

Onsager Equation Approach to Gas Flow through Porous Media

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Abstract: - Time-independent Onsager-type equations are written for a gas diffusing in a slab of porous medium subjected to temperature and pressure gradients. They are solved to obtain temperature, density and pressure profiles inside the slab. Density distribution of gas molecules inside the slab is seen to depend strongly on both temperature and pressure gradients, with a close interplay between the two. Dimensionless particle current and heat flow are computed as a function of diffusion coefficients and boundary conditions.

Key-Words: - Transport phenomena; Onsager equations; Porous materials; Gas flow; Kinetic theory; Two-temperature problem; Temperature and density profiles.

1 Introduction

The motion of fluids through porous media is often studied with equations derived from, or akin to, what is known in transport theory as diffusion approximation [1]. These equations can be arrived at with several procedures, but they share the common feature that motion is determined exclusively by density gradients; in other words, no account is taken of, or provision made for, the temperature gradients that may exist, or come into being because of the transport processes. However, and this is of special significance in the case of gases, transport phenomena are driven by density and temperature gradients alike, and neglect of the latter may lead to significant errors. In the present work, a method is presented that is based on an Onsager equations approach to the problem. Onsager equations are, originally, a phenomenological description of non-equilibrium thermodynamics [2]: but once they are written down in terms of gradients and coefficients, these latter still need to be determined for the equations to be useful. This can perhaps be done experimentally, or by yet other means: however, it is possible to derive them from kinetic theory, making suitable approximations on the distribution function and then making use of Boltzmann equation [3,4,5,6]. In this sense, they become a rigorous result of kinetic theory, and a useful tool in those physical instances in which legitimate use can be made of them, allowance being made for the assumptions and limitations introduced in their derivation.

The situation considered in the present work is as follows: a slab of porous material, having breadth and length large enough compared to thickness that the problem may be viewed as one-dimensional, is in contact with a gas. The gas has known temperature

and pressure T_0 and p_0 on one side, and T_L and p_L on the other side, as presented in Fig. 1. The gas diffuses through the porous material under the effect of density and temperature gradients: it is desired to determine density, temperature and pressure profiles once a steady state is reached. Under these conditions, pointwise thermal equilibrium is assumed between the diffusing gas and the porous medium.

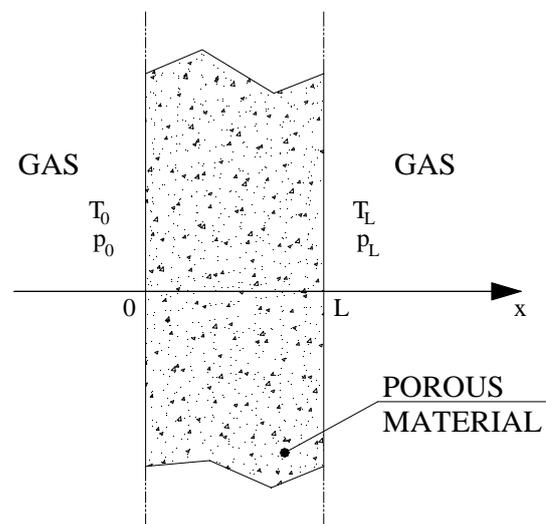


Fig.1: problem geometry

This is possibly the simplest and most straightforward problem that can be posed: however, despite its simplicity, considerable insight can be gained from its solution. Furthermore, it may represent quite accurately many real instances. Density profiles, in particular, may be of considerable interest in technological processes where porous materials are treated with gaseous substances for any purpose where the density of gas

molecules, or perhaps its distribution and uniformity, have a bearing on the success of the whole process [7].

As is customary in transport theory, interaction between gas molecules and diffusing medium will be described through cross sections. To this end some model, accurate enough but mathematically treatable enough, needs to be thought of to describe the porous medium. In the following the so called rigid sphere model will be assumed for the cross sections, and the medium will be thought of as composed of grains of varying size, as depicted schematically in Fig. 2, all interacting with gas molecules as rigid spheres. Also, grains will be very massive compared to the molecules of the gas, so that scattering is isotropic in the laboratory reference frame. Under such conditions, the transport cross section is independent of molecule velocity. Different sizes will entail different microscopic cross sections for the grains, yet they can all be compounded into one macroscopic cross section Σ_0 , independent of velocity, with the usual methods of kinetic theory.

