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Gas transport in tight porous media
Gas kinetic approach

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Abstract

We describe the flow of gas in a porous medium in the kinetic regime, where the viscous flow structure is not formed in separate pores. Special attention is paid to the dense kinetic regime, where the interactions within the gas are as important as the interaction with the porous medium. The transport law for this regime is derived by means of the gas kinetic theory, in the framework of the model of "heavy gas in light one". The computations of the gas kinetic theory are confirmed by the dimension analysis and a simplified derivation revealing the considerations behind the kinetic derivation. The role of the thermal gradient in the transport law is clarified.

Keywords: Gas; Porous media; Gas kinetic theory; Transport equation

1. Introduction

Transport of gases in tight porous media is important to a number of practical applications: chemical catalysis and chromatography; adsorption on activated carbons, molecular sieves and other microporous media; membrane transport; transport in tight natural gas reservoirs, and others [1–3]. This is the reason why this transport has been intensively studied, both theoretically and experimentally. The early history of such studies is discussed in Ref. [1]. The most widely used approaches to the multicomponent gas transport in micro- and mesoporous media are the so-called dusty-gas model [1], the phenomenological approaches based on the Maxwell–Stefan relations or the Fick law [2], and direct modeling with random walks [4,5]. The transport relations for such flows are normally considered to be well established, and the recent studies in the area are mostly experimental studies determining different coefficients in these relations [6–9].

Meanwhile, two questions remain incompletely covered in the literature. The first question is the gas behavior in the intermediate regime, between the Knudsen regime corresponding to a very rarified gas and the viscous regime where the gas in the pores flows as a continuous phase. Interpolation between the two extreme regimes is normally carried out by means of the Weber or a similar equation [8], although non-monotonous behavior of the permeability with density has been observed [10,1].

The second open question is the role of the thermal gradient in the transport equation. In the Knudsen regime the coefficient at the $\nabla(\ln T)$ is minus half the coefficient at $\nabla(\ln P)$, so that the equilibrium condition is given by $PT^{-1/2} = \text{const}$. For the viscous regime, the term proportional to the thermal gradient is usually neglected in the transport (Darcy) law. This may be proven on the basis of the rather general considerations [11], although some molecular simulation studies indicate that the thermal gradient may be influential even for this regime [12]. The intermediate behavior remains unclear.

In the present work we investigate this behavior by means of the gas kinetic theory. Several approaches to gas flow in porous media have been developed in the framework of this theory (see, for example [10,1,13–15]). We suggest a new approach to gas flow in a porous medium different from that of the dusty-gas model [1]. Our model is similar to the model of "motion of heavy gas in light one" [16], in the system of coordinates connected with the "heavy gas" particles representing the porous medium. Similar, although not fully equivalent theories have been applied to description of the phoresis of heavy (dusty)

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particles in gas [17,1]. We show that the thermal gradient is important in both the Knudsen and the intermediate regime.

Since the gas kinetic derivation is rather elaborate and is not always transparent, we also provide two other derivations of the transport law. First, we show that the dimensionality considerations make it possible to determine the transport law within the two coefficients dependent on the Knudsen number. Then we suggest a "naive", or simplified derivation, assuming the molecular velocities to be equal to their average value, as it has long been applied in the gas kinetic theory [18, Chapter 1, p. 2]. These derivations are given for illustrative purposes, in order to uncover physical considerations behind the strict gas kinetic derivation. The contribution of the thermal gradient to the transport in the intermediate regime may only be evaluated by means of the gas kinetic theory, since it depends on higher approximations in the Chapman–Enskog expansion for the Boltzmann equation for the molecular distribution.

Comparison of the three derivations makes it possible to draw some conclusions about the shape of the transport coefficients, which are discussed in the last section of the paper.

2. Transport law: dimensional analysis

The most general form of the transport law in porous media may be established on the basis of the dimensional analysis [19]. The procedure consists in determining the essential parameters of the process under study, then forming dimensionless complexes and expressing them in terms of each other.

We consider a flow of gas in an isotropic porous medium, driven by the pressure gradient ∇P and the temperature gradient ∇T. Assume that the flow is non-structured, that is, there is no correlation between the position of a molecule in the pore space and the characteristics of its motion: momentum and energy. This is a reasonable assumption if the free run of a molecule l_f is of the same order of magnitude or larger than the characteristic pore size d_p. In this case the molecules and the porous medium are assumed to be perfectly "mixed".

An opposite case considered in the literature (especially related to ground flows and transport in natural gas reservoirs) is $l_\mathrm{f} \ll d_\mathrm{p}$. In this case multiple molecules inside each pore form a viscous flow structure, with no-slip or similar conditions on the pore walls and the highest velocities close to the pore centers. On the macroscopic level transport in this regime is described by the well-known Darcy law. It will not be considered here.

The free run path for not-so-large molecules in gas is around 10^{-7} m and decreases approximately inversely proportionally to pressure (although the decrease slows down at high pressures) [18]. Thus, for the mesopores of the sizes of 10^{-8} to 10^{-9} m the flow does not exhibit the viscous structure up to the pressures of few megapascals. Moreover, if the pore size d_p is of the order of several molecular diameters d_m, the number of molecules in a pore is restricted and, again, the structure characteristic of the viscous flow is impossible.

We would like to establish the relation between the mass-averaged flow velocity of the gas $\mathbf{u}$ and the gradients of pressure and temperature in the non-structured flow. We discuss the *interstitial* velocity. To obtain the superficial velocity the result should be multiplied by porosity ϕ. Normally the flow of gas in a porous medium is rather slow and occurs under such gradients and velocities that common relations of the linear non-equilibrium thermodynamics may be applied. That is, the flow velocity depends linearly on the pressure and temperature gradients, with some coefficients K_T and K_P:

$$\mathbf{u} = K_\mathrm{T}\nabla T + K_\mathrm{P}\nabla P \tag{1}$$

This equation may be represented in another, equivalent, but more convenient form, by introducing a characteristic molecular velocity v. In terms of the molecular mass m and the Boltzmann constant k and by neglecting a multiplier of the order of unity (or considering the velocity projection on a chosen direction),

$$v = \left(\frac{kT}{m}\right)^{1/2} \tag{2}$$

Coefficients K_T and K_P are conveniently expressed in terms of the (still undetermined) coefficients l_T, l_P:

$$K_\mathrm{T} = \frac{l_\mathrm{T} v}{T}, \qquad K_\mathrm{P} = -\frac{l_P v}{P}$$

Then Eq. (1) assumes the form of

$$\frac{\mathbf{u}}{v} = l_\mathrm{T}\frac{\nabla T}{T} - l_\mathrm{P}\frac{\nabla P}{P} \tag{3}$$

Obviously, coefficients l_T, l_P have the dimension of a length. The sign of l_T, l_P is chosen such that, as shown below, these values are likely to be positive.

