/2} + \frac{147}{25}|\tau|^{3/2} + \dots$$

$$p_1 = 1 - 4|\tau| + \frac{24}{5}|\tau|^2 + \dots$$

(c) Thermodynamic potential

$$U = E$$

$$dE = TdS - PdV + \mu dN$$

$$F = E - ST \quad F = F(V, T, N)$$

$$G = F + PV \quad G = G(P, T, N)$$

$$dF = -PdV - SdT + \mu dN$$

with

$$P = -\left(\frac{\partial F(V, T)}{\partial V}\right)_{T, N}, \quad S = -\left(\frac{\partial F(V, T)}{\partial T}\right)_{V, N}$$

$$dG = -SdT + VdP + \mu dN$$

with

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

APPENDIX-II

Table The co-ordinates of the point a , b , c , d , and e in the p_r - v_r phase diagram for each reduced temperature $t_r = t_1$ (<1). a : (v_1, p_1) , b : (v_{m1}, p_{m1}) , c : (v_2, p_1) , d : (v_{m3}, p_{m3}) , and e : (v_3, p_1) . Note that p_{m1} is negative for $t_1 < 0.843$, due to the intrinsic structure of the van der Waals equation of state.

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.6	0.0868693	0.432609	-2.54746	0.535945	1.59067	0.266736	2.95057	16.7285
0.61	0.0955029	0.435602	-2.4171	0.539881	1.56434	0.277055	2.88557	15.366
0.62	0.104701	0.438683	-2.28923	0.543893	1.53902	0.287635	2.82247	14.1466
0.63	0.11448	0.441859	-2.16379	0.547982	1.51466	0.298483	2.76118	13.0519
0.64	0.124854	0.445133	-2.04074	0.552155	1.49119	0.309604	2.70161	12.0663
0.65	0.135841	0.448511	-1.92005	0.556415	1.46859	0.321005	2.64365	11.1763
0.66	0.147454	0.452	-1.80166	0.560767	1.44679	0.332691	2.58724	10.3705
0.67	0.159708	0.455605	-1.68553	0.565215	1.42577	0.34467	2.5323	9.63903
0.68	0.172618	0.459334	-1.57164	0.569767	1.40549	0.356947	2.47874	8.97341
0.69	0.186197	0.463194	-1.45995	0.574427	1.38591	0.369532	2.4265	8.36625
0.7	0.200458	0.467193	-1.35042	0.579201	1.36699	0.38243	2.37551	7.81114
0.71	0.215416	0.471341	-1.24302	0.584098	1.3487	0.39565	2.32571	7.30248
0.72	0.231083	0.475647	-1.13772	0.589125	1.33102	0.409201	2.27704	6.83537
0.73	0.247471	0.480122	-1.03451	0.594289	1.31392	0.423092	2.22942	6.40554
0.74	0.264592	0.484779	-0.933339	0.5996	1.29736	0.437333	2.18282	6.00921
0.75	0.282459	0.489631	-0.834198	0.605069	1.28133	0.451933	2.13716	5.64305
0.76	0.301082	0.494693	-0.737063	0.610706	1.2658	0.466903	2.0924	5.30412
0.77	0.320473	0.499982	-0.641912	0.616524	1.25075	0.482256	2.04847	4.98979
0.78	0.340643	0.505516	-0.548727	0.622537	1.23616	0.498003	2.00534	4.69775
0.79	0.361603	0.511317	-0.457492	0.62876	1.22201	0.514158	1.96294	4.42593

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.8	0.383362	0.517409	-0.368193	0.63521	1.20827	0.530736	1.92122	4.17246
0.801	0.385582	0.518036	-0.359369	0.635869	1.20692	0.532417	1.91709	4.14805
0.802	0.38781	0.518665	-0.350564	0.63653	1.20558	0.534103	1.91296	4.12382
0.803	0.390047	0.519298	-0.341778	0.637193	1.20423	0.535794	1.90883	4.09974
0.804	0.392291	0.519934	-0.333012	0.637859	1.20289	0.537489	1.90471	4.07583
0.805	0.394544	0.520573	-0.324265	0.638527	1.20156	0.539188	1.9006	4.05208
0.806	0.396805	0.521216	-0.315537	0.639198	1.20023	0.540892	1.8965	4.02849
0.807	0.399074	0.521862	-0.306828	0.639872	1.1989	0.5426	1.8924	4.00505
0.808	0.401351	0.522511	-0.298138	0.640548	1.19758	0.544312	1.8883	3.98178
0.809	0.403637	0.523164	-0.289468	0.641227	1.19626	0.54603	1.88421	3.95865

