Chapter 5
Critical Phenomena in Darcy and Euler Flows of Real Gases

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5.1 Introduction

In this paper, we summarize the results obtained in [1–5] for two important types of flows of real gases—the flows through porous media [6] and Euler flows.

The first significant results in the field of filtration processes were obtained in [7] and [8]. In these papers, the Darcy law was suggested to investigate flows through porous media. This approach appeared to be sufficiently effective. Such phenomena as phase transitions in filtration processes were studied in a few works, for instance, in [9] and [10]. In [9], one-dimensional nonstationary filtration of two-component mixture of hydrocarbons described by the generalized van der Waals equation was studied, but only one (thermic) equation of state was considered. In [10], the authors investigated non-equilibrium phase transitions in filtration of gas-condensate mixtures and provided the comparison with equilibrium phase transitions. In both works [9] and [10] numerical computations were used.

Comparing with [9] and [10], we consider three-dimensional, stationary, one-component filtration and provide explicit formulae for finding solutions of the Dirichlet boundary problem. Some exact solutions for nonstationary filtration together with the analysis of the symmetry algebra of corresponding equations for various media are presented in [11].

Navier–Stokes and Euler flows formed by means of source have been of great interest since the middle of the 20th century, when Landau found a new exact singular solution of incompressible Navier–Stokes equations [12] called *submerged jet*. From the physical viewpoint, this solution is formed by a source that transmits the momentum to surrounding medium in a certain direction. It has two features

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that are usually said to be the drawbacks of Landau's solution. The first one is the triviality of solution in case of ideal (inviscid) fluids, which means that solution of this type is valid only for highly viscous fluids. The second one is zero mass flux through a sphere around the source. Landau's solution was improved by Broman and Rudenko [13]. By means of symmetry methods [14, 15], they constructed some exact solutions of incompressible Navier–Stokes system corresponding to flows with non-zero mass flux and valid for inviscid fluids. It is worth to say that in [12] and [13], thermodynamics was out of consideration. One of the first authors who investigated thermodynamical properties of such flows was Squire [16]. Taking into account the equation of heat balance, he found the distribution of the temperature in the jet for incompressible fluids. Some singular solutions for incompressible and compressible fluids invariant with respect to subalgebras of the symmetry algebra of the Navier–Stokes equations were obtained in [17]. In [18], one-dimensional gas flow with phase transitions was studied, and the van der Waals equation was chosen as a model of thermodynamic state.

For modelling flows formed by means of source, we use Euler equations extended by equations of state of the medium. In case of one point source, we provide a method of finding corresponding solutions for various gases and thermodynamical processes.

This paper has the following structure. In Sect. 5.2, we show that thermodynamics is a particular case of measurement of random vectors [19]; namely, thermodynamics can be considered as a theory of measurement of extensive thermodynamical variables. Such a consideration leads us to the geometric formulation of thermodynamics previously established, for instance, in [20] an [21], but we decided to include this part, on the one hand, to show a new approach to thermodynamics based on measurement, and on the other hand, to make the paper self-contained. In Sect. 5.3, we discuss thermodynamics of gases and show how methods of contact and symplectic geometry can help us, in particular, in solution of practical issues concerning the determination of caloric equation of state for gases if we know a thermic one and description of phase transitions. In Sect. 5.4, we illustrate the methods developed on concrete models of real gases, paying special attention to phase transitions. In Sect. 5.5, we discuss basic equations describing filtration processes and Euler flows. We provide two theorems that give us solutions for the corresponding problems that can be applied to any gas as well as any process. In Sect. 5.6, we provide solutions for gases discussed in Sect. 5.4 and analyze phase transitions along the corresponding flows. In Sect. 5.7, we discuss the results.

5.2 Measurement and Thermodynamics

In this section, we describe the measurement of random vector procedure and show that the results can be naturally presented in terms of contact and symplectic geometries. The more comprehensive discussion can be found in [19].

5.2.1 Measurement of Random Vectors

Let $(\Omega, \mathcal{A}, p)$ be a probability space, i.e. Ω is a set, $\mathcal{A}$ is a σ-algebra and p is a probability measure. By a random vector, we shall mean the following map: $X\colon (\Omega, \mathcal{A}, p) \to W$, where W is a vector space, $\dim(W) = n$.

Let us suppose that we have a device that measures random vector X. It is natural to require that the result produced by such a device will be an *expectation*

$$\mathbb{E}(X) = \int\limits_{\Omega} X dp,$$

where the integration is assumed to be coordinate-wise. This is what we mean by a *measurement*.

Due to Jensen's inequality, it is easy to check that in this case, the expectation of length of vector $X - c$ for some $c \in W$ with respect to any metric g on W reaches its minimal value. Indeed,

$$\mathbb{E}\left(g(X - c, X - c)\right) \geq g(\mathbb{E}(X - c), \mathbb{E}(X - c)) = g(\mathbb{E}(X) - c, \mathbb{E}(X) - c) \geq 0,$$

and the equality to zero takes place iff $c = \mathbb{E}(X)$.

5.2.2 Information Gain

Let us now suppose that we have another probability measure q on our probability space $(\Omega, \mathcal{A}, p)$, which has the same set of measure zero sets as p has. Such measures are called *equivalent*, and we will denote it by $p \sim q$.

Define the so-called «surprise function» $s\colon \mathcal{A} \ni A \longmapsto s(A) \in \mathbb{R}$ by the following formula:

$$s(A) = -\ln(p(A)).$$

Note that this function satisfies the following properties:

1. $s(\Omega) = 0$, $s(\varnothing) = \infty$ and $s(A) \geq 0$;
2. if A and B are independent, i.e. $p(AB) = p(A)p(B)$, then $s(AB) = s(A) + s(B)$;
3. s is a continuous function of $p(A)$.

Properties (1)–(3) may also serve as a definition of the surprise function.

Let $\Omega = \{\omega_1, \ldots, \omega_n\}$ be a finite set and $p = \{p_1, \ldots, p_n\}$, $p_i = p(\omega_i)$ be a probability measure. In this case, the expectation of the surprise function is

$$S(p) = -\sum_{i=1}^{n} p_i \ln p_i .$$

The above formula coincides with Shannon's definition of entropy. Let $q = \{q_1, \ldots, q_n\}$ now be another probability measure equivalent to p. Then, the changing of the surprise function will be

$$s(p,q) = s(q) - s(p) = \left(-\sum_{i=1}^{n} \ln q_i\right) - \left(-\sum_{i=1}^{n} \ln p_i\right) = \sum_{i=1}^{n} \ln\left(\frac{p_i}{q_i}\right).$$

And the average $I(p,q)$ of $s(p,q)$ with respect to the measure p that is called *gain of information* will be

$$I(p,q) = \sum_{i=1}^{n} p_i \ln\left(\frac{p_i}{q_i}\right).$$

If $\Omega = \mathbb{R} = \bigcup_i [x_i, x_{i+1}]$ and $dp = f(x)dx$, $dq = g(x)dx$, then $I(p,q)$ takes the following form:

$$I(p,q) \approx \sum_i f(\xi_i)\Delta_i \ln\left(\frac{f(\xi_i)}{g(\xi_i)}\right),$$

where $\Delta_i = x_{i+1} - x_i$. Taking limit $\Delta_i \to 0$, $i \to \infty$, one gets

$$I(p,q) = \int_{\mathbb{R}} f(x) \ln\left(\frac{f(x)}{g(x)}\right) dx.$$

In case of arbitrary probability space $(\Omega, \mathcal{A}, p)$, the gain of information $I(p,q)$ is defined by the formula

$$I(p,q) = \int_{\Omega} \ln\left(\frac{dp}{dq}\right) dp. \tag{5.1}$$

The function $I(p,q)$ has the property $I(p,q) \geq 0$ and $I(p,q) = 0$ iff $p = q$ almost everywhere. At the same time, it cannot serve as a distance between measures p and q since it is not symmetric, i.e. $I(p,q) \neq I(q,p)$ and does not satisfy the triangle inequality.

In terms of density ρ, such that $dp = \rho dq$, (5.1) can be written as

$$I(\rho) = \int_{\Omega} \rho \ln \rho dq.$$

5.2.3 *The Principle of Minimal Information Gain*

Let $x \in W$ be a fixed vector which is expected to be the result of the measurement of random vector $X\colon (\Omega, \mathcal{A}, q) \to W$, i.e.

$$\mathbb{E}(X) = x.$$

Obviously, the given measure q may not give us the required vector x. This means that we should choose another measure p, such that $dp = \rho dq$. In other words, we are looking for a function ρ such that

$$\int\limits_{\Omega} \rho dq = 1, \quad \int\limits_{\Omega} \rho X dq = x. \tag{5.2}$$

Conditions in (5.2) are not enough to determine ρ. In addition to (5.2), we require that the new measure p is the closest one to the measure q with respect to the gain of information $I(\rho)$, i.e.

$$I(\rho) = \int\limits_{\Omega} \rho \ln \rho dq \to \min_{\rho}. \tag{5.3}$$

This is exactly what is called *the principle of minimal information gain*.

Thus, we have the following extremal problem. One needs to find the function ρ minimizing functional (5.3) under constraints in (5.2).

Theorem 5.1 *The solution of (5.2)–(5.3) is given by the following formulae:*

$$\rho = \frac{1}{Z(\lambda)} e^{\langle \lambda, X\rangle}, \quad Z(\lambda) = \int\limits_{\Omega} e^{\langle \lambda, X\rangle} dq, \tag{5.4}$$

where $\lambda \in W^*$. The results of the measurement with respect to extremal measure p belong to a manifold

$$L_H = \left\{ x = -\frac{\partial H}{\partial \lambda} \right\} \subset W \times W^*,$$

where $H(\lambda) = -\ln Z(\lambda)$.