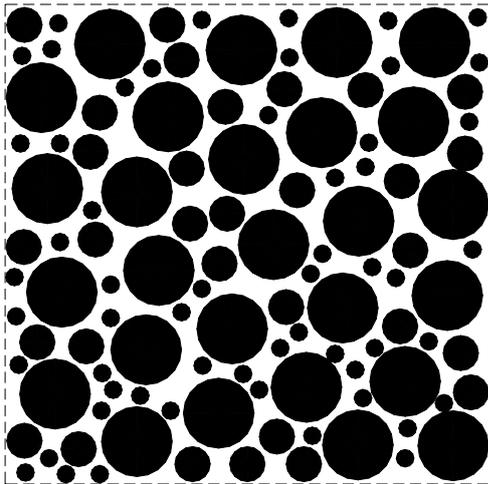


Fig.2: porous medium model

As will appear clearly in the following, the exact value of this cross section is not needed to solve the problem as was proposed, its being a constant suffices to determine the requested profiles. However, to calculate particle flow and heat flow the correct value would be required, albeit only as a multiplicative constant. Only the expressions for those two latter quantities will be written here, as the aforementioned constant will not be determined within the scope of this work.

2 Problem Formulation

As discussed above, in references [4,5,6] Onsager-type transport equations were derived from

Boltzmann equation; transport coefficients can then be determined given the appropriate cross sections. The end results will be used here, particularized to the present case of slab symmetry: the interested reader is referred to the references for further details. In Onsager equations, particle current $J(x)$ and flow of heat $Q(x)$ are given in terms of temperature and density gradients and of temperature-dependent transport coefficients.

Onsager equations, for the case at hand, can be written [4,5,6]

$$J(x) = -D(T) \frac{dn(x)}{dx} - n(x) \alpha^*(T) \frac{dT(x)}{dx} \quad (1)$$

$$Q(x) = -\gamma(T) \frac{dn(x)}{dx} - n(x) \kappa^*(T) \frac{dT(x)}{dx} \quad (2)$$

Here and in the following, temperature will be in energy units (i.e., T will be written for $K_B T$, where K_B is Boltzmann constant). Onsager equation can be supplemented with conditions on the flows of molecules and heat, i.e., the continuity and energy conservation equations. In the present case where no absorption is considered and thermal equilibrium between gas and medium is assumed, one obtains:

$$\frac{d}{dx} J(x) = 0 \quad (3)$$

$$\frac{d}{dx} Q(x) = 0 \quad (4)$$

The coefficients appearing in Eq.s 1-4 being as follows:

$$D(T) = D_c T^{\frac{1}{2}} \quad (5)$$

$$\alpha^*(T) = D_c \frac{1}{2} T^{-\frac{1}{2}} \quad (6)$$

$$\gamma(T) = D_c 2 T^{\frac{3}{2}} \quad (7)$$

$$\kappa^*(T) = D_c 3 T^{\frac{1}{2}} \quad (8)$$

with

$$D_c = \frac{1}{3\Sigma_0} \sqrt{\frac{8}{m\pi}} \quad (9)$$

Once the parameters Eq,s (5-8) are inserted in Onsager equations, the system of equations Eq,s (1-4) can be reworked to eliminate J and Q ; the third equation ensures that J is constant everywhere, constant that will be denoted J_c in the following.

Two equations can be obtained containing only n and T

$$n(x)T^{\frac{1}{2}}(x) \frac{d^2T}{dx^2} + 2 \frac{J_c}{D_c} \frac{dT}{dx} = 0 \tag{10}$$

$$n(x) = T^{-\frac{1}{2}}(x) \frac{J_c}{D_c} (a - x) \tag{11}$$

Inserting Eq. (11) into Eq. (10) an equation for T alone is obtained:

$$\frac{d^2T}{dx^2} + \frac{2}{a+x} \frac{dT}{dx} = 0 \tag{12}$$

The general solution of Eq.s (12) is found as

$$T(x) = C_3 - \frac{C_2}{a-x} \tag{13}$$

Eq. (11) yields the density: albeit the number density is the more fundamental quantity, pressure is of more practical usage, and recalling that $p = nT$,

$$p(x) = T^{+\frac{1}{2}} \times \left[C_1 + \frac{J_c}{D_c} (a - x) \right] \tag{14}$$