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.81	0.40593	0.52382	-0.280816	0.641908	1.19494	0.547751	1.88013	3.93568
0.811	0.408232	0.52448	-0.272184	0.642593	1.19363	0.549478	1.87606	3.91286
0.812	0.410542	0.525143	-0.263571	0.64328	1.19232	0.551208	1.87199	3.8902
0.813	0.41286	0.52581	-0.254976	0.643969	1.19102	0.552944	1.86792	3.86768
0.814	0.415187	0.52648	-0.246401	0.644662	1.18972	0.554684	1.86386	3.84531
0.815	0.417521	0.527154	-0.237846	0.645357	1.18842	0.556429	1.85981	3.82308
0.816	0.419864	0.527832	-0.229309	0.646055	1.18713	0.558178	1.85576	3.801
0.817	0.422215	0.528514	-0.220791	0.646756	1.18584	0.559932	1.85171	3.77907
0.818	0.424575	0.529199	-0.212292	0.64746	1.18455	0.56169	1.84768	3.75727
0.819	0.426942	0.529888	-0.203813	0.648167	1.18327	0.563454	1.84364	3.73562

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.82	0.429318	0.530581	-0.195352	0.648876	1.18199	0.565222	1.83962	3.7141
0.821	0.431703	0.531277	-0.186911	0.649589	1.18072	0.566994	1.83559	3.69273
0.822	0.434095	0.531978	-0.178488	0.650305	1.17945	0.568772	1.83158	3.67149
0.823	0.436496	0.532682	-0.170085	0.651023	1.17818	0.570554	1.82757	3.65039
0.824	0.438905	0.533391	-0.1617	0.651745	1.17692	0.572341	1.82356	3.62942
0.825	0.441323	0.534104	-0.153335	0.65247	1.17566	0.574133	1.81956	3.60859
0.826	0.443748	0.53482	-0.144989	0.653197	1.1744	0.57593	1.81556	3.58788
0.827	0.446183	0.535541	-0.136661	0.653928	1.17315	0.577731	1.81157	3.56731
0.828	0.448625	0.536266	-0.128353	0.654662	1.1719	0.579538	1.80758	3.54687
0.829	0.451076	0.536995	-0.120063	0.6554	1.17066	0.581349	1.8036	3.52656

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.83	0.453535	0.537728	-0.111793	0.65614	1.16941	0.583165	1.79962	3.50637
0.831	0.456003	0.538466	-0.103542	0.656884	1.16818	0.584986	1.79564	3.48631
0.832	0.458479	0.539208	-0.0953093	0.657631	1.16694	0.586812	1.79168	3.46638
0.833	0.460963	0.539954	-0.0870959	0.658381	1.16571	0.588643	1.78771	3.44656
0.834	0.463456	0.540705	-0.0789015	0.659135	1.16448	0.590479	1.78375	3.42687
0.835	0.465957	0.54146	-0.070726	0.659892	1.16326	0.59232	1.77979	3.40731
0.836	0.468467	0.542219	-0.0625695	0.660653	1.16204	0.594166	1.77584	3.38786
0.837	0.470985	0.542984	-0.054432	0.661417	1.16082	0.596018	1.7719	3.36853
0.838	0.473512	0.543753	-0.0463135	0.662184	1.15961	0.597874	1.76795	3.34932
0.839	0.476047	0.544526	-0.0382139	0.662955	1.1584	0.599735	1.76401	3.33023