Remark 5.1

1. The measure p defined by relations in (5.4) is called *the extremal measure*.
2. The function $Z(\lambda)$ is called *the partition function* and, obviously, exists iff $\langle \lambda, X\rangle \leq 0$ almost everywhere.

3. The integral $Z(\lambda) = \int\limits_{\Omega} e^{\langle\lambda, X\rangle} dq$ can be expressed in terms of vector space W only:

$$Z(\lambda) = \int\limits_{W} e^{\langle\lambda, t\rangle} d\mu(t),$$

where $\mu = X_*(q)$.

Proof Consider the functional

$$\mathcal{L} = \int\limits_{\Omega} \rho \ln \rho dq - \lambda_0 \left(\int\limits_{\Omega} \rho dq - 1 \right) - \left\langle \lambda, \int\limits_{\Omega} \rho X dq - x \right\rangle.$$

Since its first variation with respect to ρ should be equal to zero, we get

$$\delta\mathcal{L} = \int\limits_{\Omega} (\ln \rho + 1 - \lambda_0 - \langle\lambda, X\rangle) \delta\rho dq = 0,$$

from what follows that

$$\rho = \exp(\lambda_0 - 1 + \langle\lambda, X\rangle).$$

Taking into account that $\int\limits_{\Omega} \rho dq = 1$, we get

$$\rho = \frac{1}{Z(\lambda)} e^{\langle\lambda, X\rangle}, \text{ where } Z(\lambda) = \int\limits_{\Omega} e^{\langle\lambda, X\rangle} dq.$$

Note that

$$\frac{\partial Z}{\partial \lambda} = \int\limits_{\Omega} X e^{\langle\lambda, X\rangle} dq = \int\limits_{\Omega} X \rho Z(\lambda) dq = Z(\lambda) x,$$

from what follows that

$$\frac{\partial}{\partial \lambda} (\ln Z(\lambda)) = x.$$

Introducing the Hamiltonian $H(\lambda) = -\ln Z(\lambda)$, we get

$$x = -\frac{\partial H}{\partial \lambda}. \tag{5.5}$$

One can see that the manifold $L_H \subset (\Phi, \omega)$ is Lagrangian with respect to nondegenerate closed 2-form on $\Phi = W \times W^*$

$$\omega = d\lambda \wedge dx = \sum_{i=1}^{n} d\lambda_i \wedge dx_i,$$

i.e. $\omega|_{L_H} = 0$.

A pair (Φ, ω) represents the standard model of symplectic space. Moreover, the Lagrangian manifold L_H gives us information about both extreme measure p and expectation of random vector X; namely, λ is responsible for the corresponding extremal measure, while x represents the expectation.

Let us introduce a new function

$$J(\lambda, x) = H(\lambda) + \langle \lambda, x \rangle.$$

Using Theorem 5.1, it is easy to show that there is a following relation between I and J:

$$J|_{L_H} = I. \tag{5.6}$$

Let us consider the differential of J:

$$dJ = \sum_i \left(\frac{\partial H}{\partial \lambda_i} + x_i \right) d\lambda_i + \sum_i \lambda_i dx_i = \sum_i \left(\frac{\partial H}{\partial \lambda_i} + x_i \right) d\lambda_i + \theta,$$

where 1-form θ has the following structure:

$$\theta = \sum_i \lambda_i dx_i.$$

On the surface L_H, we have

$$dJ|_{L_H} = \theta|_{L_H}. \tag{5.7}$$

From (5.6) and (5.7), it follows that

$$\theta|_{L_H} = dI. \tag{5.8}$$

Now, we construct the contactization $\tilde{\Phi}$ of Φ as

$$\tilde{\Phi} = \mathbb{R} \times \Phi = \mathbb{R} \times W \times W^* = \mathbb{R}^{2n+1}(u, x, \lambda)$$

and equip $\tilde{\Phi}$ with the contact 1-form

$$\tilde{\theta} = du - \theta. \tag{5.9}$$

Thus, $(\tilde{\Phi}, \tilde{\theta})$ is a contact space.

Let $a = (\lambda, x) \in L_H$, and let $\tilde{L} \subset \tilde{\Phi}$ be a submanifold of dimension n such that

$$\tilde{L} = \left\{ u = I(a), \quad x = -\frac{\partial H}{\partial \lambda} \right\}. \tag{5.10}$$

Note that $\tilde{L}$, being constructed in such a way, becomes a Legendrian submanifold, i.e.

$$\tilde{\theta}|_{\tilde{L}} = 0.$$

Indeed, due to (5.8),

$$\tilde{\theta}|_{\tilde{L}} = (du - \theta)|_{\tilde{L}} = dI - \theta|_{L_H} = 0.$$

Moreover, the Legendrian manifold $\tilde{L}$ provides the knowledge about not only extreme measure p and expectation of random vector X but also information gain $I(p, q)$.

Note that in general, Eq. (5.5), being considered as an equation for λ, may have a number of roots $\lambda = \lambda^{(j)}(x)$. Let us represent vector space W as a union $W = \bigcup\limits_i D_i$, such that Eq. (5.5) can be resolved with respect to λ uniquely for any $x \in D_i$. In other words, in each domain D_i, the function x may serve as local coordinates on L_H as well as λ. This implies that the Lagrangian manifold L_H can be represented as $L_H = \bigcup\limits_i L_i$, where

$$L_i = \left\{ x \in D_i \mid x = -\frac{\partial H}{\partial \lambda}, \right\}.$$

We shall call such domains L_i *phases*.

Thus, the results of the measurement of random vectors obtained by using the minimal information gain principle can be presented by means of either Legendrian submanifold in contact space $\tilde{L} \subset (\tilde{\Phi}, \tilde{\theta})$ or Lagrangian submanifold in symplectic space $L_H \subset (\Phi, \omega = -d\tilde{\theta})$, and all necessary functions ρ, $Z(\lambda)$, $H(\lambda)$, $I(p, q)$ can be directly derived from them.

5.2.4 Variance of Random Vectors

First of all, let us recall that the *second moment* of a random vector $X\colon (\Omega, \mathcal{A}, p) \to W$ is a symmetric 2-form $\mu_2(X) \in S^2(W)$

$$\mu_2(X) = \int_{\Omega} X(\omega) \otimes X(\omega) dp.$$

Central second moment or *variance* is a symmetric 2-form $\sigma_2(X) \in S^2(W)$

$$\sigma_2(X) = \mu_2(X - \mu_1(X)) = \mu_2(X) - \mu_1(X) \otimes \mu_1(X).$$

Let $\mathrm{Hess}(H)$ be the Hessian of the Hamiltonian H:

$$\mathrm{Hess}(H) = \sum_{i,j} \frac{\partial^2 H}{\partial \lambda_i \partial \lambda_j} d\lambda_i \otimes d\lambda_j.$$

Theorem 5.2 *The variance $\sigma_2(X)$ of a random vector X is equal to $-\mathrm{Hess}(H)$:*

$$\sigma_2(X) = -\mathrm{Hess}(H).$$

Let us define the differential quadratic form κ on Φ by the following way:

$$\kappa = \frac{1}{2} \sum_i (d\lambda_i \otimes dx_i + dx_i \otimes d\lambda_i) = d\lambda \cdot dx.$$

This differential quadratic form being restricted onto the manifold L_H takes the form

$$\kappa|_{L_H} = \frac{1}{2} \sum_i (d\lambda_i \otimes dx_i + dx_i \otimes d\lambda_i)\Big|_{\left\{x = -\frac{\partial H}{\partial \lambda}\right\}} = -\mathrm{Hess}(H) = \sigma_2(X).$$

Since the variance is non-negative, the differential quadratic form $\kappa|_{L_H}$ must be non-negative.

Thus, the manifold $\Phi = W \times W^*$ is equipped with two structures:

- symplectic structure

$$\omega = d\lambda \wedge dx,$$

- pseudo-Riemannian structure of signature (n, n)

$$\kappa = d\lambda \cdot dx.$$

The measurement procedure of a random vector $X\colon (\Omega, \mathcal{A}, p) \to W$ is presented by the Lagrangian manifold $L_H \subset (\Phi, \omega)$ that has to be Riemannian manifold with respect to the quadratic differential form $\kappa|_{L_H}$. The last requirement leads us to the notion of *applicable phases*, i.e. Riemannian submanifolds of L_H, where both x and λ may serve as coordinates.

5.2.5 Thermodynamics

Here, we show that all above constructions allow us to consider thermodynamics as a measurement of extensive variables, such as energy, volume and mass.

First of all, one of the basic laws of thermodynamics, the energy conservation law, claims that the heat is consumed by the physical system for the changing of its internal energy and work, and particularly for gas-like systems, it has the form (here, we pretend that we already know the first part of the second law of thermodynamics $\delta Q = TdS$)

$$dS = T^{-1}dE + pT^{-1}dV - \gamma T^{-1}dm, \tag{5.11}$$

where S is the entropy, T is the temperature, p is the pressure, γ is the chemical potential, E is the energy, V is the volume and m is the mass.

It is absolutely clear from the physical point of view what is written in (5.11). But mathematically, we can see the identity of two 1-forms, which is possible iff $S =$ const, $V =$ const, $E =$ const and $m =$ const. Moreover, the second part of the second law of thermodynamics claims that

$$dS > 0$$

for irreversible processes, which means that we can compare differential 1-forms with zero.