A priori, the values of l_T, l_P may depend on all the parameters constituting the system: thermodynamic characteristics of the gas, its transport properties, molecular and pore sizes, characteristics of the pore shapes. We omit from this list transport properties like viscosity, since, according to our assumptions, the gas does not form a viscous flow structure. Moreover, we omit the dimensionless characteristics of the porous space from the list of parameters, since only dimensional values may be taken into consideration by the dimensional analysis. The dependence of l_T, l_P on the porosity ϕ and, probably, characteristics of the geometry of the porous space is assumed implicitly. Dependence on other parameters is expressed by

$$l_\mathrm{T} = l_\mathrm{T}(P, T, d_\mathrm{p}, d_\mathrm{m}, l_\mathrm{f}, m); \qquad l_\mathrm{P} = l_\mathrm{P}(P, T, d_\mathrm{p}, d_\mathrm{m}, l_\mathrm{f}, m)$$

Since $l_\mathrm{f} = l_\mathrm{f}(P, d_\mathrm{m}, m)$, one of these values, say, P, may be excluded. Moreover, since T is the only remaining variable having the dimension of Kelvin, it may be excluded, too. Finally, among the rest of the values, m is the only one having a dimension of a mass, hence it may also be excluded. The remaining variables have the dimension of a length. If we choose the size of a pore d_p as a characteristic length, four dimensionless complexes are formed:

$$\alpha_\mathrm{T} = \frac{l_\mathrm{T}}{d_\mathrm{p}}; \qquad \alpha_\mathrm{P} = \frac{l_\mathrm{P}}{d_\mathrm{p}}; \qquad \mathrm{Kn} = \frac{l_\mathrm{f}}{d_\mathrm{p}}; \qquad \delta = \frac{d_\mathrm{m}}{d_\mathrm{p}} \tag{4}$$

Parameter Kn is known as the Knudsen number. The dimensionless relations have the form of

$$\alpha_\mathrm{T} = \alpha_\mathrm{T}(\mathrm{Kn}, \delta); \qquad \alpha_\mathrm{P} = \alpha_\mathrm{P}(\mathrm{Kn}, \delta) \tag{5}$$

Thus, the dimensional analysis makes it possible to derive the following general relation for the non-structured gas flow in a porous medium: combining Eqs. (3)–(5), we obtain

$$\mathbf{u} = \alpha_\mathrm{T}(\mathrm{Kn}, \delta) d_\mathrm{p} v \frac{\nabla T}{T} - \alpha_\mathrm{P}(\mathrm{Kn}, \delta) d_\mathrm{p} v \frac{\nabla P}{P} \tag{6}$$

The values of α_i $(i = T, P)$ may also depend on particular dimensionless properties of the porous medium, such as porosity ϕ, characteristics of pore and particle shapes, of the packing, etc. Dimension-based considerations cannot be used to obtain a particular form of such dependence, which may be different for different particular models of a porous medium.

Expressions for α_i may be simplified for different flow regimes, that is, for different asymptotic relations between parameters δ and Kn. The value of δ may be of the order of unity or much less than unity. The case where $\delta \gg 1$, or, the same, $d_\mathrm{m} \gg d_\mathrm{p}$ is, obviously, unrealistic. The case $\mathrm{Kn} \ll 1$ is not considered here, since in this case $l_\mathrm{f} \ll d_\mathrm{p}$, which corresponds to the conditions of the viscous flow. Thus, the three asymptotic regimes may correspond to the kinetic flow regime: (1) $\delta \sim 1$; (2) $\delta \ll 1$, $\mathrm{Kn} \sim 1$; and (3) $\delta \ll 1$, $\mathrm{Kn} \gg 1$.

If $\delta \sim 1$ (the first regime), the pore sizes are comparable to the particle sizes. This is the case of a dense membrane. It is relevant to transport in zeolites, polymers and some adsorbents, and is usually studied on the basis of the different random walk models or Maxwell–Stefan relations ([20,21] and refs therein). An opposite case of the open matrix is where the molecular sizes are much smaller than the pore sizes (regimes 2 and 3). In this limit, $\delta \to 0$, dependence of the coefficients α_i on this parameter disappears, and the only varying parameter becomes the Knudsen number Kn:

$$\alpha_i = \alpha_i(\mathrm{Kn}) \quad (i = T, P)$$

Further analysis depends on the interrelation between the value of Kn, or, the same, between the relation between l_f and d_p. The regime where $l_\mathrm{f} \gg d_\mathrm{p}$ $(\mathrm{Kn} \gg 1)$ is well studied: it is the case of Knudsen flow in a porous medium. In this case the flux is proportional to $PT^{-1/2}$ [1]. For example, for the case of the isotropic "absolutely chaotic" porous medium (where no regular structure may be imposed) it has been established [1,22] that

$$\mathbf{u} = \frac{\beta\phi}{S} v \left(\frac{\nabla T}{2T} - \frac{\nabla P}{P} \right), \qquad \beta = \frac{24}{9 + 4A}\sqrt{\frac{2}{\pi}} \tag{7}$$

Here ϕ is the porosity, S the specific internal surface of the porous medium (in $\mathrm{m}^2/\mathrm{m}^3$), and A is the accommodation coefficient. The fraction A of the particles accommodates on the surface and is dispersed as an equilibrium gas with the temperature of the surface, and $1 - A$ is reflected from the surface without energy exchange. Commonly, the value of A is close to unity [23], so that $\beta = \alpha_\mathrm{P}$ is close to 1.5. The value of α_T in this case is equal to $\alpha_\mathrm{P}/2$.

