Phase transitions in filtration of real gases

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Abstract

Steady adiabatic filtration of real gases is studied. Thermodynamical states of real gases are presented by Legendrian surfaces in 5-dimensional thermodynamical contact space. The relation between phase transitions and singularities of projection of the Legendrian surfaces on the plane of intensive variables is shown. The constructive method of finding solutions of the Dirichlet filtration problem together with analysis of critical phenomena is presented. Cases of van der Waals and Peng-Robinson gases are discussed in details.

Keywords: phase transitions, thermodynamics, filtration, porous media

1 Introduction

In this paper we continue (see [1, 2]) studies of phase transitions in processes describing by nonlinear partial differential equations. Here we consider the 3-dimensional steady adiabatic filtrations of gases. The first valuable results in this area were obtained by Leibenson L.S. [3] and Muskat M. [4]. They have proposed a generalization of the Navier-Stokes equations for this case, where they substituted the Newton law by the Darcy one.

The condition for stationary of filtration not only simplifies the mathematical model but also has the practical reason because the development of such processes not only take a long time but also control of them uses the so-called cascade method.

The most complete results in this paper are obtaining for the case of filtrations in homogeneous and isotropic media, where we are able to get the explicit formulae for solutions of the Dirichlet problem.

The paper is organized in the following way. The first part is devoted to thermodynamics of gases and in the second part we apply its results to the filtration problems.
We included the part devoted to the thermodynamics of gases for the following reasons. First of all, we formulated explicitly (see also [5]) that thermodynamical states are Legendrian or Lagrangian manifolds in the corresponding contact or symplectic spaces. These manifolds equipped with a quadratic differential forms, and domains of applicability of the thermodynamic model are exactly domains where this form defines a Riemannian structure. This allows us to locate domains of applicability of our model as well as to find singularities of projections of the Lagrangian manifolds on spaces of intensive and extensive variables. They are exactly the submanifolds where the quadratic differential form changes its type.

Secondly, we use symplectic (and contact) geometry (see, for example, [6]) and corresponding Poisson and Lagrange brackets to complete equations of state to the system defining Lagrangian manifold, in the cases when we know only part of them. For the number of cases it was done by introducing and using of the Massieu-Plank potential. We show that this potential appears in the very natural way in an attempt to find caloric equation of state in the case when we know a thermic equation [7]. We show and give explicit formulae for expression of the main thermodynamical potentials, heat capacities, speed of sound as well as curves where phase transitions occur (so called coexistence curves) in terms of the Massieu-Plank potential.

To illustrate this approach we have chosen two more popular models: van der Waals and Peng-Robinson gases.

We use these models also to illustrate filtrations of these gases in more details. Especially it concerns to filtration in a domain with one source where the behaviour of gas and phase transitions are highly nontrivial.

2 Thermodynamics of real gases

2.1 Preliminaries

A thermodynamical system is described by two types of variables: extensive and intensive (the notion was proposed by Richard Tolman in 1917 [8]).

We postpone discussion of intensive variables and begin with extensives.

The defining property of extensive variables is their additivity with respect to division of a system by a disjoint union of subsystems. The main examples of extensives are: mass – \( m \), volume – \( V \), inner energy – \( E \), entropy – \( S \), etc.

Let’s denote extensive variables as \((E, S, X)\), where \( X = (X_1, ..., X_n) \), and to each extensive (except \( E \)), i.e. variables \((S, X)\) corresponds intensive variable \((T, Y)\), where \( T \) is a temperature and \( Y = (Y_1, ..., Y_n) \).

After such division the main law of thermodynamics (containing of the first and the second laws) states that differential 1-form

\[
\theta = dE - TdS + YdX
\]

should be zero.
In other words, if we consider a \((2n+3)\)-dimensional space \(\mathbb{R}^{2n+3}\) with coordinates \((E, S, X, T, Y)\) and equipped with differential form \(\theta\), then a state of thermodynamical system is such a submanifold \(L \subset \mathbb{R}^{2n+3}\) where the main law of thermodynamics holds, i.e. the restriction \(\theta|_L = 0\). The pair \((\mathbb{R}^{2n+3}, \theta)\) is the standard model of the contact space (see for example, [6]) and \(L\) is an integral manifold of \(\theta\). We’ll require that \(L\) is a maximal integral manifold, i.e. Legendrian manifold, the notion proposed by Vladimir Arnold, then \(\dim L = n + 1\).

Thus, by a *thermodynamical state* we mean a Legendrian manifold in the contact space \((\mathbb{R}^{2n+3}, \theta)\).

In the case when functions \((S, X)\) are coordinates on a Legendrian manifold \(L\), this manifold could be written in the form

\[
L = \left\{ E = F(S, X), \, T = \frac{\partial F}{\partial S}, \, Y = -\frac{\partial F}{\partial X} \right\},
\]

and the restriction of intensive variables on \(L\) plays the role of *thermodynamical forces*.

In what follows we shall mainly consider another (but equivalent) form

\[
\theta' = -T^{-1}\theta = dS - T^{-1}dE - T^{-1}Y \, dX.
\]

Then the condition to be Legendrian will be not changed, but the projection \(\pi: \mathbb{R}^{2n+3} \to \mathbb{R}^{2n+2}\), where \(\pi(E, S, X, T, Y) = (E, X, T, Y)\), allows us to eliminate \(S\) from the description of thermodynamical states. Indeed (see, for example, [6], for more details), the restriction of the projection \(\pi\) on a Legendrian manifold \(L\), \(\pi: L \to \mathbb{R}^{2n+2}\), is an immersion and the image \(\hat{L} = \pi(L) \subset \mathbb{R}^{2n+2}\) an immersed Lagrangian submanifold in the symplectic space \((\mathbb{R}^{2n+2}, \Omega)\), where the structure form \(\Omega\) equals

\[
\Omega = -d\theta' = d(T^{-1}) \wedge dE + d(T^{-1}Y) \wedge dX.
\]

In the case, when functions \((E, X)\) are coordinates on \(\hat{L}\), this Lagrangian manifold can be written in the form

\[
T = \left( \frac{\partial F}{\partial E} \right)^{-1}, \quad Y = \frac{\partial F}{\partial X} \left( \frac{\partial F}{\partial E} \right)^{-1},
\]

for some function \(F = F(E, X)\).

