Journal of Statistical Physics, Vol. 126, No. 2, January 2007 (© 2006)
DOI: 10.1007/s10955-006-9110-2

A New Momentum Equation for Gas Flow in Porous Media: The Klinkenberg Effect Seen Through the Kinetic Theory

V. Pavan[1,2] and L. Oxarango[3]

Received September 26, 2005; accepted April 3, 2006
Published Online: January 5, 2007

In this paper, an original set of transport equations for gas in porous media is developed. As far as low pressure gases or very fine grained porous media are concerned, molecular effects are likely to promote a dependency of the permeability on the pressure. These phenomena are usually modelled using the Klinkenberg correction to the Darcy's law. The retained methodology brings a new interpretation of this particular problem. The approach is based on a volume averaging scale-change methodology applied to the Boltzman equation taking into account the presence of walls. It leads to a homogenized kinetic equation describing the problem at the macroscale. A proper closure is then applied following the strategy proposed by Levermore to obtain a hydrodynamic description. The hydrodynamic force applied by the porous structure on the gas exhibits a strong non-linearity with the gas velocity. However, a linearization is proposed, recovering formally the classical Darcy's law. The validity of the resulting permeability tensor is finally discussed. As its dependency with pressure is concerned, it opens an original interpretation of the nature of the Klinkenberg effect.

KEY WORDS: kinetic theory, gas flow, porous media, Klinkenberg effect, Levermore closure hierarchy.

1. INTRODUCTION

Gas flows in porous media are well known to differ from liquid ones when the compressibility effects become significant. In such conditions, the classical Darcy's

[1] Institut de Mécanique des Fluides de Toulouse, Allée du professeur Camille Soula, 31400 Toulouse, France; e-mail: v.pavan@laposte.net
[2] Institut de Recherche Interdisciplinaire, IEMN UMR 8520, Cité scientifique avenue Poincarré, BP 60069, F-59652 Villeneuve d'Ascq, France.
[3] Laboratoire d'étude des Transferts en Hydrologie et Environnement, UMR 5564 CNRS INPG IRD UJF, BP 53, 38041 Grenoble, France.

law needs to be modified to fit the experimental measures carried out either at low pressures or in porous media featuring very small characteristic pore sizes. In his work performed in 1941, Klinkenberg[1] was among the first ones to quantify this phenomenon and to provide an empirical correction to Darcy's law by proposing a non local dependency of the permeability on the gas pressure:

$$K_g = K_l \left(1 + \frac{B}{P}\right) \tag{1}$$

Here K_g and K_l denote the so called gas and liquid permeability, B is known as the Klinkenberg factor (that must be linked to the gas properties) and P denotes the mean pressure in the porous sample. The pressure dependency of the gas permeability was originally put forward by many authors in the field of petroleum or natural gas engineering.[2] More recently, research has been carried out in various configurations with different experimental apparatus providing a collection of values for the Klinkenberg's coefficient B. To illustrate the interest of characterizing the deviation from the Darcy's law, one can mention the studies on air flows in the unsaturated zone hydrology,[3] vapour in Geysers,[4] gas flows in aerogels,[5] ceramic membranes[6] or mortars.[7] The physical interpretation of the Klinkenberg's effect appears to lie in some molecular aspects of gas transport when the Knudsen number becomes close to unity: $Kn = \lambda / l_p \approx 1$. Here λ is the mean free path of the molecules and l_p is a characteristic dimension of the flow domain. In such a configuration, the particle/wall collisions cease to be negligible compared to the particle/particle ones. To investigate these situations, recent works on microfluidics[8,9] have focused on getting rarefied gas flows in ducts. These accurate experimental set-ups have provided precious tools to understand the flow transitions in micro and nano structures and have supplied a comprehensive overview of the rarefaction effects (Fig. 1) for Kn ranging from 0.001 to 3.

The mathematical modelling of rarefied gas flows in ducts has been a major subject of interest for the last twenty years. In this field of fluid dynamics, both traditional continuum approach and molecular dynamics based on the kinetic theory have been applied.[11] Getting away from low Knudsen flows to explore rarefaction effects requires to change the classical model step by step. For $0.001 \leq Kn \leq 0.1$ numerous evidences show that the continuum point of view can be kept provided that the stick boundary conditions are replaced with the

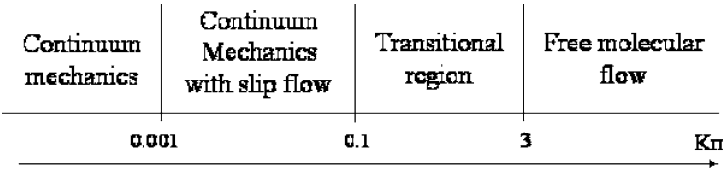

Fig. 1. Classification of flow regimes with the Knudsen number (from Ref. 10).