All these issues of mathematical nature, together with a notion that (5.11) reminds us the similar contact structure appearing in measurement theory, drive us to consider thermodynamics as a theory of measuring extensive variables $(E, V, m) \in W$. The fact that W is a vector space corresponds to the additivity properties of extensives. Then, intensives $(-T^{-1}, -pT^{-1}, \gamma T^{-1}) \in W^*$ may serve as Lagrangian multipliers λ that we have seen in the above discussion. Once we put $n = 3$ and assign $(x_1, x_2, x_3) = (E, V, m)$ and $(\lambda_1, \lambda_2, \lambda_3) = (-T^{-1}, -pT^{-1}, \gamma T^{-1})$, we are able to reformulate the laws of thermodynamics in the following way:

- **The first law of thermodynamics**
  The state of any thermodynamical system described by intensives (p, T, γ), extensives (E, V, m) and entropy S is a Legendrian manifold $\tilde{L} \subset (\tilde{\Phi}, \tilde{\theta})$, where $\tilde{\Phi} = \mathbb{R} \times W \times W^*$, i.e. maximal integral manifold of the form

$$\tilde{\theta} = d(-S) - (-T^{-1})dE - (-pT^{-1})dV - (\gamma T^{-1})dm. \tag{5.12}$$

Comparing (5.12) with (5.9) and (5.10), we conclude that the following relation holds:

$$dI = -dS. \tag{5.13}$$

The postulate that the variance of random vectors is positive gives us what we will mean by the second thermodynamical law, and what in classical thermodynamics is usually called "conditions of thermodynamical stability". Below, in Sect. 5.3, we will show the explanation.

- **The second law of thermodynamics**
  The immersed Lagrangian manifold $L \subset (\Phi, \Omega = -d\tilde{\theta})$ obtained by restriction of natural projection $\pi : \tilde{\Phi} \to \Phi, \pi(S, E, V, m, p, T, \gamma) = (E, V, m, p, T, \gamma)$, which is a local diffeomorphism, onto the Legendrian manifold $\tilde{L}$ is equipped with the differential quadratic form

  $$\kappa = d(-T^{-1}) \cdot dE + d(-pT^{-1}) \cdot dV + d(\gamma T^{-1}) \cdot dm,$$

  and the only applicable domains on L are those ones where the form κ is positive.

From (5.13), one can conclude that the well-known entropy increasing law for irreversible processes (for example, the establishment of thermodynamical equilibrium between two systems) is the principle of minimal information gain from the measurement viewpoint.

From (5.13), it also follows that

$$S = -I + \alpha_0.$$

Since the information gain I is always greater than zero, the entropy has to be $S \leq \alpha_0$. This can be interpreted as the third law of thermodynamics.

5.3 Thermodynamics of Gases

Now that we have declared that thermodynamic states are Legendrian or Lagrangian surfaces in the corresponding contact or symplectic space, and we can give a more accurate description of gases in the form appropriate for further purposes, namely, the analysis of critical phenomena in filtration processes and Euler flows.

5.3.1 Specific Variables

First of all, we introduce the so-called *specific* thermodynamic variables by the following way. Let $S = S(E, V)$ be a function on the Legendrian surface $\tilde{L}$. Due to additive properties of the entropy S, the function $S(E, V)$ has to be homogeneous of degree 1 with respect to the mass of the system, i.e.

$$S(E, V, m) = mS\left(\frac{E}{m}, \frac{V}{m}\right).$$

Introduce the notation: $e = E/m$, $v = V/m$, $S\left(\frac{E}{m}, \frac{V}{m}\right) = s(e, v)$, and call e the specific energy, v the specific volume and $s(e, v)$ the specific entropy. Then, in terms of specific variables, the form $\tilde{\theta}$ can be written as

$$\tilde{\theta} = \left(-s + T^{-1}e + pT^{-1}v - \gamma T^{-1}\right) dm + \left(-ds + T^{-1}de + pT^{-1}dv\right) m.$$

If a thermodynamic state $\tilde{L}$ is now given by a function $s = s(e, v)$, then

$$\gamma = e - Ts + pv, \quad \left(-ds + T^{-1}de + pT^{-1}dv\right)\Big|_{\tilde{L}} = 0. \tag{5.14}$$

The differential quadratic form κ on L will take the form

$$\kappa = -m\left(d(T^{-1}) \cdot de + d(pT^{-1}) \cdot dv\right),$$

and since applicable domains are defined by the positivity of κ and mass m is assumed to be positive, the applicability condition is formulated as negativity of the form $-m^{-1}\kappa$, which we will continue, denoting by κ:

$$\kappa = d(T^{-1}) \cdot de + d(pT^{-1}) \cdot dv. \tag{5.15}$$

Since $G = E - TS + pV$ is the Gibbs free energy, $\gamma = e - Ts + pv$ is the specific Gibbs free energy.

5.3.2 Legendrian and Lagrangian Manifolds for Gases

Relation (5.14) allows us to define Legendrian surfaces by means of specific variables. Indeed, consider the contact space $(\mathbb{R}^5, \theta)$ equipped with coordinates (s, e, v, p, T) and contact 1-form

$$\theta = -ds + T^{-1}de + pT^{-1}dv.$$

Then, a thermodynamic state is a Legendrian manifold $\tilde{L}$, such that $\theta|_{\tilde{L}} = 0$. For a given function $s = s(e, v)$, this manifold is defined by relations:

$$s = s(e, v), \quad T = \frac{1}{s_e}, \quad p = \frac{s_v}{s_e}.$$

In practice, we actually do not have the function $s(e, v)$, because there are no devices that would allow us to measure the specific entropy $s(e, v)$. This brings us to the necessity of eliminating s from our consideration. To this end, we introduce the projection $\pi : \mathbb{R}^5 \to \mathbb{R}^4$, $\pi(s, e, v, p, T) = (e, v, p, T)$. Its restriction onto the Legendrian manifold $\tilde{L}$ is an immersed Lagrangian manifold $L = \pi(\tilde{L})$, while $\mathbb{R}^4$ is equipped with the symplectic form

$$\Omega = d\theta = d(T^{-1}) \wedge de + d(pT^{-1}) \wedge dv,$$

which vanishes on L: $\Omega|_L = 0$. The Lagrangian manifold $L \subset (\mathbb{R}^4, \Omega)$ is given by the two functions

$$f(e, v, p, T) = 0, \quad g(e, v, p, T) = 0. \tag{5.16}$$

The condition that L is Lagrangian is expressed by vanishing of the Poisson bracket $[f, g]$ on L, i.e. $[f, g]|_L = 0$, where

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

This bracket in coordinates is of the form

$$[f, g] = \frac{1}{2}\Big(pT\left(f_p g_e - f_e g_p\right) + T^2\left(f_T g_e - f_e g_T\right) + T\left(f_v g_p - f_p g_v\right)\Big).$$

In thermodynamics of gases, the functions in (5.16) usually have the form

$$f(e, v, p, T) = p - A(v, T), \quad g(e, v, p, T) = e - B(v, T). \tag{5.17}$$

The first equation of state in (5.17) is called *thermic*, and the second one is called *caloric*. From experiments, one can obtain the first state equation, but not the second one, because we have no devices that measure the specific energy. But having known the first equation and using the compatibility condition $[f, g]|_L = 0$, one gets the caloric equation, and therefore the Lagrangian surface for a given gas becomes completely determined. Then, relations

$$T = \frac{1}{s_e}, \quad p = \frac{s_v}{s_e} \tag{5.18}$$

can be considered as an overdetermined system for $s(e, v)$, which is compatible due to $[f, g]|_L = 0$. Solving (5.18), we get unknown function $s(e, v)$ and therefore define the Legendrian manifold $\tilde{L}$ completely.

Let us take the Poisson bracket between $f(e, v, p, T)$ and $g(e, v, p, T)$ in the form (5.17). Then, we get

$$(T^{-2}B)_v = (T^{-1}A)_T,$$

from what follows that the following theorem is valid.

Theorem 5.3 *The Lagrangian manifold L is given by the Massieu–Planck potential* $\phi(v, T)$*:*

$$p = RT\phi_v, \quad e = RT^2\phi_T, \tag{5.19}$$

and the specific entropy s *and Gibbs free energy* γ *are*

$$s = R(\phi + T\phi_T), \quad \gamma = RT(v\phi_v - \phi), \tag{5.20}$$

where $R = 8.314\ J \cdot K^{-1} \cdot \mathrm{mol}^{-1}$ *is the universal gas constant.*

Using (5.19), it is easy to show that the differential quadratic form (5.15) can be expressed as follows:

$$R^{-1}\kappa = -\left(\phi_{TT} + 2T^{-1}\phi_T\right) dT \cdot dT + \phi_{vv} dv \cdot dv.$$

Hence, applicable domains are defined by inequalities

$$\phi_{TT} + 2T^{-1}\phi_T > 0, \quad \phi_{vv} < 0. \tag{5.21}$$

From (5.21) and (5.19), it follows that applicable states are also given by

$$e_T > 0, \quad p_v < 0. \tag{5.22}$$

It is worth to say that relations in (5.22) are usually called *conditions of thermodynamical stability* with respect to thermic and mechanical perturbations, respectively.