In practice, Lagrangian manifolds \(\hat{L}\) are defined by "physical laws"

\[
L = \{ f_1(E, X, T, Y) = 0, \ldots, f_{n+1}(E, X, T, Y) = 0 \},
\]

which are independent, i.e.

\[
df_1 \wedge \cdots \wedge df_{n+1} \neq 0 \quad \text{at points of} \quad \hat{L},
\]

and such that all the Poisson brackets \([f_i, f_j] = 0\), \(i, j = 1, \ldots, n + 1\), on \(\hat{L}\).
Here the Poisson brackets are taken with respect to structure form $\Omega$:

$$[f_i, f_j] \Omega^{(n+1)} \overset{\text{def}}{=} df_i \wedge df_j \wedge \Omega^n.$$ 

Remark that not all points of the Lagrangian manifold are equally good for us. Namely, if we consider a thermodynamics as a theory describing a measurement of extensive variables by random processes (see [5] for more details), then points on the Lagrangian manifolds correspond to extreme probability measures, finding by using Maximum Entropy Principle or better – Minimal Information Gain, and values of extensive are exactly the means of these measures. The second central moment corresponds to a quadratic differential form $\hat{\Omega}$. This form could be obtained by the restriction of the universal quadratic form $-\kappa$ on $\mathbb{R}^{2n+2}$, where

$$\kappa = d\left(T^{-1}\right) \cdot dE + d\left(T^{-1}Y\right) \cdot dX,$$

and dot $\cdot$ stands for symmetric product of differential 1-forms.

This means that we have a domain $D \subset \hat{L}$ of admissible points, where quadratic differential form $\kappa|_D$ is negatively defined. We’ll see later on that the boundary of the domain $D$ is the set where we’ll expect phase transitions.

### 2.2 Equilibrium

Let’s consider a system defined by extensive variables $(E, S, X)$ and let this system be a disjoint union of two subsystems $(E_1, S_1, X_1)$ and $(E_2, S_2, X_2)$ and let

$$\theta = dE - TdS - YdX, \quad \theta_1 = dE_1 - T_1dS_1 - Y_1dX_1, \quad \theta_2 = dE_2 - T_2dS_2 - Y_2dX_2$$

be the corresponding forms.

Then

$$E = E_1 + E_2, \quad S = S_1 + S_2, \quad X = X_1 + X_2,$$

and

$$\theta = \theta_1 + \theta_2 + (T_1 - T)dS_1 + (T_2 - T)dS_2 + (Y_1 - Y)dX_1 + (Y_2 - Y)dX_2.$$ 

On the given thermodynamical state we have $\theta = 0, \theta_1 = 0$ and $\theta_2 = 0$, therefore

$$T_1 = T_2 = T, \quad Y_1 = Y_2 = Y,$$

i.e. for the union of subsystems extensive variables are added but intensive should be equalized.

**Example 1 (Gibbs potential)** To describe gases we use extensives $(E, S, V, m)$ – inner energy, entropy, volume and mass and in this case

$$\theta = dE - TdS + pdV - \gamma dm,$$
where \( p \) is a pressure and \( \gamma \) is a chemical potential.

Assume that a thermodynamical state is given by function \( E = F(S, V, m) \). Then the additivity property for variables \((E, S, V, m)\) means that \( F \) is a homogeneous function of degree 1 and we’ll write it in the form

\[
F(S, V, m) = mF\left(\frac{S}{m}, \frac{V}{m}, 1\right),
\]

or in terms of specific energy \( \varepsilon = E/m \), specific entropy \( \sigma = S/m \), and specific volume \( v = V/m \) as

\[
\varepsilon = f(\sigma, v).
\]

Then

\[
\theta = m(d\varepsilon - Td\sigma + pdv) + (\varepsilon - T\sigma + pv - \gamma)dm,
\]

and for state equation (1) we have

\[
d\varepsilon - Td\sigma + pdv = 0,
\]

and

\[
\gamma = \varepsilon + pv - T\sigma.
\]

Function \( G = E + pV - TS \) is called Gibbs free energy, and therefore \( \gamma \) is a specific Gibbs free energy.

The discussed above conditions of equilibrium for gases shall take now the form:

\[
T_1 = T_2, \quad P_1 = P_2, \quad \gamma_1 = \gamma_2.
\]

### 2.3 State equations for gases

Consider a 5-dimensional contact space \( \mathbb{R}^5 \) with coordinates \((\sigma, v, \varepsilon, p, T)\), where \( \varepsilon, \sigma, v \) stand for the specific inner energy, specific entropy and specific volume respectively, \( p \) is the pressure and \( T \) is the temperature.

In this case, the above contact structure is given by differential 1-form

\[
\theta = d\sigma - T^{-1}d\varepsilon - T^{-1}pdv,
\]

and by thermodynamical states we mean Legendrian surfaces \( L \subset \mathbb{R}^5 \), i.e. surfaces where \( \theta\big|_L = 0 \), or, in other words, where the law of energy conservation holds.

As above to eliminate specific entropy \( \sigma \) from our consideration we consider a 4-dimensional space \( \mathbb{R}^4 \) with coordinates \((v, \varepsilon, p, T)\) and projection

\[
\pi: \mathbb{R}^5 \to \mathbb{R}^4,
\]

where \( \pi(\sigma, v, \varepsilon, p, T) = (v, \varepsilon, p, T) \).

The restriction of projection \( \pi \) on \( L \) is an immersion. In order to avoid extra technicalities, we’ll assume that \( \pi: L \to \tilde{L} \) is a diffeomorphism of \( L \) with a surface \( \tilde{L} \subset \mathbb{R}^4 \).
The last is a Lagrangian surface in 4-dimensional symplectic space $\mathbb{R}^4$ equipped with the symplectic 2-form

\[
\Omega = -d\theta = d (T^{-1}) \wedge d\varepsilon + d (pT^{-1}) \wedge dv = T^{-1}dp \wedge dv - T^{-2}dt \wedge (d\varepsilon + pdv),
\]

i.e. $\Omega|_{\hat{L}} = 0$.

Remark, that conditions $\theta|_{L} = 0$ and $\Omega|_{\hat{L}} = 0$ are equivalent up to a shift of $L$ along axis $\sigma$ and moreover, 2-form $d\theta$ is the pullback of $\Omega$, $\pi^*(\Omega) = d\theta$.

The Lagrangian surface $\hat{L}$ is defined by two equations (or by two thermodynamical laws)

\[ f(v, \varepsilon, p, T) = 0, \quad g(v, \varepsilon, p, T) = 0, \]

where functions $f$ and $g$ are independent and the condition $\Omega|_{\hat{L}} = 0$ is equivalent to the condition that the Poisson bracket $[f, g]$ vanishes on $\hat{L}$.