Eq.s (13) and (14) contain 4 integration constants to be determined from boundary conditions: a , J_c , C_2 and C_3 . Here, referring to the case depicted in Fig. 1, solutions can be written as

$$a = \frac{p_0 T_0^{-\frac{1}{2}}}{p_0 T_0^{-\frac{1}{2}} - p_L T_L^{-\frac{1}{2}}} L \tag{15}$$

$$J_c = -D_c \frac{p_L T_L^{-\frac{1}{2}} - p_0 T_0^{-\frac{1}{2}}}{L} \tag{16}$$

$$Q = -2D_c \frac{p_L T_L^{\frac{1}{2}} - p_0 T_0^{\frac{1}{2}}}{L} \tag{17}$$

$$T(x) = T_0 - \frac{T_0 - T_L}{L} \frac{a - L - x}{a - x} \tag{18}$$

$$p(x)T^{-\frac{1}{2}} = p_0 T_0^{-\frac{1}{2}} + \frac{p_L T_L^{-\frac{1}{2}} - p_0 T_0^{-\frac{1}{2}}}{L} x \tag{19}$$

2.1 Self-similar solution

The solution can be recast in dimensionless form, to obtain a self-similar solution. To this end dimensionless variables will be defined as follows:

$$\tilde{x} = \frac{x}{L}; \quad \tilde{a} = \frac{a}{L}; \quad \tilde{T} = \frac{T}{T_0}; \quad \tilde{p} = \frac{p}{p_0}; \quad \tilde{n} = \frac{n}{n_0}; \tag{20}$$

With these positions, the following dimensionless equations can be written

$$\tilde{a} = \frac{1}{1 - \tilde{p}_L \tilde{T}_L^{-\frac{1}{2}}} \tag{21}$$

$$\tilde{T}(\tilde{x}) = 1 - \left(1 - \tilde{T}_L\right) \frac{\tilde{a} - 1}{\tilde{a} - \tilde{x}} \tilde{x} \tag{22}$$

$$\tilde{p}(\tilde{x}) \tilde{T}^{-\frac{1}{2}} = 1 + \left(\tilde{p}_L \tilde{T}_L^{-\frac{1}{2}} - 1\right) \tilde{x} \tag{23}$$

$$\tilde{n}(\tilde{x}) = \frac{\tilde{p}(\tilde{x})}{\tilde{T}(\tilde{x})} \tag{24}$$

Dimensionless particle and heat flows as well may be defined introducing the following quantities:

$$J_0 = \frac{D_c p_0 T_0^{-\frac{1}{2}}}{L}; \quad Q_0 = 2J_0 T_0 \tag{25}$$

the dimensionless flows can then be calculated as

$$\tilde{J} = \frac{J_c}{J_0} = 1 - \tilde{p}_L \tilde{T}_L^{-\frac{1}{2}} \tag{26}$$

$$\tilde{Q} = \frac{Q}{Q_0} = 1 - \tilde{p}_L \tilde{T}_L^{+\frac{1}{2}} \tag{27}$$

3 Results

Fig.s 3 to 10 present plots of dimensionless temperature, pressure and density across the porous medium, as a function of dimensionless position \tilde{x} , for several values of \tilde{T}_L and \tilde{p}_L . The dimensionless flows, for the same combinations of temperature and pressure jumps as in the figures, are shown in Table 1.

\tilde{T}_L	\tilde{p}_L	\tilde{J}	\tilde{Q}
0.1	0.1	0.684	0.968
	0.2	0.368	0.937
0.2	0.2	0.552	0.911
	0.5	-0.118	0.776
0.5	0.2	0.717	0.859
	0.5	0.293	0.646
0.8	0.2	0.776	0.821
1.0	0.2	0.800	0.800

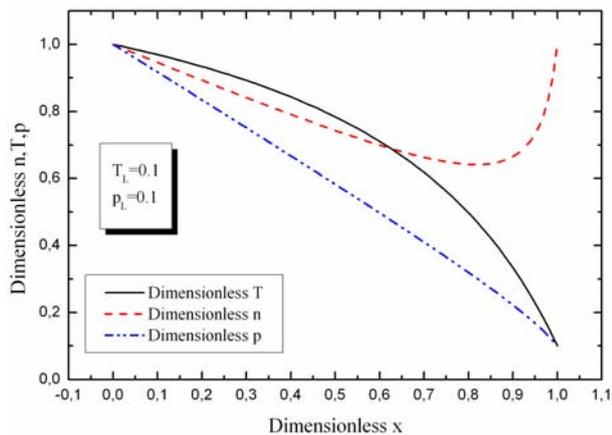


Fig. 3: \tilde{T} , \tilde{p} and \tilde{n} vs. \tilde{x} : case $\tilde{T}_L = 0.1$, $\tilde{p}_L = 0.1$