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.84	0.47859	0.545305	-0.0301333	0.66373	1.15719	0.601602	1.76008	3.31125
0.841	0.481142	0.546088	-0.0220717	0.664508	1.15599	0.603473	1.75615	3.29239
0.842	0.483702	0.546876	-0.014029	0.66529	1.15479	0.60535	1.75222	3.27365
0.843	0.486271	0.547669	-0.00600533	0.666075	1.15359	0.607232	1.7483	3.25501
0.844	0.488849	0.548466	0.00199941	0.666864	1.1524	0.609119	1.74438	3.23649
0.845	0.491434	0.549269	0.00998519	0.667657	1.15121	0.611012	1.74046	3.21808
0.846	0.494029	0.550077	0.017952	0.668454	1.15002	0.61291	1.73655	3.19977
0.847	0.496632	0.55089	0.0258999	0.669255	1.14884	0.614813	1.73264	3.18158
0.848	0.499243	0.551708	0.0338287	0.670059	1.14766	0.616721	1.72873	3.16349
0.849	0.501863	0.552532	0.0417387	0.670867	1.14648	0.618635	1.72483	3.14551

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.85	0.504492	0.55336	0.0496296	0.67168	1.14531	0.620554	1.72093	3.12764
0.851	0.507129	0.554195	0.0575016	0.672496	1.14413	0.622478	1.71704	3.10987
0.852	0.509774	0.555034	0.0653546	0.673317	1.14297	0.624408	1.71315	3.09221
0.853	0.512429	0.555879	0.0731886	0.674141	1.1418	0.626344	1.70926	3.07464
0.854	0.515091	0.55673	0.0810037	0.67497	1.14064	0.628284	1.70537	3.05718
0.855	0.517763	0.557586	0.0887998	0.675803	1.13949	0.630231	1.70149	3.03982
0.856	0.520443	0.558448	0.0965769	0.67664	1.13833	0.632183	1.69761	3.02256
0.857	0.523131	0.559316	0.104335	0.677481	1.13718	0.63414	1.69373	3.0054
0.858	0.525829	0.56019	0.112074	0.678327	1.13603	0.636103	1.68986	2.98834
0.859	0.528534	0.561069	0.119794	0.679177	1.13489	0.638072	1.68599	2.97137

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.86	0.531249	0.561955	0.127495	0.680031	1.13375	0.640046	1.68212	2.9545
0.861	0.533972	0.562847	0.135177	0.68089	1.13261	0.642026	1.67825	2.93773
0.862	0.536704	0.563744	0.142841	0.681754	1.13147	0.644012	1.67439	2.92105
0.863	0.539444	0.564648	0.150485	0.682622	1.13034	0.646003	1.67053	2.90446
0.864	0.542193	0.565559	0.15811	0.683495	1.12921	0.648	1.66667	2.88797
0.865	0.544951	0.566476	0.165716	0.684373	1.12809	0.650003	1.66281	2.87157
0.866	0.547717	0.567399	0.173303	0.685255	1.12696	0.652012	1.65895	2.85526
0.867	0.550493	0.568329	0.180871	0.686142	1.12584	0.654026	1.6551	2.83904
0.868	0.553276	0.569265	0.188419	0.687034	1.12473	0.656047	1.65125	2.82291
0.869	0.556069	0.570209	0.195949	0.687931	1.12361	0.658073	1.6474	2.80686

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.87	0.55887	0.571159	0.20346	0.688833	1.1225	0.660105	1.64356	2.79091
0.871	0.56168	0.572116	0.210952	0.68974	1.12139	0.662144	1.63971	2.77504
0.872	0.564499	0.57308	0.218424	0.690653	1.12029	0.664188	1.63587	2.75925
0.873	0.567326	0.574052	0.225877	0.69157	1.11919	0.666238	1.63202	2.74355
0.874	0.570162	0.57503	0.233312	0.692493	1.11809	0.668295	1.62818	2.72794
0.875	0.573007	0.576016	0.240727	0.693421	1.11699	0.670357	1.62434	2.71241
0.876	0.575861	0.577009	0.248123	0.694355	1.1159	0.672426	1.62051	2.69696
0.877	0.578723	0.57801	0.2555	0.695294	1.11481	0.6745	1.61667	2.68159
0.878	0.581595	0.579019	0.262858	0.696238	1.11372	0.676582	1.61283	2.66631
0.879	0.584475	0.580035	0.270196	0.697188	1.11264	0.678669	1.609	2.6511