slip ones (Refs. 12–14 or Mitsuya (1993)). In the transitional regime however ($0.1 \leq Kn \leq 3$), the Navier–Stokes equation (NSE) must be dropped in favour of the classical Boltzmann equation (CBE) solved by Monte Carlo Direct Simulations (MCDS). This association is known to provide satisfactory results and may also catch the hydrodynamic limit (with high computational costs however) as well as the free molecular flows ($Kn \geq 3$).[15–18] For the latter regime however, the deterministic molecular simulations appear to be the most relevant ones (see for instance Ref. 19). In the field of general porous media, most of the models attempting to account for the Klinkenberg effect begin with assuming that the NSE using slip boundary is valid in the pores. Following this idea, Sketjne and Auriault[20] obtained the Klinkenberg's correction to Darcy's law by using the homogenization strategy of Bensoussan *et al.*[21] and Sanchez-Palencia[22] to the Stokes flow problem. A bit later, Lasseux[23] realized comparable developments by applying the Volume Averaging scale change theory of Whitaker[24] to the same problem. For gases evolving in the transitional regime however, and following the works performed for flows in ducts, it seems preferable to drop the NSE in favour of the CBE to describe the evolution of particles inside the pores. Such an idea has been already developed in the framework of the Dusty Gas Model by Mason and Malinauskas.[25] Their model assumes that the behaviour of the gas particles can be modelled in the medium by using a Boltzmann equation for a binary mixture of light gas molecules and heavy steady particles representing the solid matrix. In such an approach, the most challenging task to obtain a correct description of the flow inside the porous medium consists in a suitable treatment of the solid/gas interactions. De Socio *et al.*[26] proposed to consider that the collisions on walls only modify the momentum of the gas particle in the direction normal to the wall. Furthermore to simplify the form of the collision integral in CBE, the porous media were modelled as a set of large square particles randomly distributed in the space. An explicit expression of the macroscopic equation governing the flow is finally obtained by using a Chapman Enskog expansion. More recently, De Socio and Ianiro[27] have extended this approach to study free flows in plane channels over a porous domain. The expression of the porous zone permeability obtained in this study is inversely proportional to the local pressure. The aim of the present work is to propose an original methodology to obtain the governing macroscopic equations of gas flows in porous media when microscopic particles evolve in the transitional regime thanks to the ideas and the concepts introduced by Levermore.[28] His method consists in a straightforward generalization of what is traditionally done to compute NSE from CBE. The remainder of the paper is organized as follows. In the first part, we derive a general homogenized kinetic equation from CBE for a set of particles trapped in a porous structure. This equation features in its second member a special term modelling the action of the porous matrix on the particles. In the second part we apply Levermore's closure strategy to get a hydrodynamic picture of the gas flowing through the porous structure. This will lead

us to generalize the Euler equations system for the ideal gas evolving in a "free" space to the case of porous media. In the third part, we are demonstrating that a proper linearization enables to formally recover the Klinkenberg permeability tensor. Numerical values are then computed and compared to some ones measured in literature.

2. PART I: A HOMOGENIZED KINETIC EQUATION FOR PARTICLES TRAPPED IN A POROUS STRUCTURE

This entire section is devoted to the derivation of a new kinetic equation modelling the behaviour of particles evolving in a porous medium. It first begins with some considerations about the Boltzmann Equation (BE) and how to add a source term modelling the action of the porous structure on the particles. This will lead us to interpret BE in the framework of *distributions* then bringing to light the inconvenience of its mathematical irregularity. To overcome this difficulty, we propose the routine regularizing strategy consisting in making the convolution product of BE with a particularly well chosen regular test function. Without any further assumption however we shall see that this basic procedure is not capable of yielding a convenient result. This problem will be nevertheless got round by introducing the assumption of small deviations. We will then be in position to feature a reasonable homogenized kinetic equation for a system of particles trapped in a porous matrix.

2.1. A Boltzmann Equation Taking into Account the Action of Walls

The classical Boltzmann equation (CBE) has been studying for decades and one can find a comprehensive description of its properties in Cercignani.[29] When particles are moving in a porous structure such that the mean pore dimensions become slightly greater than or comparable to the mean free path, the number of wall/particle collisions ceases to negligible in front of that of particle/particle and one has to add a wall/particle collision kernel $B(f)$. Without trying to give any detailed description of the latter, we can modify CBE as follows:

$$\frac{\partial}{\partial t} f + \mathbf{v} \cdot \nabla_{\mathbf{x}} f = Q(f, f) + B(f) \tag{2}$$