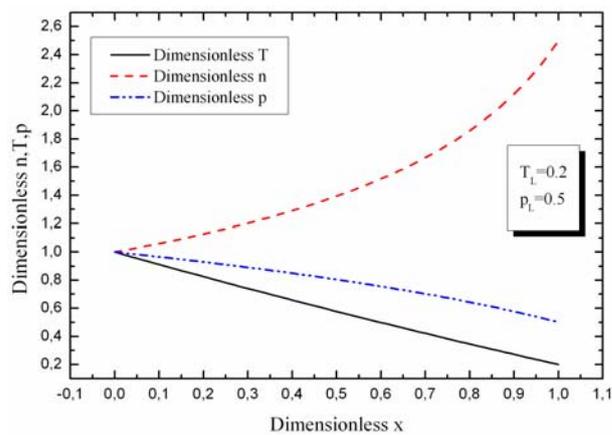


Fig. 6: \tilde{T} , \tilde{p} and \tilde{n} vs. \tilde{x} : case $\tilde{T}_L = 0.2$, $\tilde{p}_L = 0.5$

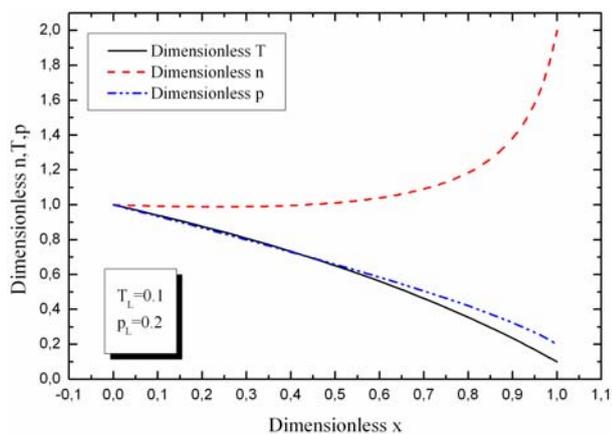


Fig. 4: \tilde{T} , \tilde{p} and \tilde{n} vs. \tilde{x} : case $\tilde{T}_L = 0.1$, $\tilde{p}_L = 0.2$

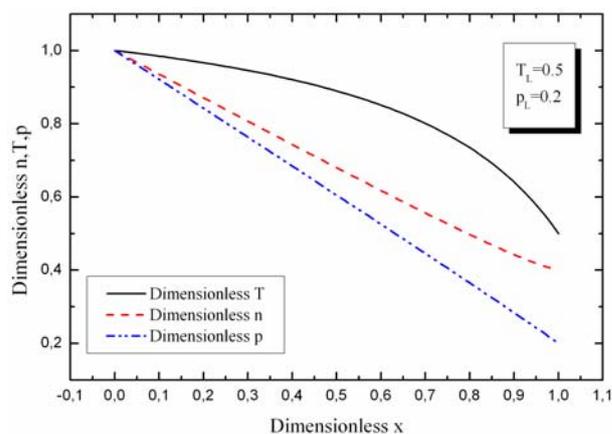


Fig. 7: \tilde{T} , \tilde{p} and \tilde{n} vs. \tilde{x} : case $\tilde{T}_L = 0.5$, $\tilde{p}_L = 0.2$

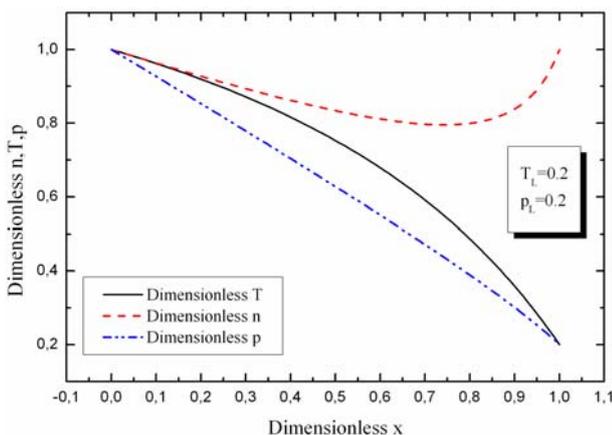


Fig. 5: \tilde{T} , \tilde{p} and \tilde{n} vs. \tilde{x} : case $\tilde{T}_L = 0.2$, $\tilde{p}_L = 0.2$