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.88	0.587363	0.581059	0.277515	0.698144	1.11156	0.680762	1.60517	2.63597
0.881	0.590261	0.582092	0.284816	0.699106	1.11048	0.682862	1.60133	2.62092
0.882	0.593168	0.583132	0.292096	0.700074	1.1094	0.684968	1.5975	2.60595
0.883	0.596083	0.584181	0.299358	0.701047	1.10833	0.687081	1.59367	2.59106
0.884	0.599007	0.585238	0.3066	0.702027	1.10726	0.6892	1.58984	2.57624
0.885	0.60194	0.586303	0.313824	0.703012	1.10619	0.691326	1.58601	2.56149
0.886	0.604881	0.587377	0.321027	0.704004	1.10513	0.693458	1.58218	2.54683
0.887	0.607832	0.58846	0.328212	0.705003	1.10407	0.695596	1.57834	2.53223
0.888	0.610791	0.589552	0.335377	0.706007	1.10301	0.697742	1.57451	2.51771
0.889	0.61376	0.590653	0.342523	0.707018	1.10196	0.699893	1.57068	2.50326

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.89	0.616737	0.591763	0.349649	0.708036	1.1009	0.702052	1.56685	2.48888
0.891	0.619723	0.592882	0.356756	0.70906	1.09985	0.704217	1.56302	2.47457
0.892	0.622718	0.594011	0.363844	0.710091	1.09881	0.706389	1.55919	2.46033
0.893	0.625722	0.595149	0.370912	0.711129	1.09776	0.708568	1.55536	2.44616
0.894	0.628735	0.596297	0.377961	0.712174	1.09672	0.710753	1.55152	2.43206
0.895	0.631756	0.597456	0.38499	0.713226	1.09568	0.712946	1.54769	2.41803
0.896	0.634787	0.598624	0.392	0.714286	1.09464	0.715145	1.54386	2.40406
0.897	0.637826	0.599802	0.39899	0.715352	1.09361	0.717352	1.54002	2.39016
0.898	0.640875	0.600992	0.405961	0.716426	1.09258	0.719565	1.53618	2.37632
0.899	0.643932	0.602191	0.412912	0.717508	1.09155	0.721786	1.53234	2.36255

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.9	0.646998	0.603402	0.419843	0.718597	1.09053	0.724013	1.5285	2.34884
0.901	0.650074	0.604624	0.426755	0.719694	1.0895	0.726248	1.52466	2.3352
0.902	0.653158	0.605856	0.433647	0.720799	1.08848	0.72849	1.52082	2.32161
0.903	0.656251	0.607101	0.44052	0.721912	1.08747	0.730739	1.51697	2.30809
0.904	0.659353	0.608356	0.447373	0.723033	1.08645	0.732996	1.51313	2.29463
0.905	0.662464	0.609624	0.454206	0.724163	1.08544	0.73526	1.50928	2.28123
0.906	0.665584	0.610904	0.461019	0.725301	1.08443	0.737531	1.50543	2.26789
0.907	0.668714	0.612196	0.467812	0.726448	1.08342	0.73981	1.50157	2.25461
0.908	0.671852	0.613501	0.474586	0.727603	1.08242	0.742097	1.49771	2.24138
0.909	0.674999	0.614818	0.481339	0.728767	1.08142	0.744391	1.49385	2.22821

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.91	0.678155	0.616148	0.488073	0.729941	1.08042	0.746692	1.48999	2.2151
0.911	0.68132	0.617492	0.494787	0.731124	1.07942	0.749002	1.48612	2.20205
0.912	0.684495	0.618849	0.50148	0.732316	1.07843	0.751319	1.48225	2.18904
0.913	0.687678	0.620219	0.508154	0.733517	1.07744	0.753644	1.47838	2.17609
0.914	0.69087	0.621604	0.514808	0.734729	1.07645	0.755976	1.4745	2.1632
0.915	0.694072	0.623003	0.521441	0.73595	1.07546	0.758317	1.47062	2.15036
0.916	0.697282	0.624417	0.528054	0.737182	1.07448	0.760666	1.46673	2.13756
0.917	0.700502	0.625846	0.534647	0.738423	1.0735	0.763023	1.46284	2.12482
0.918	0.70373	0.62729	0.54122	0.739676	1.07252	0.765388	1.45895	2.11213
0.919	0.706968	0.628749	0.547772	0.740939	1.07154	0.767761	1.45505	2.09949