In our case this bracket could be defined by the relation

\[ df \wedge dg \wedge \Omega = [f, g] \Omega \wedge \Omega, \]

and has the following form

\[ [f, g] = \frac{1}{2} (pT (f_p g_\varepsilon - f_\varepsilon g_p) + T^2 (f_T g_\varepsilon - f_\varepsilon g_T) + T (f_p g_T - f_T g_p)). \]

To find state manifolds $\hat{L}$ for real gases we’ll take the following two equations:

1. **Thermic equation of state**

   \[ p = A(v, T), \]

   and

2. **Caloric equation of state**

   \[ \varepsilon = B(v, T). \]

Then the compatibility condition for them

\[ [p - A(v, T), \varepsilon - B(v, T)] = 0 \quad \text{if} \quad \{p = A(v, T), \varepsilon = B(v, T)\} \]

is equivalent to relation

\[ (T^{-2}B)_v = (T^{-1}A)_T. \]

Solutions of the last equation we’ll present by using potential function $\phi(v, T)$ such that $T^{-1}A = R\phi_v$ and $T^{-2}B = R\phi_T$, or

\[ A = RT\phi_v, \quad B = RT^2\phi_T, \quad (3) \]

where $R$ is the universal gas constant.
In 1901 H. Kamerlingh Onnes proposed a virial model (viris=force, Latin) for thermic equation [9]:

\[ A = \frac{RT}{v} Z(v, T), \]

where \( Z(v, T) \) is a compressibility factor of the form

\[ Z(v, T) = 1 + \frac{A_1(T)}{v} + \cdots + \frac{A_k(T)}{v^k} + \cdots, \]

and \( A_k(T) \) are virial coefficients.

We have the following relation between potential function and the compressibility factor:

\[ Z = v\phi_v. \]

Therefore,

\[ \phi = \alpha(T) + \ln v - A_1(T) v^{-1} - \frac{1}{2} A_2(T) v^{-2} - \cdots - \frac{1}{k} A_k(T) v^{-k} - \cdots \]

where \( \alpha(T) \) is a smooth function.

Remark that in the case of ideal gases we have trivial virial coefficients, \( A_1 = 0 \), and

\[ B = \frac{n}{2} RT, \]

where \( n \) is the degree of freedom.

This means that

\[ T^2 \alpha_T = \frac{n}{2} T, \]

and therefore the potential function \( \phi \) has to be in the form

\[ \phi = \frac{n}{2} \ln T + \ln v - A_1(T) v^{-1} - \frac{1}{2} A_2(T) v^{-2} - \cdots - \frac{1}{k} A_k(T) v^{-k} - \cdots \quad (4) \]

In order to understand the meaning of potential function \( \phi \) let’s express the main thermodynamical functions in terms of \( \phi \).

Let’s start with the specific entropy. Condition \( \theta|_L = 0 \) gives us

\[ \sigma_T = R \left( 2\phi_T + T\phi_{TT} \right), \]
\[ \sigma_v = R \left( \phi_v + T\phi_{vT} \right), \]

and therefore (up to a constant)

\[ \sigma = R \left( \phi + T\phi_T \right). \quad (5) \]

For the specific Gibbs free energy \( \gamma \) we get

\[ \gamma = \varepsilon + pv - T\sigma = RT \left( v\phi_v - \phi \right), \quad (6) \]

and for specific enthalpy we have

\[ \eta = \varepsilon + pv = RT \left( T\phi_T + v\phi_v \right). \]

Similarly, for the Helmholtz free energy or Massieu-Plank potential we get

\[ \Xi = \sigma - \frac{\varepsilon}{T} = R\phi. \quad (7) \]

For this reason, from now and on, we’ll call \( \phi \) Massieu-Plank potential.
2.4 Riemannian structures on Lagrangian manifolds

As we have noted above, not all points of the Lagrange surface \( \hat{L} \) correspond to thermodynamical states. Namely, the fundamental quadratic differential form \( \kappa \) on the surface defines the domain of applicable states, i.e. states where \( \kappa|_{\hat{L}} \) is negative \(^5\):

In our case, this form could be written in the following way

\[
\kappa = d (T^{-1}) \cdot d\varepsilon + d (pT^{-1}) \cdot dv,
\]

and in terms of Massieu-Plank potential it has the following form

\[
\frac{1}{R} \kappa = - (\phi_{TT} + 2T^{-1}\phi_T) dT \cdot dT + \phi_{vv} dv \cdot dv.
\] (8)

**Remark 2** Let’s assume that the above quadratic differential form is non-degenerated. Then \( \kappa \) is a flat metric if and only if \( \phi (T,v) = \frac{n}{2} \ln T + \phi_0 (v) \), or if all virial coefficients are constants.

Summarizing this discussion we get the following description of the real gas states.

**Theorem 3** Thermodynamical states of real gases are defined by Massieu-Plank potential function \( \phi (T,v) \) and have the following form:

\[
p = RT \phi_v, \quad \varepsilon = RT^2 \phi_T, \quad \sigma = R (\phi + T \phi_T),
\]

where function \( \phi \) has the following expression in terms of virial coefficients

\[
\phi = \frac{n}{2} \ln T + \ln v - A_1 (T) v^{1} - \frac{1}{2} A_2 (T) v^{-2} - \cdots - \frac{1}{k} A_k (T) v^{-k} - \cdots.
\]

The domain of applicable states on the plane \( (T, v) \) is given by inequalities

\[
\phi_{vv} < 0, \quad T \phi_{TT} + 2\phi_T > 0.
\] (9)

Phase transitions occur near the curve

\[
\phi_{vv} = 0 \quad \text{or} \quad T \phi_{TT} + 2\phi_T = 0.
\]

**Remark 4** Due to the state equations we have \( \varepsilon_T = RT (T \phi_{TT} + 2\phi_T) \) and \( p_v = RT \phi_{vv} \). Therefore, applicable states belong to domain where

\[
\varepsilon_T > 0 \quad \text{or} \quad p_v < 0,
\]

or, because we expect that \( \varepsilon_T > 0 \), the phase transitions occur near the curve

\[
\phi_{vv} = 0.
\]
2.5 Singularities and phase transitions

Denote by \( L_\phi \subset \mathbb{R}^4 (\varepsilon, v, T, p) \) the Lagrangian surface that corresponds to the Massieu-Plank function \( \phi(T, v) \). This surface is given by equations

\[ p = RT \phi_v, \quad \varepsilon = RT^2 \phi_T. \]  

(10)

The projection \( L_\phi \to \mathbb{R}^2 (T, p) \) of this surface on the plane \((T, p)\) of intensive variables has singularities at points \( \Sigma_i \subset L_\phi \), where differential 2-form \( dp \wedge dT \) equals zero, or

\[ \Sigma_i = \{ \phi_{vv} = 0 \}. \]

In the similar way, singularities \( \Sigma_e \) of the projection \( L_\phi \to \mathbb{R}^2 (\varepsilon, v) \) on the plane of extensive variables correspond to the points where differential 2-form \( d\varepsilon \wedge dv \) has zeroes, i.e.

\[ \Sigma_e = \{ T \phi_{TT} + 2\phi_T = 0 \}. \]

In other words, we have singularities of two types that correspond to singularities \( \Sigma_i \) or \( \Sigma_e \). In the first case, the jumps preserve values of intensive variables and have discontinuous for extensive ones, and this is exactly what we call phase transitions, but in the second type singularities the jumps preserve extensive and we observe discontinuous for intensive variables. Remark that both these singularities are essential for us, because quadratic differential form \( \kappa \) changes its type at these points.