For the specific internal surface of the porous medium S, the value of S^{-1} is a good measure of the pore size d_p or of a grain radius r, which is usually of the same order of magnitude as d_p. For example, if the grains are spherical, and their concentration per unit volume is C, then [24]:

$$\phi = 1 - \frac{4\pi}{3} r^3 C, \qquad S = 4\pi r^2 C, \tag{8}$$

or

$$r = \frac{3(1-\phi)}{S}, \qquad C = \frac{S^3}{36\pi(1-\phi)^2}$$

For a model porous medium consisting of the cylindrical capillaries of the same diameter d_p,

$$d_\mathrm{p} = \frac{4\phi}{S}$$

In practical applications, it is more convenient to work directly with the specific surface, since it is measurable (for example, by the nitrogen adsorption). In the following, we select S^{-1} as an estimate for the value of d_p in the dimensionless parameter Kn. However, in order to better understand the transport processes, it is convenient to rewrite Eq. (7) in terms of r or d_p:

$$\mathbf{u} = -\frac{\alpha\phi}{3(1-\phi)} r v \left(\frac{\nabla T}{2T} - \frac{\nabla P}{P} \right) \quad \text{or}$$

$$\mathbf{u} = -\frac{\alpha}{4} d_\mathrm{p} v \left(\frac{\nabla T}{2T} - \frac{\nabla P}{P} \right)$$

The last regime, where $l_\mathrm{f} \sim d_\mathrm{p}$, is less studied than the other regimes. It will be called "the dense kinetic regime", or "the intermediate regime". The formulae for the Knudsen regime are not applicable to the intermediate regime, although the conditions of the non-structured flow may still be valid. Taking into account the preceding considerations, we reduce Eq. (6) to the form of

$$\mathbf{u} = \frac{\alpha_\mathrm{T}(\mathrm{Kn})}{S} v \frac{\nabla T}{T} - \frac{\alpha_\mathrm{P}(\mathrm{Kn})}{S} v \frac{\nabla P}{P}, \qquad \mathrm{Kn} = l_\mathrm{f} S \tag{9}$$

It is more convenient to represent this equation in a slightly different form:

$$S\phi^{-1} v^{-1} \mathbf{u} = \beta \left(\beta_\mathrm{T} \frac{\nabla T}{T} - \frac{1}{P} \nabla P \right) \tag{10}$$

Both β and β_T are functions of Kn. Eq. (10) is more convenient, since, as we will show, coefficients β, β_T in many cases are constants. This equation may be used to express the transport law in thermodynamic rather than kinetic variables: it is enough to substitute $(RT/M)^{1/2}$ for v, where R is the gas constant and M is the molar mass.

More detailed physical considerations are required to determine these coefficients as functions of the pore geometry and of the Knudsen number Kn. While parameter β (or α_P) is likely to be positive, the sign of β_T (or α_T) remains, a priori, indefinite. Below we apply the methods of the gas kinetic theory in order to get a more precise answer about the values of these parameters.

3. Simplified derivation

Before describing the kinetic derivation "on a full scale", we would like to present a simplified mechanistic derivation. Our goal is to clarify the logic behind the kinetic derivation and to show how the description of the non-structured flow, within a multiplier of the order of unity, may be obtained from the relatively simple considerations, similar to those applied by the founders of the gas kinetic theory, Clausius and Maxwell.

For a simplified derivation, it is necessary to assume a model of the porous medium. There are two principal types of such models: a porous medium as a capillary network, or as a system of solid particles—a granular packing. In Section 3.1 we repeat, briefly and as generally as possible, the known derivation of the flow equation for a capillary network and show that a system of obvious assumptions may in this case only lead to the equations of the Knudsen regime.

Then we proceed to the model of the porous medium as a granular packing and show that a simplified description of the dense kinetic flow regime (apart from the thermal effect) is possible for this model.

3.1. Knudsen regime

Let us briefly remind of the well-known derivation of the flow equation for the Knudsen flow regime. Consider a cylindrical volume of a homogeneous porous medium directed parallel to the flow. The height of the cylinder is l, and the cross-section is A.

Consider the fluxes j_{R} and j_{L} entering the section from the right and from the left, correspondingly (axis x is directed from the left to the right, as usual). Obviously, these fluxes are proportional to the particle concentration (numerical density) N and to the average molecular velocity v. Porosity should enter the expression, since the flow occurs only through part ϕ of the surface. The resulting expression for the flux through the section is

$$j = j_{\mathrm{L}} - j_{\mathrm{R}} = \alpha\phi(N_{\mathrm{L}}v_{\mathrm{L}} - N_{\mathrm{R}}v_{\mathrm{R}}) \approx -\alpha\phi l \frac{\partial(Nv)}{\partial x} \tag{11}$$

The last transition is possible if the value of l is small, or if the gradient is uniform. A non-trivial assumption of the whole derivation is that l cannot tend to zero, otherwise the flux per unit area vanishes. A characteristic value of l is usually selected to be equal to the pore size d_{p}, or to the inverse specific internal surface S^{-1}. The numerical multiplier α is a constant determined by a particular model of the porous medium [1]. An expression for the superficial flux (unlike Eq. (11) for the interstitial flux j) requires an additional multiplier ϕ on the right-hand side.

Eq. (11) expresses the well-known Knudsen law for gas flow in a porous medium. In view of Eq. (2), it predicts that the flux is proportional to the gradient of $NT^{1/2}$or, the same, $PT^{-1/2}$. This is true for the Knudsen regime, but not for the intermediate kinetic regime, as will be shown below.

This indicates the limits of a "naive" derivation of the transport equation based on a capillary network model. Any such derivation is reduced to the considerations above and, thus, results in the equations for the Knudsen regime. The reason is that we implicitly assume that fluxes j_{R} and j_{L} do not interact. This assumption is violated for denser flows, especially, if l_{f} becomes of the order of d_{p}. In order to generalize the approach, it is necessary to introduce the interactions between j_{R} and j_{L}. However, this seems to be a non-trivial task within a capillary network model.

3.2. Dense kinetic regime

As shown in Section 3.1, the governing equation for this regime cannot be derived from the "capillary network" point of view. Alternatively, we may consider a porous medium as a system of solid grains, as in the dusty-gas model [1].