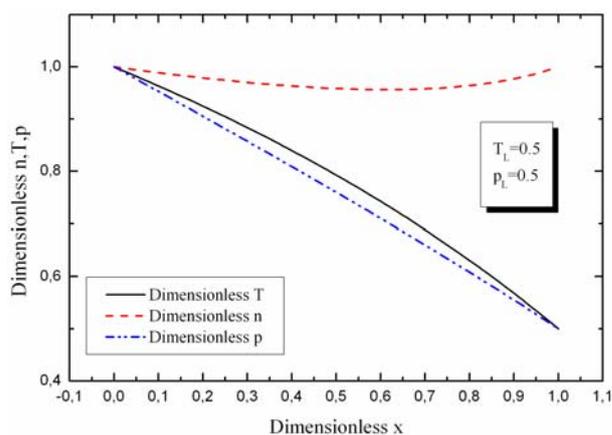


Fig. 8: \tilde{T} , \tilde{p} and \tilde{n} vs. \tilde{x} : case $\tilde{T}_L = 0.5$, $\tilde{p}_L = 0.5$

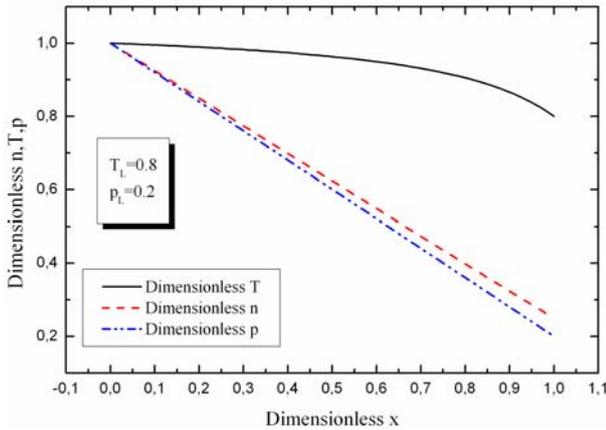


Fig. 9: \tilde{T} , \tilde{p} and \tilde{n} vs. \tilde{x} : case $\tilde{T}_L = 0.8$, $\tilde{p}_L = 0.2$

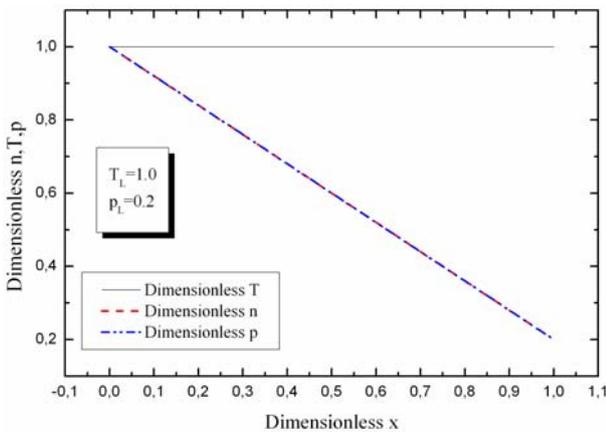


Fig. 10: \tilde{T} , \tilde{p} and \tilde{n} vs. \tilde{x} : case $\tilde{T}_L = 1$, $\tilde{p}_L = 0.2$

4 Conclusions

As can be gathered from the results presented, density profiles are very sensitive to the pressure and temperature ratios at the two sides of the slab. This suggests the possibility that gas density be tuned somehow at will by a cunning choice of temperatures and pressures on the boundaries. This might be of technical interest where control of the density is meaningful to successful treatments. On the contrary, the trends of temperature and pressure profiles do not exhibit any similar variability. It must be underlined that neglecting the compound effect of temperature and pressure gradients (as done, for instance, in the diffusion equation and related approximations) would lead to overlook completely the effect of temperature-driven diffusion with the result that density profiles would be markedly inaccurate. Finally, one word on distribution functions: were they desired, as they may become of use in investigating the chemistry of reactions (particularly threshold reactions) between the gas and the

medium, they are easily determined within the present method, and with the same level of approximation.

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