5.3.3 Singularities of Lagrangian Manifolds and Phase Transitions

Let us now explore singularities of projections of the Lagrangian manifold L to spaces of intensive variables (p, T) and extensive variables (v, e). The singularities of the first type occur where the differential form $dp \wedge dT$ degenerates and coincides with the set where $\phi_{vv} = 0$. The singularities of the second type are the points where $de \wedge dv = 0$, or, equivalently, $\phi_{TT} + 2T^{-1}\phi_T = 0$. Thus, the set where the Lagrangian manifold L has singularities is exactly the set where the differential quadratic form κ degenerates. We will consider such Lagrangian manifolds that (e, v) serve as global coordinates on them. This means that L in our consideration will have no singularities of the second type, and since κ has to be negative, the inequality $\phi_{TT} + 2T^{-1}\phi_T > 0$ holds everywhere on L. Domains of the manifold L that have no singularities and on which the form κ is negative definite, we have already called *applicable phases*. Consequently, if κ is nondegenerate and negative on the entire manifold L, and therefore L has no singularities of its projections to the space of intensive variables as well, then a thermodynamical system corresponding to such a Lagrangian manifold L has only one phase, otherwise it has a number of phases, separated from one another by the set where κ is non-negative, or, where $\phi_{vv} \geq 0$. In the last case, thermodynamical system has a remarkable property called *phase transitions of the first type*.

Definition 5.1 A jump from one applicable point $(e_1, v_1) \in L$ to another applicable point $(e_2, v_2) \in L$, governed by the intensive variables (p, T) and the specific Gibbs potential γ conservation law, is called *phase transition of the first type*.

A set of points where phase transition occurs is a curve on the Lagrangian manifold L, which is called *coexistence* or *binodal* curve. Using (5.19) and (5.20), one gets the following equations for the coexistence curve $\Gamma \subset \mathbb{R}^3(p, v, T)$ [4]:

$$\phi_v(v_2, T) = \frac{p}{RT}, \quad \phi_v(v_1, T) = \frac{p}{RT}, \tag{5.23}$$

$$\phi(v_2, T) - \phi(v_1, T) - v_2\phi_v(v_2, T) + v_1\phi_v(v_1, T) = 0. \tag{5.24}$$

Thus, solving (5.23), we define the location for phases of thermodynamical system on the corresponding Lagrangian manifold L.

5.4 Examples of Gases

In this section, we discuss various models of real gases and show how above methods can be applied to the analysis of gases. We provide a detailed description for models of real gases, which are extremely important for applications—van der Waals, Peng–Robinson and Redlich–Kwong models.

5.4.1 Ideal Gases

We start with the simplest model of gases—ideal gases. The Lagrangian manifold L for ideal gases is given by equations

$$f(e, v, p, T) = p - Rv^{-1}T, \quad g(e, v, p, T) = e - \frac{nRT}{2}, \tag{5.25}$$

where n is the degree of freedom. The first equation in (5.25) is called *Mendeleev–Clapeyron* equation.

The Legendrian manifold $\tilde{L}$ is defined by (5.25) extended by

$$s = R\ln\left(T^{n/2}v\right) + \frac{Rn}{2}.$$

The Massieu–Planck potential coincides with the specific entropy s (up to a multiplicative constant R):

$$\phi = \ln\left(T^{n/2}v\right).$$

And finally, the differential quadratic form κ for ideal gases is

$$\kappa = -\frac{Rn}{2T^2}dT \cdot dT - Rv^{-2}dv \cdot dv.$$

One can see that κ is negative; therefore, the Lagrangian manifold L for ideal gases has no singularities, and there are no phase transitions.

5.4.2 *Van der Waals Gases*

The van der Waals model is historically the first one admitting phase transitions of gas–liquid type. The thermic equation is of the form:

$$f(e, v, p, T) = p - \frac{RT}{v-b} + \frac{a}{v^2},$$

where a and b are constants responsible for the interaction between particles and their volume, respectively. Note that in case $a = 0$ and $b = 0$, one gets the ideal gas state equation.

To find out the second equation of state, we assume that $g(e, v, p, T) = e - B(v, T)$ and take the Poisson bracket $[f, g]$. Since it should be zero on the Lagrangian surface, we get the following equation for $B(v, T)$:

$$v^2 B_v - a = 0,$$

from what follows that $B(v, T) = F(T) - a/v$. Putting $a = 0$ and $b = 0$, we get an ideal gas, and the caloric equation for van der Waals gases is of the form

$$g(e, v, p, T) = e - \frac{nRT}{2} + \frac{a}{v}.$$

Let us now resolve system (5.18) for van der Waals gases. The result will be (up to additive constant)

$$s(v,T) = R\ln\Big(T^{n/2}(v-b)\Big) + \frac{Rn}{2}.$$

The Massieu–Planck potential has the following form:

$$\phi(v,T) = \ln\Big(T^{n/2}(v-b)\Big) + \frac{a}{vRT}.$$

Finally, the differential quadratic form κ for van der Waals gases is [1, 4]

$$\kappa = -\frac{Rn}{2T^2}dT\cdot dT - \frac{v^3RT - 2a(v-b)^2}{v^3T(v-b)^2}dv\cdot dv.$$

We can see that the first component of κ is negative, while the second one can change its sign. Therefore, the Lagrangian manifold has singularities of projections to the plane of intensive variables (p, T). The curve in coordinates (T, v) where the differential quadratic form κ changes its sign, which is also called *spinodal curve* given by

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

This function has a maximum at point $v_{\text{crit}} = 3b$, and it equals $T_{\text{crit}} = 8a/27Rb$. The temperature T_{crit} is called *critical temperature*, and if $T > T_{\text{crit}}$, the differential quadratic form κ is negative. The corresponding critical values for pressure p_{crit}, energy e_{crit} and entropy s_{crit} could be found as well. It is more convenient to work with dimensionless thermodynamic variables. To this end, we introduce the following contact scale transformation:

$$T \longmapsto \frac{T}{T_{\text{crit}}}, \quad v \longmapsto \frac{v}{v_{\text{crit}}}, \quad p \longmapsto \frac{p}{p_{\text{crit}}}, \quad e \longmapsto \frac{e}{e_{\text{crit}}}, \quad s \longmapsto \frac{s}{s_{\text{crit}}},$$

where T_{crit}, v_{crit}, p_{crit}, e_{crit} and s_{crit} are critical parameters for van der Waals gases:

$$T_{\text{crit}} = \frac{8a}{27Rb}, \quad v_{\text{crit}} = 3b, \quad p_{\text{crit}} = \frac{a}{27b^2}, \quad e_{\text{crit}} = \frac{a}{9b}, \quad s_{\text{crit}} = \frac{3R}{8};$$

then, we get the reduced equations of state in new dimensionless coordinates, which we will continue, denoting by p, T, e and v:

$$p = \frac{8T}{3v-1} - \frac{3}{v^2}, \qquad e = \frac{4n}{3}T - \frac{3}{v}.$$

One can easily show that the Massieu–Planck potential and the specific entropy for van der Waals gases take the form:

$$\phi = \ln\left(T^{n/2}(3v-1)\right)+\frac{9}{8vT}+C_\phi, \quad s = \ln\left(T^{4n/3}\,(3v-1)^{8/3}\right)+C_s, \tag{5.26}$$

where constants C_ϕ and C_s are

$$C_\phi = \ln\left(\left(\frac{2}{3}\right)^{3n/2}\left(\frac{a}{bR}\right)^{n/2} b\right), \quad C_s = \frac{4n}{3} + \ln\left(\left(\frac{2}{3}\right)^{4n}\left(\frac{a}{bR}\right)^{4n/3} b^{8/3}\right).$$

And the differential quadratic form becomes

$$\kappa = -\frac{Rn}{2}\frac{dT^2}{T^2} - \frac{9R(4Tv^3 - 9v^2 + 6v - 1)}{4Tv^3(3v-1)^2}dv^2.$$

The spinodal curve together with the coexistence curve in coordinates (p, T) for van der Waals gases is presented in Fig. 5.1. The equations for the coexistence curve in reduced coordinates have the form [4]:

$$\begin{aligned}\frac{3p}{8T} &= \frac{3}{3v_{1,2}-1} - \frac{9}{8v_{1,2}^2T}, \quad \frac{(3v_1-1)(3v_2-1)(v_1+v_2)}{v_1-v_2}\ln\left(\frac{3v_2-1}{3v_1-1}\right)\\ &= 3(v_1+v_2-6v_1v_2),\end{aligned}$$

and the coexistence curve together with the spinodal curve for van der Waals gases in coordinates (p, v) is presented in Fig. 5.2.

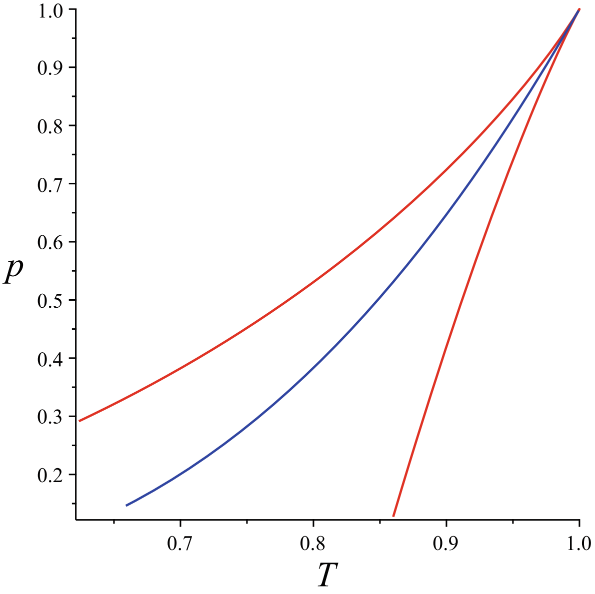
Both curves on the Lagrangian manifold for van der Waals gases are shown in Fig. 5.3. The area on the left of the coexistence curve corresponds to the liquid phase, and the right area is the gas phase. The area inside the coexistence curve is a condensation of the gas, and the area between the coexistence and spinodal curves corresponds to possible thermodynamic states, but dramatically unstable. On the left, such states are called *overheated liquid*, while the right one is *overcooled gas*.