We assume that all the grains are similar. This assumption may be shown to be non-restrictive. Moreover, for the present simplified derivation it is convenient to consider the grains of a cylindrical shape, with the cross-section A_{g} orthogonal to flow, and length (height) l_{g}. Assuming so, we obtain an answer within an order of magnitude, which we do anyway. In Section 4 we will generalize these results onto nearly arbitrary grain shapes.

If the numerical concentration of the solid grains is C, their number in volume V is CV. Additionally, if $V_{\mathrm{g}} = A_{\mathrm{g}}l_{\mathrm{g}}$ is the volume of a single grain, then

$$CV_{\mathrm{g}} = 1 - \phi \tag{12}$$

Instead of computing the mass balance, as in the previous subsection, we will consider the momentum balance. The total force acting on the gas in the volume V is

$$F = (P_{\mathrm{L}} - P_{\mathrm{R}})A \approx -V\frac{\mathrm{d}P}{\mathrm{d}x} \tag{13}$$

Instead of the total force F it is convenient to consider force F_1 acting on each grain of the porous medium:

$$F = CVF_1$$

Comparing this equation to Eq. (13), we obtain

$$-\frac{\mathrm{d}P}{\mathrm{d}x} = CF_1 \tag{14}$$

Another expression for F_1 may be obtained by considering the flowing gas. Assume that its average convective velocity is u. Then the average molecular rate in the direction of the flow is $v + u$ (within a certain approximation). Let subscripts 'L' and 'R' mean to the right and to the left from a single grain of the porous medium. The average number of the particle collisions with the left face of the grain per time unit is $N_{\mathrm{L}}(v_{\mathrm{L}} + u)/2$. Here the multiplier 1/2 is introduced, since half of the molecules move in the opposite direction. Assume that a molecule accommodates on the surface, that is, it is reflected with the average equilibrium velocity $-v_{\mathrm{L}}$. Then a single molecule transfers in one collision a momentum equal to $m(2v_{\mathrm{L}} + u)$. The overall momentum transferred *from the left* to the grain per time unit is

$$M_{\mathrm{L}} = \frac{1}{2}mN_{\mathrm{L}}(v_{\mathrm{L}} + u)(2v_{\mathrm{L}} + u)$$

Similarly, the momentum per time unit transferred to the particle *from the right* is

$$M_{\mathrm{R}} = \frac{1}{2}mN_{\mathrm{R}}(v_{\mathrm{R}} - u)(2v_{\mathrm{R}} - u)$$

The difference $M_L - M_R$ should be equal to force F_1. After some rearrangement, it may be reduced to the form of

$$F_1 = F_P + F_v \tag{15}$$

$$F_P = A_g[mN_L v_L^2 - mN_R v_R^2],$$
$$F_v = 3A_g m \frac{N_L v_L + N_R v_R}{2} u \tag{16}$$

In order to simplify the expression for F_P, let us notice that the value of $mNv^2 = NkT$ is exactly the pressure of an ideal gas. Thus,

$$F_P = A_g(P_L - P_R) \approx -V_g \frac{dP}{dx}$$

In order to calculate F_v, the sum $N_L v_L + N_R v_R$ on the right-hand side of Eq. (16) may be substituted by its mean value Nv, which is possible due to the small grain sizes. Substituting everything back to Eq. (14) and taking into account Eq. (12), we obtain the transport equation in the form of

$$-\phi \frac{dP}{dx} = 3CA_g \rho v u$$

For the grains of regular shapes, the value of CA_g may, within a numerical multiplier, be identified with the internal surface S. Finally, we obtain

$$-\phi \frac{dP}{dx} = \alpha' S \rho v u \tag{17}$$

Here α' is a numerical multiplier depending on the grain shapes and other parameters of geometry of the porous space.

For isothermal flows, Eq. (17) is similar to Eq. (11) for the Knudsen regime (although the multipliers α and α' may be different). However, there is an important difference between these two flow equations: The Knudsen regime equation (11) contains a term proportional to the temperature gradient, while Eq. (17) does not contain such a term, similar to the well-known Darcy law for viscous regime. A reason why we do not obtain the thermal gradient contribution in the dense kinetic regime is that in the derivation of this section we have implicitly assumed that, in spite of the presence of the thermal gradient, the gas is in thermal equilibrium. It is known, however, that the thermal gradient introduces corrections to the gas distribution, which may be evaluated on the basis of the Chapman–Enskog expansion of the Boltzmann equation (see below). These corrections are difficult to introduce in the framework of the empirical derivation. It is necessary to carry out the full-scale kinetic derivation in order to account for the effect of the thermal gradient in the kinetic regime. Such a kinetic derivation is presented below.

4. Gas kinetic derivation

4.1. Basic assumptions

The kinetic derivation needs precise definition of the physical conditions and underlying assumptions. We consider a steady-state flow of a single-component gas in the intermediate regime. The flow conditions are such that collisions between the gas molecules are more frequent than collisions with the pore walls. However, the viscous flow structure is not formed. In this assumption, the system considered becomes similar to the case of "motion of a heavy gas in a light gas", which is described in a system of coordinates connected to heavy molecules [16]. This approach is different from the approach of the "dusty-gas" model [1] where expansion is carried out around the equilibrium state corresponding to zero gas velocity $\mathbf{u} = 0$. Equilibration in gas is achieved much faster than between the gas and the porous medium. In zero approximation, the distribution of the molecular rates $\mathbf{v}$ is the common Maxwell distribution corresponding to numerical particle density N, temperature T and average gas velocity $\mathbf{u}$:

$$f^{(0)}(\mathbf{v}|T, \mathbf{u}) = N\left(\frac{2\pi kT}{m}\right)^{-3/2} \exp\left(-\frac{m\mathbf{V}^2}{2kT}\right),$$
$$\mathbf{V} = \mathbf{v} - \mathbf{u} \tag{18}$$

In Ref. [25] it was shown that $f^{(0)}$ is a zero approximation to the real distribution of the gas molecules in the porous medium. Subsequent approximations may be obtained by the multiscale expansion procedure similar to the Chapman–Enskog method. In the first approximation to function f the term $f^{(1)}$ proportional to the thermal gradient has the same form as in the common Chapman–Enskog expansion for the gas in free space. The porous medium introduces into the expansion additional terms proportional to $\mathbf{u}$, which contribution to the transport equations may be neglected compared to the contribution of the zero-order term. The term proportional to the thermal gradient cannot be neglected, since, as shown below, the zero-order approximation $f^{(0)}$ does not contribute to the thermal force. Combination of the equations from Chapter 7 of [27] shows that the main term in the expansion of $f^{(1)}$ by Sonine polynomials is equal to

$$f^{(1)} = -\frac{1}{\rho}\frac{2m^2}{5(kT)^2}\lambda\left(\frac{m\mathbf{V}^2}{2kT} - \frac{5}{2}\right) f^{(0)}(\mathbf{V}\nabla T) \tag{19}$$

Here λ is the gas heat conductivity, in J/(m s grad).