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.92	0.710215	0.630225	0.554305	0.742213	1.07057	0.770143	1.45114	2.0869
0.921	0.71347	0.631716	0.560816	0.743498	1.0696	0.772532	1.44723	2.07435
0.922	0.716735	0.633224	0.567307	0.744795	1.06863	0.774931	1.44331	2.06185
0.923	0.72001	0.634749	0.573778	0.746103	1.06766	0.777337	1.43939	2.0494
0.924	0.723293	0.636292	0.580228	0.747423	1.0667	0.779752	1.43546	2.03699
0.925	0.726585	0.637852	0.586658	0.748755	1.06574	0.782176	1.43153	2.02462
0.926	0.729887	0.63943	0.593067	0.7501	1.06478	0.784609	1.42759	2.0123
0.927	0.733197	0.641027	0.599455	0.751457	1.06382	0.78705	1.42364	2.00002
0.928	0.736517	0.642642	0.605822	0.752828	1.06287	0.789501	1.41968	1.98778
0.929	0.739846	0.644277	0.612168	0.754211	1.06192	0.79196	1.41572	1.97559

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.93	0.743184	0.645932	0.618494	0.755608	1.06097	0.794428	1.41174	1.96343
0.931	0.746531	0.647608	0.624798	0.757019	1.06002	0.796905	1.40776	1.95131
0.932	0.749887	0.649304	0.631082	0.758444	1.05908	0.799392	1.40378	1.93923
0.933	0.753253	0.651021	0.637344	0.759883	1.05813	0.801888	1.39978	1.92719
0.934	0.756628	0.652761	0.643585	0.761338	1.05719	0.804393	1.39577	1.91518
0.935	0.760012	0.654523	0.649805	0.762807	1.05626	0.806908	1.39175	1.90321
0.936	0.763405	0.656308	0.656003	0.764292	1.05532	0.809432	1.38773	1.89127
0.937	0.766807	0.658117	0.662181	0.765793	1.05439	0.811966	1.38369	1.87936
0.938	0.770219	0.65995	0.668336	0.76731	1.05346	0.81451	1.37964	1.86749
0.939	0.77364	0.661808	0.67447	0.768845	1.05253	0.817063	1.37558	1.85564

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.94	0.77707	0.663692	0.680582	0.770396	1.0516	0.819627	1.37151	1.84383
0.941	0.780509	0.665602	0.686673	0.771965	1.05068	0.8222	1.36743	1.83205
0.942	0.783958	0.66754	0.692741	0.773552	1.04976	0.824784	1.36333	1.82029
0.943	0.787415	0.669505	0.698788	0.775158	1.04884	0.827379	1.35922	1.80856
0.944	0.790882	0.6715	0.704812	0.776783	1.04792	0.829983	1.3551	1.79685
0.945	0.794359	0.673524	0.710815	0.778427	1.04701	0.832598	1.35096	1.78517
0.946	0.797844	0.675578	0.716795	0.780092	1.0461	0.835224	1.34681	1.77351
0.947	0.801339	0.677664	0.722752	0.781778	1.04519	0.837861	1.34264	1.76187
0.948	0.804843	0.679783	0.728688	0.783486	1.04428	0.840508	1.33846	1.75025
0.949	0.808357	0.681935	0.7346	0.785215	1.04338	0.843167	1.33425	1.73865

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.95	0.811879	0.684122	0.74049	0.786967	1.04247	0.845837	1.33004	1.72707
0.951	0.815411	0.686345	0.746357	0.788743	1.04157	0.848518	1.3258	1.7155
0.952	0.818953	0.688605	0.752201	0.790543	1.04067	0.851211	1.32154	1.70395
0.953	0.822503	0.690903	0.758022	0.792369	1.03978	0.853915	1.31727	1.69241
0.954	0.826063	0.693241	0.76382	0.79422	1.03888	0.856631	1.31297	1.68088
0.955	0.829632	0.69562	0.769594	0.796098	1.03799	0.859359	1.30865	1.66936
0.956	0.833211	0.698042	0.775344	0.798004	1.0371	0.8621	1.30431	1.65784
0.957	0.836799	0.700508	0.781071	0.799939	1.03621	0.864852	1.29994	1.64633
0.958	0.840396	0.70302	0.786774	0.801904	1.03533	0.867617	1.29555	1.63482
0.959	0.844003	0.70558	0.792453	0.803899	1.03444	0.870395	1.29114	1.62332