5.4.3 Peng–Robinson Gases

Another very important model of real gases is Peng–Robinson model proposed in [22]. It appeared to be effective in description of hydrocarbons. The first state equation has the following form:

$$f(p, T, e, v) = p - \frac{RT}{v-b} + \frac{a}{(v+b)^2 - 2b^2},$$

Fig. 5.1 Spinodal curve (red) and coexistence curve (blue) for van der Waals gases in coordinates (p, T)



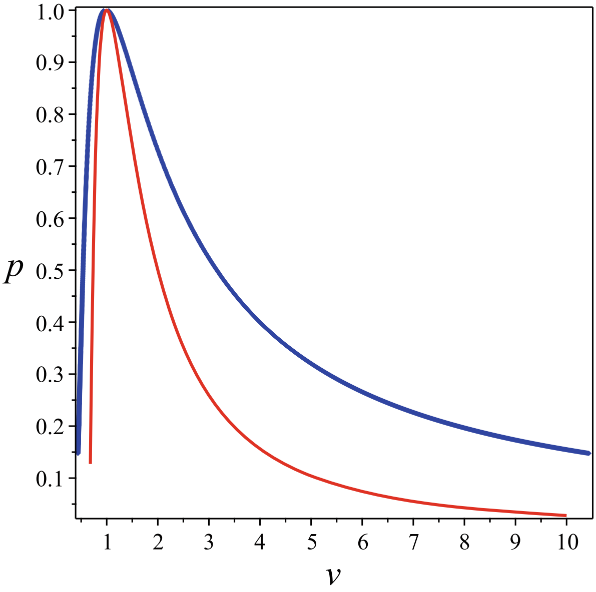


Fig. 5.2 Spinodal curve (red) and coexistence curve (blue) for van der Waals gases in coordinates (p, v)

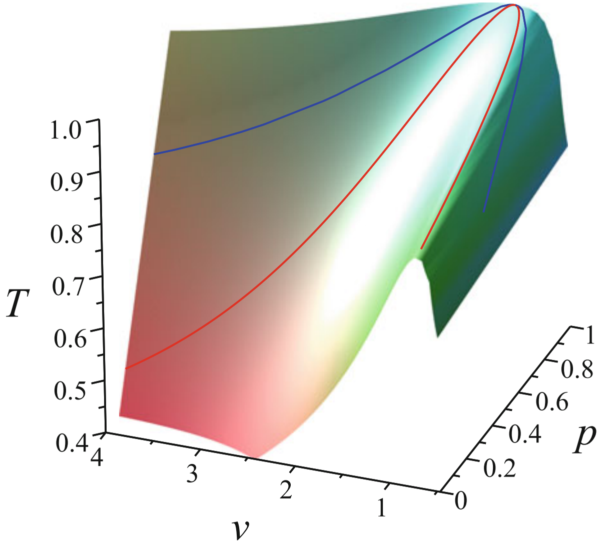


Fig. 5.3 Lagrangian manifold for van der Waals gases together with spinodal (red) and coexistence (blue) curves

where constants a and b are responsible for particles' interaction and their volume, respectively, as in the van der Waals model. The compatibility condition leads us to the following caloric equation of state:

$$g(p, T, e, v) = e - \frac{nRT}{2} - \frac{a\sqrt{2}}{4b} \ln\left(\frac{v + b - \sqrt{2}b}{v + b + \sqrt{2}b}\right).$$

As in case of van der Waals gases, let us introduce the contact scale transformation

$$p \longmapsto \frac{a}{b^2}p, \quad T \longmapsto \frac{a}{bR}T, \quad e \longmapsto \frac{a}{b}e, \quad v \longmapsto bv, \quad s \longmapsto Rs.$$

The reduced Peng–Robinson state equations are

$$p = \frac{T}{v-1} - \frac{1}{(v+1)^2 - 2}, \quad e = \frac{nT}{2} + \frac{\sqrt{2}}{4} \ln\left(\frac{v + 1 - \sqrt{2}}{v + 1 + \sqrt{2}}\right),$$
$$s = \ln\left(T^{n/2}(v-1)\right) + \frac{n}{2} + \ln\left(\left(\frac{a}{bR}\right)^{n/2} b\right).$$

The Massieu–Planck potential ϕ for Peng–Robinson gases is

$$\phi(v,T)=\ln\left(T^{n/2}(v-1)\right)-\frac{\sqrt{2}}{4T}\ln\left(\frac{(3-2\sqrt{2})(v\sqrt{2}+v-1)}{v\sqrt{2}-v+1}\right)+\ln\left(\left(\frac{a}{bR}\right)^{n/2}b\right).$$

The differential quadratic form κ has the form

$$R^{-1}\kappa=-\frac{n}{2T^2}dT\cdot dT-\frac{Tv^4+2(2T-1)v^3+2(T+1)v^2-2(2T-1)v+T-2}{T(v-1)^2(v^2+2v-1)^2}dv\cdot dv.$$

Therefore, the singular set of the Lagrangian manifold for Peng–Robinson gases can be found from

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

As in case of van der Waals gases, there is a critical point $(T_{\text{crit}}, v_{\text{crit}})$, such that if $T > T_{\text{crit}}$, then the differential quadratic form κ is negative for any v.

Theorem 5.4 ([3]) *The critical temperature for Peng–Robinson gases* T_{crit} *and the corresponding critical volume* v_{crit} *are defined as follows:*

$$v_{\text{crit}}=1+2(4+2\sqrt{2})^{-1/3}+(4+2\sqrt{2})^{1/3},\quad T_{\text{crit}}=\frac{2(v_{\text{crit}}+1)(v_{\text{crit}}-1)^2}{(v_{\text{crit}}^2+2v_{\text{crit}}-1)^2}.$$

The coexistence curve for Peng–Robinson gases in coordinates (p, v, T) is presented in Fig. 5.4 and is of similar form as for van der Waals gases.

5.4.4 Redlich–Kwong Gases

The next model of real gases is the Redlich–Kwong model. It was proposed in [23] and became of wide popularity in filtration processes. The thermic equation of state for Redlich–Kwong gases is

$$f(p,T,v,e)=p-\frac{RT}{v-b}+\frac{a}{\sqrt{T}v(v+b)}. \tag{5.27}$$

If one takes the Poisson bracket $[f,g]|_L$, where $g(e,v,p,T)=e-B(v,T)$, one gets the following equation for $B(v,T)$:

$$3a-2v\sqrt{T}(v+b)B_v=0,$$

which has solution

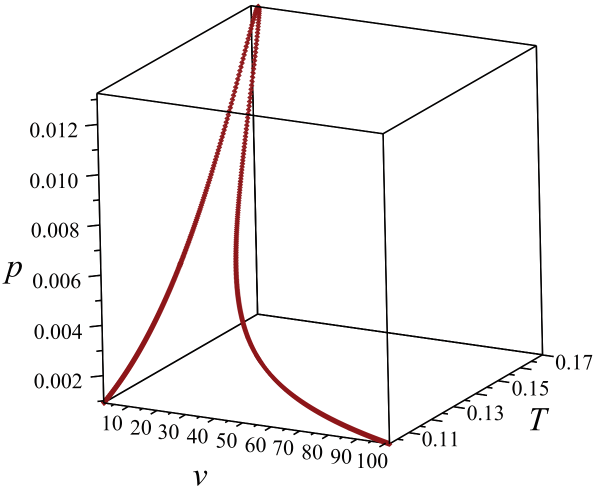


Fig. 5.4 Coexistence curve for Peng–Robinson gases

$$B(v,T)=F(T)+\frac{3a}{2b\sqrt{T}}\ln\left(\frac{v}{v+b}\right).$$

Again, $F(T)$ has to be defined as $F(T)=nRT/2$, and the Lagrangian manifold for Redlich–Kwong gases is given by (5.27) together with [2]

$$g(p,T,v,e)=e-\left(\frac{nRT}{2}+\frac{3a}{2b\sqrt{T}}\ln\left(\frac{v}{v+b}\right)\right). \tag{5.28}$$

Resolving the equation for the specific entropy s as described in Sect. 5.2, we get

$$s(v,T)=\frac{Rn}{2}\ln T+R\ln(v-b)+\frac{a}{2bT^{3/2}}\ln\left(\frac{v}{v+b}\right)+\frac{Rn}{2}. \tag{5.29}$$

Thus, the Legendrian manifold $\tilde{L}$ is defined by (5.27), (5.28) and (5.29).