The total distribution of the gas molecules by velocities will be approximated by

$$f = f^{(0)} + f^{(1)}$$

Further approximations will be omitted.

The collisions of the gas molecules with the internal surface of the porous medium are described by the *reflection kernel* $B(\mathbf{v}_1 \to \mathbf{v}_2|\mathbf{n}, T_P)$. This is the probability density of the event that a molecule with velocity $\mathbf{v}_1$ after collision with the surface with external normal $\mathbf{n}$ acquires velocity $\mathbf{v}_2$. Here T_P is the temperature of the porous medium, which, in principle, may or may not be equal to the gas temperature T. The temperature equilibration is a relatively fast process [25]. Indeed, equilibration of the temperature in solid is fast, since its heat diffusivity is much higher than that of the gas. Equilibration of the temperature between the gas and the porous medium is also rather fast. It is proportional to the contact surface S between gas and solid, which is rather large for most porous media. Thus, we assume that $T = T_P$, as in Section 3.2. Additional introduction of the difference $T - T_P$ would not change the momentum balance, at least, in the first approximation, in view of the vector character of this balance.

Kernel B is normalized to unity:

$$\int_{\mathbf{v}_2\mathbf{n}>0} B(\mathbf{v}_1 \to \mathbf{v}_2|\mathbf{n}, T)\,\mathrm{d}\mathbf{v}_2 = 1, \quad (\mathbf{v}_1\mathbf{n} < 0) \tag{20}$$

For particular calculations we will use a model for B of the type of full accommodation (dispersive reflection). If the molecules colliding with the surface "forget" their past and assume equilibrium distribution with the temperature of the surface, then [23]:

$$B(\mathbf{v}_1 \to \mathbf{v}_2|\mathbf{n}, T) = \left(\frac{2\pi m}{kT}\right)^{1/2} N^{-1} F(\mathbf{v}_2|T)(\mathbf{v}_2\mathbf{n}),$$
$$(\mathbf{v}_1\mathbf{n} < 0, \quad \mathbf{v}_2\mathbf{n} > 0) \tag{21}$$

Here N is the number density, and f_0 is the Maxwell distribution corresponding to zero velocity $\mathbf{u}$:

$$f_0(\mathbf{v}|T) = N\left(\frac{2\pi kT}{m}\right)^{-3/2} \exp\left(-\frac{mv^2}{2kT}\right) \tag{22}$$

In this or any other particular case, B obeys the principle of microreversibility [16]:

$$|\mathbf{v}_1\mathbf{n}| f_0(\mathbf{v}_1|T) B(\mathbf{v}_1 \to \mathbf{v}_2|\mathbf{n})$$
$$= |\mathbf{v}_2\mathbf{n}| f_0(\mathbf{v}_2|T) B(-\mathbf{v}_2 \to -\mathbf{v}_1|\mathbf{n}) \tag{23}$$

As shown below, this principle makes it possible to find most of the expressions involved without referring to particular form of the kernel B. Taking into account that the accommodation coefficient is normally close to unity, especially for the "rough" surfaces, it may be concluded that assumption about complete accommodation does not influence very much the calculated values of the transfer coefficients.

Another general property of kernel B is the conservation law for the particles in a collision:

$$\int B(\mathbf{v}_1 \to \mathbf{v}_2|\mathbf{n})\,\mathrm{d}\mathbf{v}_2 = 1 \tag{24}$$

4.2. *Outline of the derivation*

The goal of this subsection is to express the transport law in terms of the distributions introduced above. First, let us consider distribution $f_a(\mathbf{v}|T, \mathbf{u}, \mathbf{n})$ of the molecules attacking the porous surface at a certain point, and distribution $f_r(\mathbf{v}|T, \mathbf{u}, \mathbf{n})$ of the molecules reflected from this surface (both distributions normalized to the numbers of such particles; we take into account that $T = T_P$). Function f_a is expressed as

$$f_a(\mathbf{v}|T, \mathbf{u}, \mathbf{n}) = |\mathbf{v}\mathbf{n}| f(\mathbf{v}|T, \mathbf{u}), \quad \mathbf{v}\mathbf{n} < 0 \tag{25}$$

Function f_r is expressed in terms of f_a and the reflection kernel B:

$$f_r(\mathbf{v}|T, \mathbf{u}, \mathbf{n}) = \int_{\mathbf{v}_1\mathbf{n}<0} B(\mathbf{v}_1 \to \mathbf{v}|\mathbf{n}, T) f_a(\mathbf{v}_1|T, \mathbf{u}, \mathbf{n})\,\mathrm{d}^3\mathbf{v}_1$$
$$= \int_{\mathbf{v}_1\mathbf{n}<0} |\mathbf{v}_1\mathbf{n}| B(\mathbf{v}_1 \to \mathbf{v}|\mathbf{n}, T) f(\mathbf{v}_1|T, \mathbf{u})\,\mathrm{d}^3\mathbf{v}_1 \tag{26}$$

As in the previous section, we derive the transport law from the momentum balance for an elementary volume V of a cylindrical shape, with cross-section A and height (length) l. We choose the direction of the cylinder to be parallel to the unit vector $\mathbf{n}_P$ of the pressure gradient. The gas in the volume is affected by the pressure force $\mathbf{F}$, equal to the difference of pressures applied to area A from different sides of the cylinder:

$$\mathbf{F} = -A\Delta P\mathbf{n}_P \approx -Al\nabla P = -V\nabla P \tag{27}$$