We say that distinct points \((v_1, p_1, \varepsilon_1, T_1)\) and \((v_2, p_2, \varepsilon_2, T_2)\) on the Lagrangian surface \( L_\phi \) are phase equivalent iff

\[ p_1 = p_2, \quad T_1 = T_2, \quad \gamma (v_1, T_1) = \gamma (v_2, T_2). \]

Remark 5 We have \( \gamma = \varepsilon + pv - T \sigma \), and

\[ d\gamma = vdp - \sigma dT \mod (\theta). \]

This relation explains the Maxwell rule of equal areas on the plane \((v, p)\) (or \((\sigma, T)\)) that used to apply to find phase equivalent points.

In terms of the Massieu-Plank potential phase equivalent points \((v_1, T)\) and \((v_2, T)\) on surface \( L_\phi \) could be found from the following system of equations:

\[ \phi_v (v_2, T) - \phi_v (v_1, T) = 0, \]
\[ \phi (v_2, T) - \phi (v_1, T) - v_2 \phi_v (v_2, T) + v_1 \phi_v (v_1, T) = 0. \]  

(11)

Eliminating \( v_2 \) from the above equations and putting \( v_1 = v \) we get phase transition or coexistence curve \( \Gamma_\phi \subset \mathbb{R}^2 (v, T) \) which shows \((v, T)\) points of phase transitions, and eliminating \( T \) we get phase transition curve \( \Gamma_\phi \subset \mathbb{R}^2 (v_1, v_2) \) shows the specific volumes of phase transitions.

Moreover, if we consider the equivalent equations

\[ \phi_v (v_2, T) = \frac{p}{RT}, \quad \phi_v (v_1, T) = \frac{p}{RT}, \]
\[ \phi (v_2, T) - \phi (v_1, T) - v_2 \phi_v (v_2, T) + v_1 \phi_v (v_1, T) = 0, \]  

(12)

9
and eliminate \((v_1, v_2)\) from these equations we get phase transition curve \(\Gamma_\phi \subset \mathbb{R}^2(p, T)\) that shows the pressures and temperatures when phase transitions occur.

These equations also allow us to find jumps in heat, inner energy and work on phase transitions:

\[
\begin{align*}
\Delta Q &= T (S(v_2, T) - S(v_1, T)) = RT (\Delta \phi + T \Delta \phi_T), \\
\Delta W &= -P(v_2 - v_1) = -RT \phi_v \Delta v = -RT \Delta \phi, \\
\Delta \varepsilon &= \varepsilon(v_2, T) - \varepsilon(v_1, T) = RT^2 \Delta \phi_T = \Delta Q + \Delta W.
\end{align*}
\]

### 2.6 Heat capacities and speed of sound

In this section we compute heat capacities and speed of sound in terms of potential function \(\phi\).

Recall that heat capacity measures the amount of heat required to change temperature by a given amount. There are two types of heat capacities: \(C_v\) – heat capacity at fixed volume, \(C_p\) – heat capacity at fixed pressure.

We begin with computation of \(C_v\). Following to the above saying, we define it by the relation

\[
Td\sigma - C_v dT \equiv 0 \mod \langle dv \rangle,
\]

on \(L_\phi\).

Using the description of the Lagrangian surface \(L_\phi\) we get

\[
d\sigma - R (2\phi_T + T \phi_{TT}) dT \equiv 0 \mod \langle dv \rangle,
\]

and therefore

\[
C_v = RT (2\phi_T + T \phi_{TT}) = \varepsilon_T.
\]

In the similar way we define \(C_p\) by the following relation:

\[
Td\sigma - C_p dT \equiv 0 \mod \langle dp \rangle.
\]

We have

\[
\begin{align*}
dp &= R (T \phi_{vv} dv + (\phi_v + T \phi_{Tv}) dT) \quad (13) \\
Td\sigma &= RT ((2\phi_T + T \phi_{TT}) dT + (\phi_v + T \phi_{Tv}) dv). \quad (14)
\end{align*}
\]

Therefore,

\[
dl \equiv - \frac{\phi_v + T \phi_{Tv}}{T \phi_{vv}}dT \mod \langle dp \rangle
\]

and

\[
C_p = \frac{R}{\phi_{vv}} \left(T^2 (\phi_{TT} \phi_{vv} - \phi_{Tv}^2) + 2T (\phi_T \phi_{vv} - \phi_v \phi_{Tv}) - \phi_v^2\right) = \varepsilon_T - \frac{p_v^2 T}{\rho_v},
\]

also

\[
C_p - C_v + \frac{p_v^2 T}{\rho_v} = 0.
\]
The speed of sound $c$ is defined as $c^2 = C_s$, where
\[ dp - C_s dv^{-1} \equiv 0 \mod (d\sigma). \]
In our case,
\[ dT \equiv -\frac{\varepsilon_v + p}{\varepsilon_T} dv \mod (d\sigma), \]
and therefore
\[
C_s = v^2 \left( \frac{\varepsilon_v p_T - \varepsilon_T p_v}{\varepsilon_T} + \frac{1}{2} \frac{(p^2)_T}{\varepsilon_T} \right) = R v^2 \frac{T^2 (\phi_v^2 - \phi_T \phi_v v) + 2T (\phi_v \phi_v T - \phi_T \phi_v v) + \phi_v^2}{2\phi_T + T \phi_T T}.
\]
It is easy to check that all the quantities $C_v, C_p$ and $C_s$ are connected by the following relation
\[ T^{-1} C_s C_v + R v^2 \phi_v v C_p = 0. \]
As a by-product of this equality we get the following observation.