The contact scale transformation

$$p\longmapsto\left(\frac{Ra^2}{b^5}\right)^{1/3}p,\quad T\longmapsto\left(\frac{a}{Rb}\right)^{2/3}T,\quad v\longmapsto bv,$$

$$e\longmapsto\left(\frac{Ra^2}{b^2}\right)^{1/3}e,\quad s\longmapsto Rs$$

gives us reduced state equations [2]:

$$p=\frac{T}{v-1}-\frac{1}{\sqrt{T}v(v+1)},\quad e=\frac{nT}{2}+\frac{3}{2\sqrt{T}}\ln\left(\frac{v}{v+1}\right), \tag{5.30}$$

$$s = \ln\left(T^{n/2}(v-1)\right) + \frac{1}{2T^{3/2}}\ln\left(\frac{v}{v+1}\right) + \frac{n}{2} + \ln\left(\left(\frac{a}{Rb}\right)^{n/3} b\right). \quad (5.31)$$

The Massieu–Planck potential is of the form

$$\phi(v,T) = \ln\left(T^{n/2}(v-1)\right) - \frac{1}{T^{3/2}}\ln\left(\frac{v}{v+1}\right) + \ln\left(b\left(\frac{a}{Rb}\right)^{n/3}\right).$$

The differential quadratic form κ is

$$\begin{aligned}\kappa R^{-1} = &-\left(\frac{n}{2T^2} + \frac{3}{4T^{7/2}}\ln(1+v^{-1})\right) dT \cdot dT \\ &- \frac{v^2(v+1)^2T^{3/2} - 2v^3 + 3v^2 - 1}{T^{3/2}(v+1)^2v^2(v-1)^2} dv \cdot dv.\end{aligned}$$

Note that in case of Redlich–Kwong gases, the first component of the differential quadratic form κ depends on the specific volume v. But since pressure p and temperature T are assumed to be positive, from (5.30), it follows that only $v > 1$ have sense, and therefore, the component mentioned is negative, and the projection of the Lagrangian manifold to (e, v) for Redlich–Kwong gases has no singularities.

Spinodal and coexistence curves for Redlich–Kwong gases can be elaborated in the same way as for van der Waals and Peng–Robinson gases and can be found in [2].

5.5 Basic Equations

Thermodynamics of real gases discussed in previous sections forms a base for the analysis of gas dynamics, since, as we will see further, equations describing dynamics significantly depend on thermodynamical properties. In this section, we formulate the problem and provide general solutions for stationary Darcy and Euler flows.

The system of equations describing one-component filtration of gases in porous media (Darcy flows) or inviscid gas flow (Euler flow) consists of [6–8]

1. The momentum conservation law
    - the Darcy law (for filtration processes)

$$\mathbf{u} = -\frac{k}{\mu}\nabla p, \quad (5.32)$$

where $\mathbf{u}(x) = (u_1, u_2, u_3)$ is the velocity field, $x \in D \subset \mathbb{R}^3$, $p(x)$ is the pressure, $k = k(v, T)$ and $\mu = \mu(v, T)$ are the coefficients of permeability and viscosity, respectively, which are the functions of the medium.

- the Euler equation (for inviscid gases)

$$\rho(\mathbf{u}, \nabla)\mathbf{u} = -\nabla p, \tag{5.33}$$

where $\rho(x) = v^{-1}(x)$ is the density.

2. The mass conservation law

$$\mathrm{div}(\rho \mathbf{u}) = 0. \tag{5.34}$$

In addition to (5.32), (5.33) and (5.34), we assume that the flows of both kinds are adiabatic, i.e. the specific entropy s is constant along the trajectories of the velocity field $\mathbf{u}$:

$$(\mathbf{u}, \nabla s) = 0. \tag{5.35}$$

One can see that the system (5.32) or (5.33) together with (5.34) and (5.35) is incomplete. It is quite expectable, since we have not yet specified the medium above Eqs. (5.32)–(5.35) are written for. It can be done by means of equations of state (Legendrian manifold)

$$p = RT\phi_v, \quad e = RT^2\phi_T, \quad s = R(\phi + T\phi_T), \tag{5.36}$$

where $\phi(v, T)$ is given.

Then, system of equations including (5.32) or (5.33), together with (5.34)–(5.36) is complete

Using equations of state together with equations describing dynamics not only makes the system complete but also allows us to investigate how thermodynamic properties, especially phase transitions, appear in solutions of equations. Indeed, having solution of basic equations, one gets thermodynamical variables as functions in D, and therefore coexistence curves for various gases can be moved from the Lagrangian manifold to D. This allows us to define the location for different phases of gases and the set of points in D where phase transition occurs.

Suppose that the domain D contains a number of sources located at points $a_i \in D$, having intensities J_i. We will denote the source as a pair (a_i, J_i), $i = \overline{1, N}$. Then, D can be represented as a union of domains $D = \cup D_k$, where each D_k contains sources with common specific entropy s_0, while filtrations in D_k are independent [4]. Therefore, we can restrict ourselves on case $s(x) = s_0$. We can also say that the gas is involved in an adiabatic process.

Geometrically, thermodynamical processes can be understood as contact transformations of $(\mathbb{R}^5, \theta)$ preserving the Legendrian manifold $\tilde{L}$, or, from infinitesimal viewpoint, as contact vector fields X tangent to $\tilde{L}$. Integral curve of X is a curve l on $\tilde{L}$, which we will mean by a thermodynamical process.

5.5.1 Darcy Flows

In case of Darcy flows, the following theorem is valid.

Theorem 5.5 *Let the thermodynamic state of the gas be given by $\tilde{L}$ and $l \subset \tilde{L}$ be a thermodynamical process. Then, filtration equations (5.32), (5.34) and (5.36) are equivalent to the Dirichlet problem*

$$\Delta(Q(\tau)) = 0, \quad \tau|_{\partial D} = \tau_0,$$

where

$$Q(\tau) = -\int v^{-1}(\tau)\frac{k(\tau)}{\mu(\tau)}p'(\tau)d\tau,$$

τ is a parameter on l and Δ is the Laplace operator.

Proof Let τ be a parameter on a given process l. Then, all the thermodynamic variables can be expressed in terms of τ, in particular,

$$p = p(\tau), \quad v = v(\tau), \quad T = T(\tau), \quad k = k(\tau), \quad \mu = \mu(\tau). \tag{5.37}$$

From (5.32) and (5.34), one gets

$$\begin{aligned} 0 = \operatorname{div}(v^{-1}\mathbf{u}) &= \operatorname{div}\left(v^{-1}(\tau)\left(-\frac{k(\tau)}{\mu(\tau)}\nabla p\right)\right) = \operatorname{div}\left(v^{-1}(\tau)\left(-\frac{k(\tau)}{\mu(\tau)}p'(\tau)\nabla\tau\right)\right) \\ &= \operatorname{div}\left(Q'(\tau)\nabla\tau\right) = \operatorname{div}\left(\nabla Q(\tau)\right) = \Delta(Q(\tau)), \end{aligned}$$

where $Q(\tau) = -\int v^{-1}(\tau)\frac{k(\tau)}{\mu(\tau)}p'(\tau)d\tau$. □

This theorem is a generalization of that in [1–4]. The result of this theorem gives an explicit method of finding solutions for the Dirichlet filtration problem. Note that this result is of general form for all gases and all processes. All we need is to find the function $Q(\tau)$ for a given gas and a given process.

In case of N sources (a_i, J_i) and $D = \mathbb{R}^3$, one has

$$\tau(x) = Q^{-1}\left(\sum_{i=1}^{N}\frac{J_i}{4\pi|x - a_i|} + Q(\tau_0)\right).$$

By means of (5.37), we have $p = p(x)$, $v = v(x)$, $T = T(x)$ and so on and therefore get a complete solution for Darcy flows. The conditions for the invertibility of $Q(\tau)$ will be formulated for concrete gases.

5.5.2 Euler Flows

For Euler flows, we analyze in detail the case of one point isotropic source (a, J) in D and have the same theorem as for Darcy flows [5].

Theorem 5.6 *Let the thermodynamic state of the gas be given by $\tilde{L}$ and $l \subset \tilde{L}$ be a thermodynamical process. Then, the solution for problems (5.33), (5.34) and (5.36) is given implicitly by the following formula:*

$$\frac{v^2(\tau)}{2|x-a|^4} + \left(\frac{4\pi}{J}\right)^2 \Psi(\tau) = 0, \tag{5.38}$$

where τ is a parameter on l and

$$\Psi(\tau) = \int v(\tau) p'(\tau) d\tau.$$

Proof Let $r = |x - a|$ be a distance from the source, $x - a = \mathbf{r}$, and let $\mathbf{n} = \mathbf{r}/r$. Since the source is isotropic, one has

$$\mathbf{u} = U(r)\mathbf{r}, \quad \nabla = \mathbf{n}\partial_r.$$

The intensity of the source is equal to J, which means that the mass flux through a sphere S_a of radius r with a centre at a is equal to J:

$$J = \int_{S_a} v^{-1}(\tau(r))(\mathbf{u}, \mathbf{n}) dS = 4\pi r^3 v^{-1}(\tau(r)) U(r),$$

from what follows that

$$U(r) = \frac{J}{4\pi r^3} v(\tau(r)).$$

Then, Eq. (5.33) due to (5.37) takes the form

$$v^{-1}(\tau)\left(\frac{J}{4\pi}\right)^2 \frac{v(\tau)}{r^2}\frac{d}{dr}\left(\frac{v(\tau)}{r^2}\right) = -p'(\tau)\frac{d\tau}{dr},$$

which in turn becomes

$$\frac{d}{dr}\left(\frac{v^2(\tau)}{2r^4}\right)+\left(\frac{4\pi}{J}\right)^2 v(\tau)p'(\tau)\frac{d\tau}{dr}=0,$$

from what follows the statement of the theorem. □

Once one computes the function $\Psi(\tau)$, one gets a complete solution for the stationary Euler problem.

In our case, the specific volume v can be chosen as a parameter τ on adiabatic process $l_{\mathrm{adiab}} \subset \tilde{L}$. Indeed, due to (5.20), we have the following relation:

$$s_0 = R(\phi + T\phi_T),$$

which can be considered as an equation for $T(v)$ since the derivative of the right-hand side is positive in an applicable domain. Therefore, all the thermodynamical variables can be expressed in terms of v.