Force $\mathbf{F}$ should be equal to momentum per time unit $\mathbf{M}$, which is transferred from the molecules to the solid particles. This momentum is evaluated as

$$\mathbf{M} = \mathbf{M}_a - \mathbf{M}_r, \qquad \mathbf{M}_a = \int \mathrm{d}^2S \int_{\mathbf{v}\mathbf{n}<0} m\mathbf{v} f_a \mathrm{d}^3\mathbf{v},$$
$$\mathbf{M}_r = \int \mathrm{d}^2S \int_{\mathbf{v}\mathbf{n}>0} m\mathbf{v} f_r \mathrm{d}^3\mathbf{v}, \tag{28}$$

Here f_a and f_r are functions introduced in Eqs. (25) and (26). Each of these functions is a sum of the two addenda corresponding to the approximations $f^{(0)}$ and $f^{(1)}$ in the Chapman–Enskog expansion for f (see Eqs. (18) and (19)). In the following, we present only computations corresponding to approximation $f^{(0)}$. Computations for $f^{(1)}$ are fully similar. Later in Section 4.5 we bring formula for the contributions $\mathbf{M}_a^{(1)}$, $\mathbf{M}_r^{(1)}$ of $f^{(1)}$.

Direct calculation of the integrals involved in the expressions for $\mathbf{M}_a^{(0)}$ and $\mathbf{M}_r^{(0)}$ is hardly possible. It becomes possible, however, if we expand the Maxwell distribution (18) with regard to velocity $\mathbf{u}$. Applying Eq. (22) gives

$$f^{(0)}(\mathbf{v}|T, \mathbf{u}) = f_1 + f_2 + o(\mathbf{u}), \qquad f_1 = f_0(\mathbf{v}|T),$$
$$f_2 = f_0(\mathbf{v}|T)\frac{m(\mathbf{v}\mathbf{u})}{kT} \tag{29}$$

In view of expansion (29), distributions f_a, f_r, and the corresponding force momenta $\mathbf{M}_a$, $\mathbf{M}_r$ are also split into the two addenda: $\mathbf{M}_{a1}$, $\mathbf{M}_{a2}$, and $\mathbf{M}_{r1}$, $\mathbf{M}_{r2}$, correspondingly. The resulting force balance, accounting for Eqs. (27) and (28) may be represented in the form of

$$-V\nabla P + \mathbf{M}_{r1} - \mathbf{M}_{a1} + \mathbf{M}_r^{(1)} - \mathbf{M}_a^{(1)} = \mathbf{M}_{a2} - \mathbf{M}_{r2} \tag{30}$$

The left-hand side of the last equation depends only on the thermodynamic variables, while the right-hand side is proportional to velocity $\mathbf{u}$.

Computation of the integrals $\mathbf{M}_{ai}$, $\mathbf{M}_{ri}$, $\mathbf{M}_a^{(1)}$, $\mathbf{M}_r^{(1)}$ consists in multiple integration and is rather straightforward, apart from a few details. First, we will split the integration over velocity

$\int \mathrm{d}^3\mathbf{v}$ into the product of the integral $\int v^2\,\mathrm{d}v$ over the absolute velocity value and the integral $\int \mathrm{d}^2\mathbf{n}_v$ over a unit vector parallel to velocity:

$$\int \mathrm{d}^3\mathbf{v} = \int v^2 \mathrm{d}v \int \mathrm{d}^2\mathbf{n}_v \tag{31}$$

Integration over d^2S in $\mathbf{M}_{\mathrm{r}1}$, $\mathbf{M}_{\mathrm{a}1}$ may be carried out directly, without any assumption about the internal surface. This is shown in the next subsection. For $\mathbf{M}_{\mathrm{a}2}, \mathbf{M}_{\mathrm{r}2}$, an additional assumption about the structure of the internal surface is needed. We assume that the surface is *isotropic and equally accessible to the molecules*, that is, that all the directions of the normal $\mathbf{n}$ to the surface are equiprobable. In this case, by definition of the specific surface S,

$$\int \mathrm{d}^2S = \frac{VS}{4\pi} \int \mathrm{d}^2\mathbf{n} \tag{32}$$

The unit vector $\mathbf{n}$ is normal to the surface and directed into the porous space. Thus, integrations $\int \mathrm{d}^2\mathbf{n}_v$, $\int \mathrm{d}^2\mathbf{n}$ are carried out over a unit sphere.

The assumption about equal accessibility of all the internal points of the surface is rather restrictive. It may be violated in structured porous media and in porous media with wide pore size distributions. There may be small or narrow pores where the particles are entrapped, or tortuous capillaries where they are entangled. Moreover, the assumption may be violated in cases of strong interactions between the gas particles in the porous walls. In the last cases, the particles may be adsorbed on the walls or form non-uniform adjacent layers [26]. Surface flows also become important in these cases. Most of the mentioned phenomena may be incorporated into the model being developed. However, we do not consider them here, trying to present as simple model as possible. Possible extensions are subject to a separate work.

4.3. Integrals $\boldsymbol{M}_{r1}$, $\boldsymbol{M}_{a1}$

The goal of this subsection is to show that integrals $\mathbf{M}_{\mathrm{r}1}$, $\mathbf{M}_{\mathrm{a}1}$ are neither dependent on the distribution of the internal surface (the shapes of the grains), nor on the character of collisions (kernel B). More particularly, we will show that

$$\mathbf{M}_{\mathrm{r}1} = -\mathbf{M}_{\mathrm{a}1} = \frac{1}{2}(1-\phi)V\nabla P, \tag{33}$$

so that

$$\mathbf{M}_{\mathrm{r}1} - \mathbf{M}_{\mathrm{a}1} = CV_{\mathrm{g}}\nabla P = (1-\phi)V\nabla P \tag{34}$$

First, let us exclude the collision kernel B. This kernel enters $\mathbf{M}_{\mathrm{r}1}$, through $f_{\mathrm{r}1}$ (see Eqs. (26) and (28)):

$$f_{\mathrm{r}1} = \int_{\mathbf{v}_1\mathbf{n}<0} |\mathbf{v}_1\mathbf{n}| B(\mathbf{v}_1 \to \mathbf{v}|\mathbf{n}) f_0(\mathbf{v}_1|T)\,\mathrm{d}^3\mathbf{v}_1,$$