**Theorem 6** The speed of sound vanishes on singular set $\Sigma_i$.

### 2.7 Relations with Monge-Ampere equations

Formula (15) for $C_s$ gives us a method to find equations of state for a media with known speed of sound:
\[ c^2 = R F (v, T) v^2. \]

Indeed, in this case the formula shows that the Massieu-Plank potential $\phi (T, v)$ satisfies the following Monge-Ampere differential equation
\[
T^2 (\phi_v^2 - \phi_T \phi_v v) + 2T (\phi_v \phi_v T - \phi_T \phi_v v) + \phi_v^2 - F (v, T) (2\phi_T + T \phi_T T) = 0.
\]
Thus, for example, equation of state for ultrarelativistic fluids has the form
\[ pv = c^2 \]
and the last equation takes the form
\[
vT (\phi_v^2 - \phi_T \phi_v v) + 2v (\phi_v \phi_v T - \phi_T \phi_v v) + vT^{-1} \phi_v^2 - \phi_v (2\phi_T + T \phi_T T) = 0.
\]
Also the virial expansion could be used to find approximations to solutions for the obtained Monge-Ampere equations.
Thus, for main thermodynamical functions we have

\[
\varepsilon = RT \left( \frac{n}{2} - TA_1' - \frac{TA_2'}{2v^2} \right) + O \left( \frac{1}{v^3} \right),
\]

\[
p = RT \left( \frac{1}{v} + A_1' \right) + O \left( \frac{1}{v^3} \right),
\]

\[
C_v = \frac{Rn}{2} - \frac{RT}{v} (TA_1'' + 2A_1') - \frac{RT}{2v^2} (TA_2'' + 2A_2') + O \left( \frac{1}{v^3} \right)
\]

\[
C_p = \frac{R(n + 2)}{2} - \frac{RT^2 A_1''}{v} + O \left( \frac{1}{v^2} \right),
\]

\[
C_s = \frac{RT(n + 2)}{n} + \frac{4RT}{vn^2} \left( T^2 A_1'' + (n + 2) \left( TA_1' + \frac{n}{2} A_1 \right) \right) + O \left( \frac{1}{v^2} \right).
\]

2.8 Examples

2.8.1 Ideal gas.

The equations of state are the following

- Clapeyron-Mendeleev equation

\[ pv = RT, \]

and

- equation for internal energy

\[ \varepsilon = \frac{n}{2} RT, \]

where \( n \) is the degree of freedom.

The potential function \( \phi \) for this case we’ll find from equations \[10\]. We get

\[
\phi = \ln \left( T^{n/2}v \right), \quad \sigma = R \ln \left( T^{n/2}v \right),
\]

\[
C_v = \frac{Rn}{2}, \quad C_p = \frac{Rn}{2} + R, \quad C_s = RT \frac{n + 2}{2}.
\]

The quadratic differential form equals

\[
\kappa = \frac{Rn}{2} \frac{dT^2}{T^2} - \frac{R}{v^2} \frac{dv^2}{v^2}.
\]

It is negative, and there are no phase transitions.
2.8.2 van der Waals gas.

In this case state equations are
\[ p = \frac{RTv^2 - a(v - b)}{v^2(v - b)}, \quad \varepsilon = \frac{n}{2}RT - \frac{a}{v}. \]

Let us introduce following scale contact transformation
\[ T = \frac{T}{T_{\text{crit}}}, \quad v = \frac{v}{v_{\text{crit}}}, \quad p = \frac{p}{p_{\text{crit}}}, \quad \varepsilon = \frac{\varepsilon}{\varepsilon_{\text{crit}}}, \quad \sigma = \frac{\sigma}{\sigma_{\text{crit}}}, \]
where \( T_{\text{crit}}, v_{\text{crit}}, p_{\text{crit}}, \varepsilon_{\text{crit}}, \sigma_{\text{crit}} \) are critical parameters for van der Waals gases:
\[ T_{\text{crit}} = \frac{8a}{27Rb}, \quad v_{\text{crit}} = \frac{3b}{2}, \quad p_{\text{crit}} = \frac{a}{27b^2}, \quad \varepsilon_{\text{crit}} = \frac{a}{9b}, \quad \sigma_{\text{crit}} = \frac{3R}{8}. \]

then, we get the reduced equations of state in new dimensionless coordinates, which we shall continue denoting by \( p, T, \varepsilon, v \):
\[ p = \frac{8T}{3v - 1} - \frac{3}{v^2}, \quad \varepsilon = \frac{4n}{3}T - \frac{3}{v}. \]

One may show that the Massieu-Plank potential and the specific entropy for van der Waals gases are of the form:
\[ \phi = \ln \left( T^{n/2}(3v - 1) \right) + \frac{9}{8vT}, \quad \sigma = \ln \left( T^{4n/3} (3v - 1)^{8/3} \right). \] (17)

Therefore, heat capacities for van der Waals gases have the following form:
\[ C_v = \frac{n}{2}R, \quad C_p = \frac{C_{p,n}}{C_{p,d}}R, \]
where
\[ C_{p,n} = 4T(n + 2)v^3 - 9nv^2 + 6nv - n, \]
\[ C_{p,d} = 8Tv^3 - 18v^2 + 12v - 2, \]
and
\[ C_s = \frac{2aC_{p,n}}{3bv(3v - 1)^2}. \]

The corresponding quadratic differential form equals
\[ \kappa = -\frac{Rn}{2} \frac{dT^2}{T^2} - \frac{9R(4Tv^3 - 9v^2 + 6v - 1)}{4Tv^3(3v - 1)^2} dv^2. \]

Therefore, the domain of applicable states is given by the inequality
\[ 4Tv^3 - 9v^2 + 6v - 1 > 0, \quad \text{or} \quad T > \frac{(3v - 1)^2}{4v^3}, \]
Figure 1: Applicable domain for van der Waals gases.

and the phase transitions occur near the curve

\[ T = \frac{(3v - 1)^2}{4v^3}. \]

White domain in figure 1 corresponds to the domain of applicable states. Recall, that the coexistence curve or binodal curve may be obtained by means of Massieu-Plank potential using formulae (11) and (12). Both these forms of equations of coexistence curves are essential for us, because they allow us to get such curves in different coordinates.

System (11) for van der Waals gases has the following form:

\[
\frac{(3v_1 - 1)(3v_2 - 1)(v_1 + v_2)}{v_1 - v_2} \ln \left( \frac{3v_2 - 1}{3v_1 - 1} \right) = 3(v_1 + v_2 - 6v_1v_2), \tag{18}
\]

\[ T = \frac{(v_1 + v_2)(3v_1 - 1)(3v_2 - 1)}{8v_1^2v_2^2}. \tag{19}\]

Equation (18) defines a curve \( \Gamma_\phi \subset \mathbb{R}^2(v_1, v_2) \) of specific volumes of phase transition, which is shown in figure 2 and equation (19) allows to find the corresponding temperature.

Eliminating \( v_1 \) and \( v_2 \) from (12) we get a binodal curve \( \Gamma_\phi \subset \mathbb{R}^2(p, T) \), which is presented in figure 3(a) and eliminating \( v_1 \) and putting \( v_2 = v \) we get a curve \( \Gamma_\phi \subset \mathbb{R}^2(T, v) \). It is presented in figure 3(b). Since it is a difficulty to eliminate specific volumes, these curves have been obtained numerically.