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.96	0.847619	0.708189	0.798108	0.805927	1.03356	0.873186	1.28669	1.61181
0.961	0.851244	0.710851	0.803739	0.807988	1.03268	0.875989	1.28222	1.60029
0.962	0.854879	0.713566	0.809344	0.810084	1.03181	0.878806	1.27772	1.58878
0.963	0.858523	0.716338	0.814925	0.812217	1.03093	0.881637	1.27319	1.57725
0.964	0.862176	0.719169	0.820481	0.814387	1.03006	0.884481	1.26862	1.56571
0.965	0.865839	0.722061	0.826012	0.816596	1.02919	0.887339	1.26402	1.55415
0.966	0.869511	0.725018	0.831517	0.818847	1.02832	0.890211	1.25939	1.54258
0.967	0.873193	0.728042	0.836997	0.821141	1.02746	0.893098	1.25471	1.53098
0.968	0.876884	0.731138	0.842451	0.823479	1.02659	0.896	1.25	1.51936
0.969	0.880584	0.734308	0.847878	0.825866	1.02573	0.898917	1.24524	1.50771

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.97	0.884294	0.737556	0.853279	0.828302	1.02487	0.901849	1.24044	1.49603
0.971	0.888014	0.740887	0.858653	0.83079	1.02401	0.904796	1.23559	1.48431
0.972	0.891742	0.744306	0.864	0.833333	1.02316	0.90776	1.23069	1.47254
0.973	0.89548	0.747817	0.86932	0.835935	1.0223	0.91074	1.22574	1.46073
0.974	0.899228	0.751427	0.874611	0.838598	1.02145	0.913736	1.22073	1.44886
0.975	0.902985	0.755141	0.879875	0.841327	1.0206	0.91675	1.21566	1.43693
0.976	0.906752	0.758965	0.88511	0.844125	1.01975	0.919781	1.21053	1.42493
0.977	0.910528	0.762909	0.890316	0.846997	1.01891	0.92283	1.20533	1.41286
0.978	0.914313	0.766979	0.895493	0.849948	1.01806	0.925897	1.20005	1.40071
0.979	0.918108	0.771185	0.90064	0.852983	1.01722	0.928984	1.19469	1.38846

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.98	0.921912	0.775539	0.905756	0.856109	1.01638	0.932089	1.18925	1.3761
0.981	0.925726	0.78005	0.910841	0.859333	1.01554	0.935215	1.18371	1.36363
0.982	0.92955	0.784734	0.915895	0.862663	1.01471	0.938361	1.17808	1.35103
0.983	0.933383	0.789606	0.920917	0.866108	1.01387	0.941529	1.17233	1.33828
0.984	0.937225	0.794682	0.925905	0.869679	1.01304	0.944718	1.16646	1.32536
0.985	0.941077	0.799984	0.93086	0.873387	1.01221	0.947931	1.16046	1.31226
0.986	0.944938	0.805536	0.935781	0.877248	1.01139	0.951167	1.15431	1.29896
0.987	0.948809	0.811367	0.940665	0.881278	1.01056	0.954427	1.14799	1.28541
0.988	0.95269	0.817511	0.945514	0.885498	1.00974	0.957714	1.1415	1.27159
0.989	0.95658	0.824009	0.950324	0.889931	1.00891	0.961027	1.13479	1.25746