5.6 Solutions

In this section, we discuss solutions of Darcy and Euler equations for concrete gases using the analysis of their thermodynamic properties in Sect. 5.4. For simplicity, the permeability coefficient k and the viscosity μ are assumed to be constants.

5.6.1 Darcy Flows

5.6.1.1 Ideal Gases

First of all, let us express all the thermodynamic variables in terms of v. For ideal gases, we have

$$T(v)=\exp\left(\frac{2s_0}{Rn}\right)v^{-2/n},\quad p(v)=R\exp\left(\frac{2s_0}{Rn}\right)v^{-2/n-1}. \tag{5.39}$$

Therefore, the function $Q(v)$ equals

$$Q(v)=-\frac{Rk}{2\mu}\exp\left(\frac{2s_0}{Rn}\right)\frac{n+2}{n+1}v^{-2/n-2}.$$

And finally, the solution $v(x)$ has the following form:

$$v(x) = \left(Q(v_0) - \frac{2\mu}{Rk} \exp\left(-\frac{2s_0}{Rn} \right) \frac{n+1}{n+2} \sum_{i=1}^{N} \frac{J_i}{4\pi |x - a_i|} \right)^{-\frac{n}{2(n+1)}},$$

where v_0 is the specific volume at infinity.

5.6.1.2 van der Waals Gases

For van der Waals gases, the expressions for $T(v)$ and $p(v)$ are of the form:

$$T(v) = \exp\left(\frac{3s_0}{4n}\right)(3v-1)^{-1-2/n}, \quad p(v) = 8\exp\left(\frac{3s_0}{4n}\right)(3v-1)^{-1-2/n} - \frac{3}{v^2}.$$

And the function $Q(v)$ is defined by the relation [4]

$$-\frac{\mu}{k} Q(v) = -\frac{2}{v^3} + 8\exp\left(\frac{3s_0}{4n}\right)\frac{(3v-1)^{-\alpha}}{v} + 8\exp\left(\frac{3s_0}{4n}\right)\int (3v-1)^{-\alpha} v^{-2} dv,$$

where $\alpha = 1 + 2/n$.

For van der Waals gases, the conditions for invertibility of $Q(v)$ are given by the following theorem [1, 4].

Theorem 5.7 *The function $Q(v)$ is invertible if the specific entropy constant s_0 satisfies the following inequality:*

$$\exp\left(\frac{3s_0}{4n}\right) > \frac{1}{4\alpha}(1+\alpha)^{1+\alpha}(2-\alpha)^{2-\alpha}.$$

Thus, if the above condition holds, the solution is uniquely determined, otherwise, there are a number of possibilities in filtration development. The case of multivalued solution for one source is considered in detail in [4]. Here, we concentrate on a uniquely determined solution for a number of sources. As we have said, having solution for the filtration problem, one can find the location of different phases. It is presented in Fig. 5.5. We can see that the condensation process is observed in the neighbourhood of the sources.

5.6.1.3 Peng–Robinson Gases

In case of Peng–Robinson gases, the expressions for $T(v)$ and $p(v)$ have the following form:

$$T(v) = \exp\left(\frac{2s_0}{n}\right)(v-1)^{-2/n}, \quad p(v) = \exp\left(\frac{2s_0}{n}\right)(v-1)^{-1-2/n} - \frac{1}{(v+1)^2 - 2}.$$

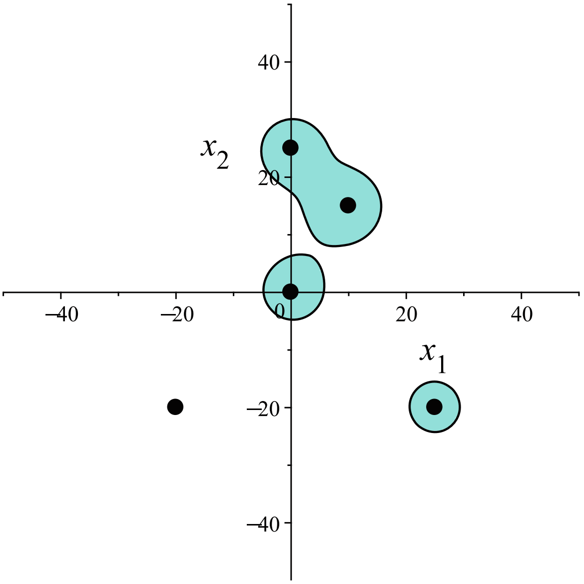


Fig. 5.5 Distribution of phases for van der Waals gases. Coloured domain corresponds to the condensation process, and white domain corresponds to gas phase

Therefore, the function $Q(v)$ is

$$-\frac{\mu}{k}Q(v) = \frac{3\sqrt{2}}{4}\ln\left(\frac{v+1+\sqrt{2}}{v+1-\sqrt{2}}\right) + \ln\left(\frac{v^2}{v^2+2v-1}\right) -$$
$$-\frac{v+2}{v^2+2v-1} - \exp\left(\frac{2s_0}{n}\right)\left(1+\frac{2}{n}\right)\int\frac{dv}{v(v-1)^{2+2/n}}.$$

Invertibility conditions for $Q(v)$ in this case can be given by the following theorem [3].

Theorem 5.8 *The function* $Q(v)$ *is invertible if the specific entropy constant* s_0 *satisfies the inequality:*

$$\exp\left(\frac{2s_0}{n}\right) > \frac{2n(v_0+1)(v_0-1)^{2+2/n}}{(n+2)(v_0+2v_0-1)^2},$$

where v_0 *is the root of the equation:*

$$(2-n)v^3 + 3(n+2)v^2 + (3n+2)v + 3n - 2 = 0. \tag{5.40}$$

There exists a real root of (5.40), $v_0 > 1$.

The distribution for phases has the same form as in case of van der Waals gases and can be found in [3].

5.6.1.4 Redlich–Kwong Gases

For Redlich–Kwong gases, the given level of the specific entropy s_0 leads us to the following relation:

$$s_0 = \ln\left(T^{n/2}(v-1)\right) + \frac{1}{2T^{3/2}}\ln\left(\frac{v}{v+1}\right). \tag{5.41}$$

We cannot get an explicit expression for $T(v)$ from (5.41), but nevertheless, one can estimate the asymptotic behaviour for $p(v)$, $T(v)$ and $Q(v)$ when $v \to 1$ or $v \to \infty$ [2].

Theorem 5.9 *If $v \to 1$, then asymptotics for $T(v)$, $p(v)$ and $Q(v)$ have the following form:*

$$T(v) = \frac{B^{2/3}}{(v-1)^{2/3}} + O\left((v-1)^{1/3}\right), \quad p(v) = \frac{B^{2/3}}{(v-1)^{5/3}} + O\left(\frac{1}{(v-1)^{2/3}}\right),$$

$$Q(v) = -\frac{kB^{2/3}}{\mu(v-1)^{5/3}} + O\left(\frac{1}{(v-1)^{2/3}}\right),$$

where $B = \exp(s_0)$.

Theorem 5.10 *If $v \to +\infty$, then asymptotics for $T(v)$, $p(v)$ and $Q(v)$ have the following form:*

$$T(v) = \frac{1}{(B^* v)^{2/3}} + O\left(\frac{1}{v^{5/3}}\right), \quad p(v) = \frac{c}{v^{5/3}} + O\left(\frac{1}{v^{8/3}}\right),$$

$$Q(v) = -\frac{5kc}{8\mu v^{8/3}} + O\left(\frac{1}{v^{11/3}}\right),$$

where B^* is the root of the equation

$$-s_0 = B/2 + \ln B,$$

and

$$c = \left(B^*\right)^{-2/3} - \left(B^*\right)^{1/3}.$$

Let us now analyze the invertibility conditions for $Q(v)$. We need to find actually the conditions for s_0 when $Q(v)$ is monotonic for all v that have sense, i.e. $v > 1$. In other words, $Q'(v)$ should have no zeroes for $v > 1$. But since the relations $Q'(v) = 0$ and $p'(v) = 0$ are equivalent, one has to explore $p'(v)$ including s_0 as a parameter. First of all, using equation of state $p(T, v)$, one has

$$\frac{dp}{dv} = \frac{\partial p}{\partial v} + \frac{\partial p}{\partial T}\frac{dT}{dv}. \tag{5.42}$$

The derivative $T'(v)$ can be obtained by means of (5.41). Once we substitute it in (5.42), the equation $p'(v) = 0$ will take the form

$$AZ^2 + BZ + C = 0, \tag{5.43}$$

where $Z = T^{3/2}$ and

$$A = 2(n+2)v^2(v+1)^2, \quad C = (v-1)^2\left(1 - 3(2v+1)\ln\left(1+v^{-1}\right)\right),$$
$$B = 3v^2(v+1)^2\ln\left(1+v^{-1}\right) + 2(v-1)((v+1)(2v+n) - 2nv^2).$$

Since $A > 0$ and $C < 0$, the discriminant of (5.43) is positive, and therefore, there are two real roots. But since $B > 0$, one of them is negative and is out of consideration. Thus, from equation $p'(v) = 0$, we have

$$T(v) = \left(\frac{-B + \sqrt{B^2 - 4AC}}{2A}\right)^{2/3}. \tag{5.44}$$

Substituting the root (5.44) in (5.41), we get the relation

$$s_0 = H(v). \tag{5.45}$$

If the specific entropy level s_0 is such that (5.45) has no solution $v^* > 1$, then $Q(v)$ is invertible. An example for $H(v)$ in case of $n = 3$ is presented in Fig. 5.6. Numerical computation shows that if $s_0 > -0.5$, then $Q(v)$ is invertible [2]. The distribution of phases is very similar to the case of van der Waals gases and can be found in [2].