Moreover, it is possible to lift these curves into the space \( \mathbb{R}^3(p, v, T) \), which is shown in figure 4.
2.8.3 Peng-Robinson gas.

The Peng-Robinson EOS is the most popular equation of state for real gases in the petroleum industry.

The first equation of state

\[ p = \frac{RT}{v - b} - \frac{\alpha}{(v + b)^2 - 2b^2} \]

was found by D.B. Robinson and his PhD student D. Peng [10] in 1976.

To find the second equation \( \varepsilon = B(v, T) \), we, as above, shall take the Poisson
Figure 4: Coexistence curve $\Gamma_\phi \subset \mathbb{R}^3(p,v,T)$ for van der Waals gases.

bracket $[p - A(v,T), \varepsilon - B(v,T)]$, where

$$A = \frac{RT}{v-b} - \frac{\alpha}{(v+b)^2 - 2b^2},$$

and require that this bracket equals zero if $p = A, \varepsilon = B$.

This condition gives differential equation on function $B$:

$$(b^2 - 2bv - v^2) B_v + \alpha = 0,$$

with solution

$$B = F(T) - \frac{\alpha}{\sqrt{2b}} \arctanh \left( \frac{v+b}{\sqrt{2b}} \right),$$

where $F(T)$ is an arbitrary smooth function.

Using the above virial coefficients arguments we take

$$\varepsilon = \frac{n}{2} RT - \frac{\alpha}{\sqrt{2b}} \arctanh \left( \frac{v+b}{\sqrt{2b}} \right)$$

as the second state equation.

By the following scale contact transformation

$$T \to \frac{\alpha}{bR} T, \quad \varepsilon \to \frac{\alpha}{b} \varepsilon, \quad p \to \frac{\alpha}{b^2} p, \quad v \to bv, \quad \sigma \to R\sigma$$
we transform the equations of state to the reduced form:

\[ p = \frac{T}{v - 1} - \frac{1}{(v + 1)^2 - 2}, \]
\[ \varepsilon = \frac{n}{2}T - \frac{\text{arctanh} \left( \frac{v+1}{\sqrt{2}} \right)}{\sqrt{2}}. \]

It is easy to check that the following function

\[ \phi = \ln \left( T^{\frac{n}{2}} (v - 1) \right) + T^{-1} \frac{\text{arctanh} \left( \frac{v+1}{\sqrt{2}} \right)}{\sqrt{2}}, \]

is the Massieu-Plank potential for the Peng-Robinson gases, and

\[ \sigma = \ln \left( T^{\frac{n}{2}} (v - 1) \right). \]

Therefore, we have for the Peng-Robinson gases

\[ C_v = \frac{n}{2}R, \]
\[ C_p = \frac{C_{p,n}}{C_{p,d}}R, \]

where

\[ C_{p,n} = T(n + 2)v^4 + 2(2(n + 2)T - n)v^3 + 2((n + 2)T + n)v^2 - 2(2(n + 2)T - n)v + T(n + 2) - 2n, \]
\[ C_{p,d} = 2(Tv^4 + 2(2T - 1)v^3 + 2(T + 1)v^2 - 2(2T - 1)v + T - 2), \]

and

\[ C_s = \frac{\alpha v^2}{bn} \frac{C_{p,n}}{(v - 1)^2 (v^2 + 2v - 1)^2}. \]

The corresponding quadratic differential form equals

\[ \kappa = -\frac{Rn \, dT^2}{2 \, T^2} - \frac{RT \, v^4 + (4T - 2) \, v^3 + (2T + 2) \, v^2 + (2 - 4T) \, v + T - 2}{(v - 1)^2 (v^2 + 2v - 1)^2} \, dv^2. \]

Therefore, the domain of applicable states is given by the inequality

\[ Tv^4 + (4T - 2) \, v^3 + (2T + 2) \, v^2 + (2 - 4T) \, v + T - 2 > 0, \]

and the phase transitions occur near the curve

\[ T = \frac{2(v + 1)(v - 1)^2}{(v^2 + 2v - 1)^2}. \]

White domain in figure 5 corresponds to the domain of applicable states.
3 Steady adiabatic filtration of real gases

3.1 Basic equations

Steady gas filtration in homogeneous porous 3-dimensional media is described by the following system of differential equations \[3, 4, 11\]:

- Darcy law or conservation of momentum
  \[ \mathbf{U} = -\frac{k}{\mu} \nabla p, \]  \hspace{1cm} (20)

  for gas flow in anisotropic porous media, where \( \rho \) is the density of gas, \( p \) – pressure, \( \mu \) – dynamic viscosity, \( k = \|k_{ij}\| \) – permeability tensor, \( \mathbf{U} \) – vector field of filtration rate, and \( \nabla p \) – the gradient of pressure.

- conservation of mass
  \[ \text{div} (\rho \mathbf{U}) = 0, \]  \hspace{1cm} (21)

  where \( \rho = \nu^{-1} \).

- In addition to these equations, we assume that the filtration is adiabatic,
  \[ \mathbf{U} (\sigma) = 0, \]  \hspace{1cm} (22)

  where \( \sigma \) is a specific entropy, and by \( \mathbf{U} (f) \) we denoted the derivative of a function \( f \) along vector field \( \mathbf{U} \).
It is worth to note that the last condition in the cases of sources leads us to local constancy of entropy in neighborhoods of the sources. We extend this observation and propose some kind of “ergodicity hypothesis”. Namely, we’ll consider a domain $D \subset \mathbb{R}^3$ with sources $\{a_i\}$, having the common constant specific entropy $\sigma_0$.

More precisely, consider a domain $D \subset \mathbb{R}^3$ with sources $\{a_i\}$, then under condition (22) we represent $D$ as a union of domains $D_k$, $k = 1, 2, \ldots$, such that the ergodicity hypothesis holds for each domain $D_k$, i.e. all sources in this domain have the same entropy, and the rest $D' = D \setminus \bigcup D_k$ contains no sources. Filtrations in these domains are independent. Thus, we may restrict ourselves by the case of domains, where the ergodicity hypothesis holds.

The permeability tensor $k$ is a symmetric positive tensor depending on media, $k = k(v, T)$, as well as viscosity $\mu$.

3.2 Filtration Equations

Proposition 7 The following formulae

$$dp \equiv -v^{-2}c^2 \, dv \bmod \langle \sigma \rangle,$$

and

$$v^{-2}c^2 = R \frac{T^2 (\phi_{vv}^2 - \phi_{vT} \phi_{tv}) + 2T (\phi_v \phi_{vT} - \phi_T \phi_{vv}) + \phi_v^2}{2 \phi_T + T \phi_{TT}}$$

are valid.