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.99	0.960479	0.830914	0.955095	0.894609	1.00809	0.964369	1.12784	1.24295
0.991	0.964388	0.83829	0.959826	0.899571	1.00728	0.967741	1.12061	1.22802
0.992	0.968307	0.846223	0.964513	0.904864	1.00646	0.971144	1.11306	1.21257
0.993	0.972235	0.854822	0.969156	0.910555	1.00565	0.974581	1.10511	1.19649
0.994	0.976173	0.864242	0.973752	0.916735	1.00483	0.978055	1.09668	1.17962
0.995	0.98012	0.874706	0.978297	0.923531	1.00402	0.981569	1.08764	1.16176
0.996	0.984077	0.886555	0.982787	0.931145	1.00321	0.985128	1.07778	1.14254
0.997	0.988043	0.900365	0.987216	0.939911	1.00241	0.988736	1.06678	1.1214
0.998	0.992019	0.917266	0.991576	0.950485	1.0016	0.992403	1.05397	1.09721
0.999	0.996005	0.940177	0.995851	0.964562	1.0008	0.996143	1.03766	1.06704

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.999	0.996005	0.940177	0.995851	0.964562	1.0008	0.996143	1.03766	1.06704
0.9991	0.996404	0.943088	0.996273	0.966329	1.00072	0.996523	1.03567	1.06341
0.9992	0.996803	0.946184	0.996694	0.968204	1.00064	0.996903	1.03358	1.05959
0.9993	0.997202	0.9495	0.997113	0.970207	1.00056	0.997284	1.03135	1.05555
0.9994	0.997602	0.953087	0.997531	0.972366	1.00048	0.997667	1.02897	1.05124
0.9995	0.998001	0.957015	0.997948	0.974723	1.0004	0.998051	1.02639	1.04659
0.9996	0.998401	0.961394	0.998363	0.977342	1.00032	0.998437	1.02355	1.04149
0.9997	0.9988	0.966409	0.998776	0.980328	1.00024	0.998824	1.02034	1.03575
0.9998	0.9992	0.972419	0.999187	0.983889	1.00016	0.999213	1.01656	1.02902
0.9999	0.9996	0.980354	0.999595	0.988563	1.00008	0.999605	1.01166	1.02037

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.9999	0.9996	0.980354	0.999595	0.988563	1.00008	0.999605	1.01166	1.02037
0.99991	0.99964	0.981345	0.999636	0.989145	1.00007	0.999644	1.01106	1.0193
0.99992	0.99968	0.982395	0.999677	0.98976	1.00006	0.999683	1.01042	1.01818
0.99993	0.99972	0.983515	0.999717	0.990416	1.00006	0.999723	1.00974	1.01699
0.99994	0.99976	0.984721	0.999758	0.991122	1.00005	0.999762	1.00901	1.01571
0.99995	0.9998	0.986036	0.999798	0.99189	1.00004	0.999802	1.00822	1.01432
0.99996	0.99984	0.987493	0.999839	0.992741	1.00003	0.999841	1.00735	1.01279
0.99997	0.99988	0.989153	0.999879	0.993709	1.00002	0.999881	1.00636	1.01106
0.99998	0.99992	0.991127	0.99992	0.994858	1.00002	0.99992	1.00519	1.00902
0.99999	0.99996	0.993711	0.99996	0.99636	1.00001	0.99996	1.00366	1.00636

t1	p1	v1	pm1	vm1	v2	pm3	vm3	v3
0.99999	0.99996	0.993711	0.99996	0.99636	1.00001	0.99996	1.00366	1.00636
0.999991	0.999964	0.994032	0.999964	0.996546	1.00001	0.999964	1.00347	1.00603
0.999992	0.999968	0.994372	0.999968	0.996743	1.00001	0.999968	1.00327	1.00569
0.999993	0.999972	0.994734	0.999972	0.996953	1.00001	0.999972	1.00306	1.00532
0.999994	0.999976	0.995123	0.999976	0.997178	1.	0.999976	1.00284	1.00492
0.999995	0.99998	0.995546	0.99998	0.997424	1.	0.99998	1.00259	1.00449
0.999996	0.999984	0.996014	0.999984	0.997695	1.	0.999984	1.00231	1.00401
0.999997	0.999988	0.996547	0.999988	0.998003	1.	0.999988	1.002	1.00347
0.999998	0.999992	0.997179	0.999992	0.998369	1.	0.999992	1.00164	1.00284
0.999999	0.999996	0.998004	0.999996	0.998846	1.	0.999996	1.00116	1.002