Application of the principle of microscopic reversibility (23) and integration over $-\mathbf{v}_1$ by use of Eq. (24) result in

$$f_{\mathrm{r}1} = |\mathbf{vn}| f_0(\mathbf{v}|T) = f_{\mathrm{a}1}$$

From this equation and Eq. (28) it follows that $\mathbf{M}_{\mathrm{r}1} = -\mathbf{M}_{\mathrm{a}1}$, and only one of these integrals must be calculated. We have

$$\mathbf{M}_{\mathrm{a}1} = m \int \mathrm{d}^2S \int_{\mathbf{vn}<0} \mathrm{d}^3\mathbf{v}\,\{|\mathbf{vn}| f_0(\mathbf{v}|T)\mathbf{v}\}$$

Integration over $\mathrm{d}^3\mathbf{v}$ with the help of Eq. (31) and standard integrals (see Appendix A) results in

$$\mathbf{M}_{\mathrm{a}1} = -\frac{1}{2}\int \mathbf{n}NkT\mathrm{d}^2S = -\frac{1}{2}\int P\mathbf{n}\mathrm{d}^2S$$

Here integration is carried out over the external surface of the grains of the porous medium. With the help of the Gauss theorem, this integral may be transformed to the integral over the volume of the grains:

$$\mathbf{M}_{\mathrm{a}1} = -\frac{1}{2}\int \nabla P \mathrm{d}^3V_{\mathrm{g}}$$

Considering the pressure gradient to be approximately constant over the selected elementary volume and taking into account that $V_{\mathrm{g}} = (1-\phi)V$, we reduce the last equation to the form (33). Thus, both this equation and Eq. (34) are proven.

The fact that the difference $\mathbf{M}_{\mathrm{r}1} - \mathbf{M}_{\mathrm{a}1}$ is always the same is not surprising. Indeed, this difference expresses the pressure force acting on the grains of the porous medium. Another term on the left-hand side of Eq. (30), $-V\nabla P$, expresses the pressure force acting on the whole volume containing porous medium + gas. The rest part of the force, $-\phi V\nabla P$, acts only on gas. This explains the appearance of the porosity ϕ on the left-hand sides of Eqs. (7) and (17) (and, later, Eq. (37)).

4.4. Integrals $\boldsymbol{M}_{r2}$, $\boldsymbol{M}_{a2}$

Computation of these integrals is straightforward, but cumbersome. The answer depends on the structure of the internal surface and, for $\mathbf{M}_{\mathrm{r}2}$, also on the reflection kernel. For example, for the case of complete accommodation (21) and isotropic internal surface (32) integral $\mathbf{M}_{\mathrm{r}2}$ assumes the form of

$$\begin{aligned} \mathbf{M}_{\mathrm{r}2} = {} & -mNVS2^{-9/2}\pi^{-7/2}\left(\frac{kT}{m}\right)^{-7/2} \int \mathrm{d}^2\mathbf{n} \int_{\mathbf{vn}>0} \mathrm{d}v \\ & \times \int \mathrm{d}\mathbf{n}_v \int_{\mathbf{n}_{v1}\mathbf{n}<0} \mathrm{d}^2\mathbf{n}_{v1} \int_0^\infty \mathrm{d}v_1 \Big\{ (\mathbf{n}_{v1}\mathbf{n})(\mathbf{n}_v\mathbf{n})(\mathbf{n}_{v1}\mathbf{u})v_1^4 v^4 \\ & \times \exp\left(-\frac{mv^2}{2kT}\right) \exp\left(-\frac{mv_1^2}{2kT}\right) \mathbf{n}v \Big\} \end{aligned}$$

Further integration is carried out by application of the integrals listed in the Appendix A. The results are

$$\mathbf{M}_{\mathrm{a}2} = \frac{4}{3}\sqrt{\frac{2}{\pi}} V\rho S \left(\frac{kT}{m}\right)^{1/2} \mathbf{u},$$

$$\mathbf{M}_{r2} = -\frac{\sqrt{2\pi}}{12} V\rho S \left(\frac{kT}{m}\right)^{1/2} \mathbf{u} \tag{35}$$

4.5. Contribution of the first approximation

Computation of the integrals arising from the first approximation is similar to the computation of $\mathbf{M}_{r2}$, $\mathbf{M}_{r2}$. It may be derived that

$$\mathbf{M}_{\mathrm{r}}^{(1)} - \mathbf{M}_{\mathrm{a}}^{(1)} = \frac{4}{15}\sqrt{\frac{2}{\pi}}VS\lambda\left(\frac{kT}{m}\right)^{-1/2}\nabla T \qquad (36)$$

4.6. Final result

Substitution of Eqs. (34) and (35) into Eq. (30) results in

$$-V\nabla P + (1-\phi)V\nabla P + \frac{4}{15}\sqrt{\frac{2}{\pi}}VS\lambda\left(\frac{kT}{m}\right)^{-1/2}\nabla T$$
$$= \frac{4}{3}\sqrt{\frac{2}{\pi}}V\rho S\left(\frac{kT}{m}\right)^{1/2}\mathbf{u} + \frac{\sqrt{2\pi}}{12}V\rho S\left(\frac{kT}{m}\right)^{1/2}\mathbf{u},$$

or

$$-\phi\nabla P + \frac{4}{15}\sqrt{\frac{2}{\pi}}S\lambda\left(\frac{kT}{m}\right)^{-1/2}\nabla T = \frac{16+\pi}{6\sqrt{2\pi}}S\rho\left(\frac{kT}{m}\right)^{1/2}\mathbf{u} \qquad (37)$$

This is the final expression for the gas transport law in the dense kinetic regime.