Proof. First of all, by the definition of the speed of sound we have

$$dp \equiv c^2 d(v^{-1}) \bmod \langle \sigma \rangle \equiv -v^{-2}c^2 \, dv \bmod \langle \sigma \rangle.$$

The second relation follows from the above formula for $C_s$.

Define a new tensor $\|Q_{ij} (v, \sigma_0)\|$ as follows.

Assume that a fixed level $\sigma_0$ of entropy $\sigma$ is given and define function $T = \tau (v, \sigma_0)$ as a solution of the equation $\sigma = R\sigma_0$, i.e.

$$\phi + T \phi_T = \sigma_0.$$

The derivative of the left hand side of this equation in $T$ equals $R^{-1} \varepsilon_T$, that is positive in applicable domain, and therefore the function $\tau$ exists and smooth.

Now we put

$$Q_{ij} (v, \sigma_0) = \int \frac{c^2 k_{ij}}{v^3 \mu} \, dv,$$

where all functions under integral are functions in $v$.

As the integral of positive tensor the above tensor is also positive and symmetric.
Theorem 8 Basic equations of adiabatic filtration with a given level of specific entropy $R_{\sigma_0}$ are equivalent to equation

$$\sum_{i,j} \frac{d^2 Q_{ij}}{dx_i dx_j} = 0.$$  \hspace{1cm} (24)

Proof. Indeed,

$$-\text{div} \left( \frac{k}{\mu} (\nabla p) \right) = -\text{div} \left( \sum_{ij} k_{ij} \frac{\partial p}{\partial x_i} \frac{\partial p}{\partial x_j} \right) = \text{div} \left( \sum_{ij} c_k^2 k_{ij} v^2 \frac{\partial v}{\partial x_i} \frac{\partial v}{\partial x_j} \right) =$$

$$\text{div} \left( \sum_{ij} \frac{dQ_{ij}}{dx_i} \frac{\partial}{\partial x_j} \right) = \sum_{ij} \frac{d^2 Q_{ij}}{dx_i dx_j}.$$

Let’s rewrite equation (24) in more details. To this end let us introduce two symmetric matrices:

$$\text{Hess} v = \left\| \frac{\partial^2 v}{\partial x_i \partial x_j} \right\|, \quad \left( \frac{\partial v}{\partial x} \right)^2 = \left\| \frac{\partial v}{\partial x_i} \frac{\partial v}{\partial x_j} \right\|.$$

Then,

$$\frac{dQ_{ij}}{dx_k} = Q'_{ij} \frac{\partial v}{\partial x_k}, \quad \frac{d^2 Q_{ij}}{dx_k dx_l} = Q'_{ij} \frac{\partial^2 v}{\partial x_k \partial x_l} + Q''_{ij} \frac{\partial v}{\partial x_k} \frac{\partial v}{\partial x_l},$$

and therefore equation (24) takes the form

$$\text{Tr} \left( Q' \cdot \text{Hess} v + Q'' \cdot \left( \frac{\partial v}{\partial x} \right)^2 \right) = 0,$$  \hspace{1cm} (25)

where $Q' = \| Q'_{ij} \|$ and $Q'' = \| Q''_{ij} \|$.

The following two cases shall be important for us.

1. The porous media is isotropic, i.e. $k_{ij} = k \delta_{ij}$, where $\delta_{ij}$ is the Kronecker symbol. Then,

$$Q_{ij} = Q \delta_{ij},$$

where

$$Q(v) = \int \frac{c_k^2}{v^3} dv.$$

Theorem 9 Basic equations of adiabatic filtration in isotropic media with a given level of specific entropy $R_{\sigma_0}$ are equivalent to equation

$$\Delta (Q(v)) = 0,$$  \hspace{1cm} (26)

where $\Delta$ is the Laplace operator.
2. The porous media is non isotropic but homogeneous, i.e. \( k_{ij} \) are constants. Then
\[
Q_{ij} = k_{ij} q,
\]
where
\[
q = \int \frac{c^2}{\rho^3} \mu dv.
\]

**Theorem 10** Basic equations of adiabatic filtration in non isotropic but homogeneous media with a given level of specific entropy \( R\sigma_0 \) are equivalent to equation
\[
\text{Tr}(k \cdot \text{Hess}(q)) = 0,
\]
(27)
where \( \text{Hess}(q) \) is the Hessian matrix of \( q \).

**Remark 11** By applying an orthogonal transformation we can transform matrix \( k \) to the diagonal form and in these coordinates equation (27) takes the form
\[
k_1 \frac{d^2 q}{dx_1^2} + k_2 \frac{d^2 q}{dx_2^2} + k_3 \frac{d^2 q}{dx_3^2} = 0,
\]
(28)
where \( k_1, k_2, k_3 \) are eigenvalues of \( k \).

**Remark 12** A solution of all these equations gives us \( v \) and \( T \) as functions in the domain \( D \) and by using the state equations we’ll find also \( p \) and \( \varepsilon \). Substituting these values in the equations of the phase transitions curves give us equations for points in \( D \) where we expect phase transitions.

### 3.3 Integration of basic equations for isotropic and homogeneous media

Here we consider the isotropic case, the case of homogeneous media may be elaborated in the similar manner.

Formula (26) shows that solutions of the basic system of equations for adiabatic filtration (of the given level of entropy \( \sigma_0 \)) could be found in the following way.

Take a harmonic function \( u \) in some domain \( D \subset \mathbb{R}^3 \), and define, in general multivalued, function \( v \) such that
\[
u = Q(v, \sigma_0).
\]

Remark, that function \( u \) is defined outside of a subset \( \Sigma_u \subset D \) of singular points, where \( \{c^2 = 0\} \), and this set consists of points in \( D \), where \((v, T) \in \Sigma_i \).

Outside of this singular set all branches of the multivalued function \( v \) are smooth and satisfy the basic equations. Also phase transitions occur at points \( x^{(1)} \) and \( x^{(2)} \), where corresponding values of one of branches of \( v \) satisfy equations (11).
3.3.1 Model of source.

Let’s consider first solutions that correspond to sources of given intensity \( I \). It means that

\[
    u(x) = \frac{I}{4\pi} |x - a|^{-1},
\]

if the source is located at point \( a \in D \), or

\[
    v(x) = Q^{-1} \left( \frac{I}{4\pi} |x - a|^{-1}, \sigma_0 \right).
\]  

(29)

This is a multivalued solution such that its branches are smooth outside of \( \Sigma_u \) and phase transitions occur at points where equations (11) hold.

3.3.2 Dirichlet boundary problem.

Consider an open and connected domain \( D \subset \mathbb{R}^3 \) with a smooth boundary \( \partial D \), equipped with a set \( A = \{ a_i, i = 1, \ldots, N \} \subset D \) of points, which are the locations of sources, with given intensities \( I_i \).