5.6.2 Euler Flows

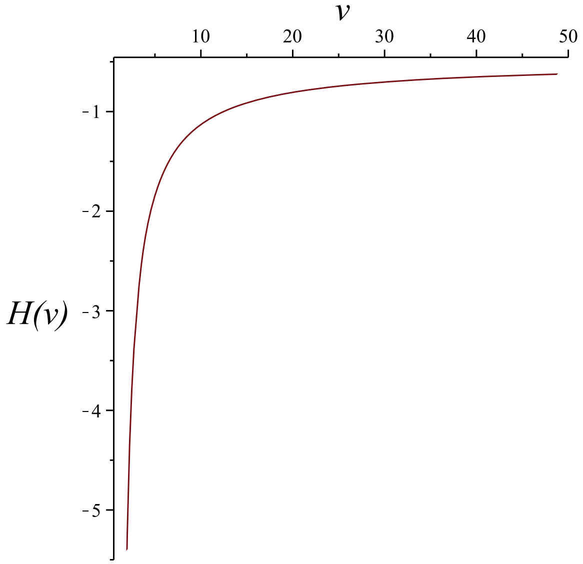
Here, we discuss the solution for Euler flows of ideal and van der Waals gases. Peng–Robinson and Redlich–Kwong models can be elaborated in the same way.

First of all, we take $D = \mathbb{R}^3$ assuming that the specific volume is given at infinity $v|_{|x-a|\to\infty} = v_0$. Since we take v as a parameter on the process l_{adiab}, the general formula (5.38) takes the form [5]:

$$\frac{v^2}{2|x-a|^4} + \left(\frac{4\pi}{J}\right)^2 \Psi(v) = 0,$$

where $\Psi(v) = \int vp'(v)dv$.

Fig. 5.6 Graph of function $H(v)$



5.6.2.1 Ideal Gases

Using (5.39), one can show that the function $\Psi(v)$ for ideal gases has the following form:

$$\Psi(v) = \frac{R(n+2)}{2} \exp\left(\frac{2s_0}{Rn}\right) v^{-2/n}.$$

Therefore, the solution for ideal gases has the form (it is more convenient to work in terms of density $\rho = v^{-1}$ here):

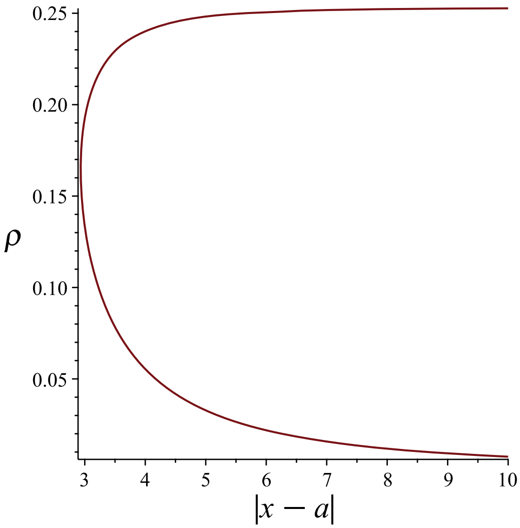
$$\frac{1}{2|x-a|^4\rho^2} + \left(\frac{4\pi}{J}\right)^2 \exp\left(\frac{2s_0}{Rn}\right) \frac{R(n+2)}{2}\rho^{2/n} = C_0,$$

where C_0 is a constant depending on $\rho|_{|x-a|\to\infty} = \rho_0$.

Theorem 5.11 ([5]) *If $\rho_0 = 0$, then the asymptotic behaviour of $\rho(x)$ at infinity is of the form:*

$$\rho(x) = \frac{1}{\sqrt{2C_0}|x-a|^2} + o\left(\frac{1}{|x-a|^2}\right),$$

Fig. 5.7 The distribution of the density for ideal gases



and if $\rho_0 \neq 0$*, then*

$$\rho(x) = \left(\frac{J}{4\pi}\right)^n \left(\frac{2C_0}{R(n+2)} \exp\left(-\frac{2s_0}{Rn}\right)\right)^{n/2} + \sum_{i=1}^{\infty} \frac{\beta_i}{|x-a|^{4i}}.$$

Thus, the solution obtained is regular at infinity in both cases. The distribution of the density is shown in Fig. 5.7.

We can see that the solution is multivalued. Moreover, it exists not for any x [5].

Theorem 5.12 *The solution* $\rho(x)$ *exists if*

$$|x-a| > \left(2\rho_*^2 \left(C_0 - R\left(\frac{4\pi}{J}\right)^2 \exp\left(\frac{2s_0}{Rn}\right)(n/2+1)\rho_*^{2/n}\right)\right)^{-1/4},$$

where

$$\rho_* = \left(\frac{J}{4\pi}\right)^n \left(\exp\left(-\frac{2s_0}{Rn}\right)\frac{2nC_0}{R(n+1)(n+2)}\right)^{n/2}.$$

5.6.2.2 van der Waals Gases

In case of van der Waals gases, the solution is given by the following formula [5]:

$$\frac{1}{2|x-a|^4\rho^2} + \left(\frac{4\pi}{J}\right)^2 \times$$
$$\left(4\exp\left(\frac{3s_0}{4n}\right)(3\rho^{-1}-1)^{-(1+2/n)}\left(\rho^{-1}(n+2) - \frac{n}{3}\right) - 6\rho\right) = C_0.$$

Fig. 5.8 The distribution of phases for van der Waals gases. Variable $y = 1$ is the liquid phase, and variable $y = 0.5$ is the condensation process

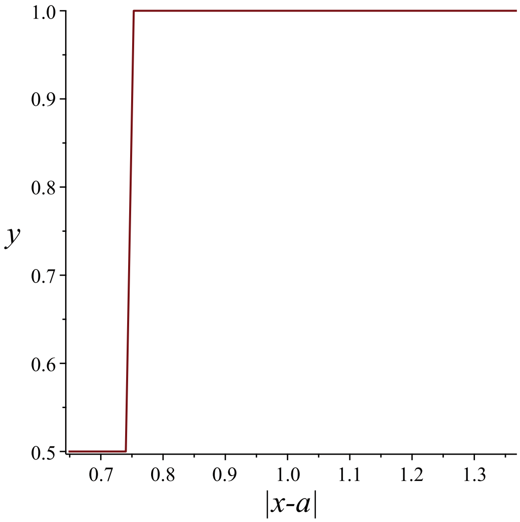
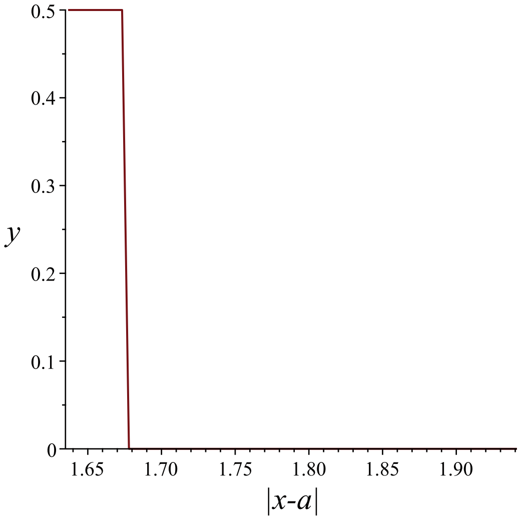


Fig. 5.9 The distribution of phases for van der Waals gases. Variable $y = 0$ is the gas phase, and variable $y = 0.5$ is the condensation process



We analyze phase transitions in two cases, for "small" and "big" levels of the specific entropy constant s_0. Let us start with the higher branch of solution.

If $s_0 = 0.5$, the distribution of phases is shown in Fig. 5.8. We observe the condensation process near the source, while far from the source, the medium is in a liquid phase.

If $s_0 = 200$, the distribution of phases is shown in Fig. 5.9. We again observe the condensation process near the source, but at large distances from the source, the medium is in a gas phase.

For the lower branch of solution, in both cases, the gas condensates.

5.7 Conclusions

In this paper, we presented the analysis of critical phenomena in two types of stationary gas flows—filtration flows described by the Darcy law and flows of inviscid gases described by Euler equations. We showed that thermodynamics plays a crucial role in modelling of gas dynamics, and since taking into account thermodynamic properties of the medium expressed by state equations, we not only make the system of continuous media equations complete but also get an opportunity to investigate how these properties influence the flow. We provided constructive methods of finding solutions for Darcy and Euler flows, which are of general form not only for various gases but also for thermodynamical processes these gases are involved in. We also showed that the solutions of both Darcy and Euler system are, in general, multivalued, and for Darcy flows, the conditions for uniquely determined solution can be formulated, while in case of Euler flows, the solution is always multivalued, but each branch is determined by the conditions at infinity, and therefore only one of them can be realized physically. Another important property of solutions is their regularity at infinity, usually accepted in physics as “correctness”. The analysis of critical phenomena showed that Darcy and Euler flows have the same distribution of phases in case of “big level” of the specific entropy.

Further investigations in this field can be connected with the analysis of critical phenomena in case of, in some sense, distributed sources, i.e. the source is no longer assumed to be a point but occupies some domain. Another direction could be, on the one hand, the exploration of gas flows on Riemannian manifolds, and on the other hand, the investigation of flows for media with more complicated thermodynamics, namely, phase transitions of the higher order, which requires in turn the more detailed analysis of geometric structures on the corresponding Legendrian and Lagrangian manifolds.

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