5. Discussion of the results

We have the transport law for gas in a tight porous medium in different regimes, using, subsequently, dimensionality considerations, simple mechanistic considerations, and the gas kinetic theory. Not surprisingly, the resulting expressions are similar. All of them may be represented in the common form (10), which we repeat for convenience:

$$S\phi^{-1}v^{-1}\mathbf{u} = \beta\left(\beta_{\mathrm{T}}\frac{\nabla T}{T} - \frac{1}{P}\nabla P\right)$$

Coefficient β is constant in all the regimes considered. This constant, however, is different for the different regimes (Knudsen or intermediate, Eqs. (7) and (37), correspondingly). For the case of complete accommodation, it is equal to $(24/13)\sqrt{2/\pi} \approx 1.5$ for the Knudsen regime, and $6\sqrt{2\pi}/(16+\pi) \approx 0.8$ for the dense kinetic regime. The fact that for the dense kinetic regime β is lower corresponds to the well-known minimum of the gas permeability at intermediate pressures [1]. Our approach seems to be rather advantageous for description of this minimum, clearly evaluating its value.

It should be taken into account that constant β was calculated for fully chaotic porous media, where the collisions with all the points of the internal surface are equally probable, and this surface is isotropic. For more ordered media this constant may also depend on the assumed shapes of the grains or capillaries, although this dependence is not very strong [1].

The value of β_{T} behaves less trivially. While it is equal to 1/2 for the Knudsen regime, for the dense regime it is expressed as follows (cf. Eqs. (10) and (37)):

$$\beta_{\mathrm{T}} = \frac{8\lambda S}{15\sqrt{2\pi}vRN\phi}$$

Thus, β_{T} depends on both the thermodynamic parameters of gas and the porous medium. The value of β_{T} may also be expressed as a function of porosity and dimensionless parameter $\mathrm{Kn} = l_{\mathrm{f}}S$ introduced in Section 2. In order to do so, the well-known kinetic expression for heat conductivity, $\lambda = \psi N c_v v l_{\mathrm{f}}$, is used. Here c_v is gas heat capacity at constant volume, and ψ dimensionless parameter depending on the type of collisions (close to 1/3). Substitution of the last expression for λ results in

$$\beta_{\mathrm{T}} = \frac{8\psi\gamma\mathrm{Kn}}{15\sqrt{2\pi}\phi} \approx 0.07\frac{\gamma\mathrm{Kn}}{\phi}, \qquad \gamma = \frac{c_v}{R}$$

Thus, in the dense kinetic regime the value of β_{T} is proportional to Kn. This results in a rather non-trivial transport law under constant pressure (not density!) in this regime:

$$\mathbf{u} = \frac{48\lambda}{15(16+\pi)P}\nabla T \qquad (38)$$

As in the Knudsen regime, the gas flows from the cold to the hot side. However, unlike the Knudsen regime, the transport coefficient in the dense kinetic regime is independent of the properties of the porous medium (at least for the case where this porous medium is fully non-structured and isotropic). This is explained by the fact that Eq. (38) is obtained by equating two forces: the friction force of the moving gas and the "thermal force" arising from the non-equilibrium gas temperature distribution. Both forces are proportional to the specific surface, which, thus, disappears when they are equated. In a different way, this independence of the parameters of the porous medium may be illustrated by considering the friction and the thermal force per one grain of the porous medium and then summing over all the grains.

Experimental determination of the value of β_{T} is possible in a steady-state flow experiment. The steady-state condition is given by

$$PT^{-\beta_{\mathrm{T}}} = \mathrm{const} \qquad (39)$$

A necessity for experimental determination of β_{T} (as well as β) arises from the fact that the transition from the Knudsen to the dense kinetic regime and further to the Darcy regime (where β_{T} is traditionally considered to be equal to zero) is not clear. As discussed in Section 2, all the three regimes correspond to certain asymptotics where the different parameters tend to zero or to infinity. Intermediate cases cannot be described in this way. Generally speaking, neither kinetic derivation can fully describe transition from the kinetic to the Darcy regime, from the non-structured molecular to the structured flow. Correct description of the Darcy regime is obtained by averaging of the 'Stokes equations in the porous space (for example, similar to [11]). Transition between the regimes is achieved by application of the additivity assumption [1], or, almost equivalently, by an interpolation formula [8]. Most of these approaches do not account for minimum of permeability caught by our approach. A rigorous theory for transition between the Knudsen and the Darcy regimes probably requires an innovative approach and is still to be developed.

6. Conclusion

We have developed a gas kinetic approach to the description of the gas flow in a porous medium in the intermediate flow regime. The computations based on the gas kinetic theory are confirmed by a simplified derivation, as well as by the analysis of dimensions. Special attention was paid to the contribution of the thermal gradient to the transport law. It was proven that this gradient is important to both the Knudsen and the dense kinetic regimes, although it plays totally different roles in these regimes. Experiments are needed in order to confirm or to disprove this statement, and to check the involvement of the thermal gradient for gas flow in different thermodynamic conditions.

The developed theory may be generalized onto phoresis of heavy particles in gas. However, additional developments are needed in order to do so, and additional thermal effects may be involved. Another generalization to be considered separately is the flow of the gas mixtures.

Appendix A. Calculation of the kinetic integrals

In this appendix we list the integrals which are used for computations in Sections 4.3 and 4.4. The integral over the absolute value of velocity v is carried out with the help of the standard integrals of the type of $\int v^{\beta}\exp(-\alpha v^2)\,\mathrm{d}v$. Integrals over d$\mathbf{n}$, d$\mathbf{n}_v$, d$\mathbf{n}_{v1}$ should be taken in a certain order: first, over d$\mathbf{n}_{v1}$, then over d$\mathbf{n}_v$, and afterwards over d$\mathbf{n}$. In these calculations, the following integrals are applied (similar to those used in the Enskog theory of dense gases [18]):

$$-\int_{\mathbf{n}_1\mathbf{n}<0} \mathrm{d}^2\mathbf{n}_1(\mathbf{n}_1\mathbf{n}) = \int_{\mathbf{n}_1\mathbf{n}>0} \mathrm{d}^2\mathbf{n}_1(\mathbf{n}_1\mathbf{n}) = 2\pi;$$

$$\int_{\mathbf{n}_1\mathbf{n}<0} \mathrm{d}^2\mathbf{n}_1(\mathbf{n}_1\mathbf{n})\mathbf{n}_1 = \int_{\mathbf{n}_1\mathbf{n}>0} \mathrm{d}^2\mathbf{n}_1(\mathbf{n}_1\mathbf{n})\mathbf{n}_1 = \frac{2\pi}{3}\mathbf{n}$$

(These equalities are easy to check by selecting $\mathbf{n} = (0, 0, 1)$).

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