We are looking for a solution \( v \) of Dirichlet boundary problem of the basic system in domain \( D \setminus A \), for a real gas with Massieu-Plank potential function \( \phi(T, v) \), having given intensities \( I_i \) at points \( a_i \), given entropy level \( \sigma_0 \), and given values of specific volume (or temperature) on the boundary:

\[
    v|_{\partial D} = v_0.
\]

To this end we take a harmonic in the domain \( D \setminus A \) function \( u \) such that

\[
    u = \sum_i \frac{I_i}{4\pi} |x - a_i|^{-1} + u_0,
\]

where \( u_0 \) is the harmonic function in \( D \) with the following boundary conditions

\[
    u_0|_{\partial D} = Q(v_0) - \left( \sum_i \frac{I_i}{4\pi} |x - a_i|^{-1} \right)|_{\partial D}.
\]

Then the multivalued function \( Q^{-1}(u) \) gives us the solution of the Dirichlet boundary problem.

3.4 Examples

Here we apply above methods to the van der Waals and Peng-Robinson gases filtration.
3.4.1 van der Waals gases.

Given level of the specific entropy $\sigma_0$ allows us to express the temperature $T$ and the pressure $p$ as functions of the specific volume $v$ using (17). For van der Waals gases we get:

$$T(v) = c(3v - 1)^{-\alpha}, \quad p(v) = 8c(3v - 1)^{-\alpha} - \frac{3}{v^2},$$

where

$$\alpha = 1 + \frac{2}{n}, \quad c = \exp\left(\frac{3\sigma_0}{4n}\right).$$

Function $Q(v)$ is defined by the following relation:

$$-\frac{\mu}{k}Q(v) = -\frac{2}{v^3} + 8c\frac{(3v - 1)^{-\alpha}}{v} + 8c \int (3v - 1)^{-\alpha}v^{-2}dv.$$

As it has already been shown, to get an explicit solution we have to invert $Q(v)$. For this reason it is essential for us to figure out the invertibility conditions for $Q(v)$.

**Theorem 13** Function $Q(v)$ is invertible if the specific entropy constant $c$ satisfies the following inequality:

$$c > \frac{1}{4\alpha}(1 + \alpha)^{1+\alpha}(2 - \alpha)^{2-\alpha}.$$  

**Proof.** We need to define a condition when the function $Q(v)$ is monotonic if $v > 1/3$. This means that its derivative must not be equal to zero. As the conditions $Q'(v) = 0$ and $p'(v)$ are equivalent, it easy to check that

$$Q'(v) = 0 \iff w(v) = 4c\alpha,$$

where $w(v) = (3v - 1)^{1+\alpha}v^{-3}$. Function $w(v)$ has a maximum at the point $v_0$, which is derived from the equation $w''(v) = 0$ and it equals

$$v_0 = \frac{1}{2 - \alpha}.$$  

Therefore, $w(v_0) = (1 + \alpha)^{1+\alpha}(2 - \alpha)^{2-\alpha}$.  

Having a solution we can move the coexistence curve from the space of thermodynamical variables to the $\mathbb{R}^3(x_1, x_2, x_3)$. Let’s suppose that we have a point source at the point $x_0$. Then, in case of invertible function $Q(v)$ we have the picture presented by figure [6].

Figure [6] shows that in the neighbourhood of the source condensation of the gas is observed.

In case of irreversibility of the function $Q(v)$ the picture is much more complicated. First of all, solution is multivalued. It is shown in figure [7]. This means that there is a number of possibilities for the gas filtration development.
Figure 6: Phases in space for van der Waals gases if $Q(v)$ is invertible. If variable $y = 0$, the domain $|x - x_0|$ corresponds to the gas phase. If $y = 0.5$, the domain $|x - x_0|$ corresponds to the intermediate state (condensation process).

Figure 7: Dependence of temperature on the distance from the source for van der Waals gases: (a) represents low temperatures; (b) represents high temperatures.

In figure 7, the temperature under the critical point is uniquely determined, which leads to the uniqueness in phase under the critical point. It is shown in figure 8. We can see that the picture is similar to the previous one.

But in figure 9, the temperature under the critical point is multivalued. This means that we can expect that at the same point there can be different phases. It is shown in figure 10.

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Figure 8: Phases in space for van der Waals gases if $Q(v)$ is irreversible. If variable $y = 0$, the domain $|x - x_0|$ corresponds to the gas phase. If $y = 0.5$, the domain $|x - x_0|$ corresponds to the intermediate state (condensation process).

Figure 9: Dependence of temperature on the distance from the source for van der Waals gases: (a) represents low temperatures; (b) represents high temperatures.

3.4.2 Peng-Robinson gases.

In case of Peng-Robinson gases the pressure $p$ and the temperature $T$ can be expressed as functions of the specific volume $v$ as follows:

$$T(v) = c(v - 1)^{-\alpha + 1}, \quad p(v) = c(v - 1)^{-\alpha} - \frac{1}{v^2 + 2v - 1}.$$
Figure 10: Phases in space for van der Waals gases if $Q(v)$ is irreversible. If variable $y = 0$, the domain $|x - x_0|$ corresponds to the gas phase, if $y = 0.5$, the domain $|x - x_0|$ corresponds to the intermediate state (condensation process), if $y = 1$, the domain $|x - x_0|$ corresponds to the liquid phase.

where
\[ c = \exp \left( \frac{2\sigma_0}{n} \right), \quad \alpha = 1 + \frac{2}{n}. \]

Function $Q(v)$ is defined by the following relation:
\[
-\frac{\mu}{k}Q(v) = \frac{c}{v(v-1)^\alpha} - \frac{v + 2}{v^2 + 2v - 1} + \ln \left( \frac{v^2}{v^2 + 2v - 1} \right) + \\
+ \frac{3}{\sqrt{2}} \text{arctanh} \left( \frac{v + 1}{\sqrt{2}} \right) + c \int (v - 1)^{-\alpha}v^{-2}dv.
\]

Finally, invertibility condition can be formulated as follows.

**Theorem 14** Function $Q(v)$ is invertible if the specific entropy constant $c$ satisfies the following inequality:
\[
c > \frac{2}{\alpha} \frac{(v_0 + 1)(v_0 - 1)^{\alpha+1}}{(v_0^2 + 2v_0 - 1)^2},
\]

where $v_0$ is the root of the equation:
\[
(\alpha - 2)v^3 + 3\alpha v^2 + (\alpha + 2)v - \alpha + 4 = 0.
\]

There exists a real root of the above equation if $\alpha < 2$, or, equivalently, $n > 2$.

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