Here, the new source term $B(f)$, describing the action of the walls on the particles velocity, is clearly linear with f and proportional to the Dirac distribution of the surface separating pores and obstacles as established in detail in the Appendix A.1. The linearity of the wall/particle collision operator with respect to the *pdf* f also occurs when the Dusty Gas model is used to derive the wall/particle interaction (Ref. 27, Eq. 7). But contrary to what is underlined here, the action of the wall is then distributed everywhere in the volume. Mathematically, the specific location

of the wall action on the particles can be nicely interpreted by considering Eq. (2) in the sense of distributions. Since $f(\mathbf{x}, \mathbf{v}, t)$ is null in the obstacles volume (where it is obviously impossible to find any particle) and strictly positive in the pores volume, a jump term is likely to appear when differentiating in the sense of distribution. The accurate description of the action of the porous matrix on particles requires to consider the way molecules are reflected by the walls. Following Cercignani[29] and Sharipov[30] this can be achieved by introducing the *scattering kernels* $R(\mathbf{v}' \to \mathbf{v}, \mathbf{n})$. The way particles are interacting with the walls is then described by a relation linking the molecules going to the wall to those getting away from it ($\mathbf{n}(\mathbf{x})$ is oriented from wall to pre):

$$\forall \mathbf{v}, \quad \mathbf{v} \cdot \mathbf{n}(\mathbf{x}) \geq 0,$$

$$|\mathbf{v} \cdot \mathbf{n}(\mathbf{x})| f(\mathbf{x}, \mathbf{v}, t) = \int\limits_{\mathbf{v}' \cdot \mathbf{n}(\mathbf{x}) \leq 0} |\mathbf{v}' \cdot \mathbf{n}(\mathbf{x})| R(\mathbf{v}' \to \mathbf{v}, \mathbf{n}) f(\mathbf{x}, \mathbf{v}', t) d\mathbf{v}' \tag{3}$$

There are three main scattering kernels modelling the wall/particle interactions: the specular scattering kernel (RSK), the pure diffusive scattering kernel (DSK) and the Maxwell scattering kernel (MSK) that is in fact a normalized weighted sum of the others. They are respectively defined by:

$$\text{RSK}: \; R_R(\mathbf{v}' \to \mathbf{v}, \mathbf{n}) \hat{=} \delta_{\mathbf{0}}(\mathbf{v}' - [\mathbf{v} - (2\mathbf{v} \cdot \mathbf{n})\, \mathbf{n}]), \quad \delta_0 \text{ Dirac distribution at } \mathbf{0} \tag{4}$$

$$\text{DSK}: \; R_D(\mathbf{v}' \to \mathbf{v}, \mathbf{n}) \hat{=} \frac{m^2 \mathbf{v} \cdot \mathbf{n}}{2\pi \left(k_B T_W\right)^2} \exp\left(-\frac{m\mathbf{v}^2}{2k_B T_W}\right)$$

$$\text{MSK}: \; \exists \alpha \in [0, 1], \, R_M(\mathbf{v}' \to \mathbf{v}, \mathbf{n}) \hat{=} \alpha R_R(\mathbf{v}' \to \mathbf{v}, \mathbf{n}) + (1 - \alpha) R_D\left(\mathbf{v}' \to \mathbf{v}, \mathbf{n}\right)$$

2.2. The Homogenization Procedure

The whole strategy for regularizing Eq. (2) is described in Appendix A.1 as well as the computations to achieve it. It basically consists in making the convolution product of (2) with a regular test function. It leads to define a new *pdf*, denoted by $F(\mathbf{y}, \mathbf{v}, t)$, as the mean value of $f(\mathbf{x}, \mathbf{v}, t)$ in a well chosen $\mathbf{y}$-centred neighbourhood, traditionally referred as the *E.R.V.* (Elementary Representative Volume). $F(\mathbf{y}, \mathbf{v}, t)$ appears as a new *pdf*, but defined at another volume scale. As convolution an differentiation commute, the regularization of (2) leads quickly to a new kinetic equation written for F and reading as:

$$\frac{\partial}{\partial t} F(\mathbf{y}, \mathbf{v}, t) + \mathbf{v} \cdot \nabla_{\mathbf{y}} F(\mathbf{y}, \mathbf{v}, t) = \left[\left(Q(f, f) + B(f)\right) \psi\right](\mathbf{y}) \tag{5}$$

Of course, the key point of the homogenization procedure remains that of expressing the second member of (5) as an operator acting on $F(\mathbf{y}, \mathbf{v}, t)$. Such a problem

is very similar to the closure problems appearing in the development of the volume averaging scale change method for transport in porous media.[24] Nevertheless, the closure procedure that is applied here is probably the simplest one can imagine and is described in the Appendix A.1. It basically assumes that fluctuations of the "microscopic *pdf*" $f(\mathbf{x}, \mathbf{v}, t)$ are not significant so that it can be approximated by its mean value everywhere in the *E.R.V.* An easy sequence of calculations shows then (see A.1):

$$Q(f, f) * \psi = \frac{Q(F, F)}{\varepsilon(\mathbf{y})} \hat{=} \frac{1}{\varepsilon(\mathbf{y})} \int_{\mathbf{n}\in S} \int_{\mathbf{v}_1} b\,(|(\mathbf{v} - \mathbf{v}_1) \cdot \mathbf{n}|)(F_1^* F^* - F_1 F) d\mathbf{n}\, d\mathbf{v}_1$$

$$B(f) * \psi = \frac{W(F)}{\varepsilon(\mathbf{y})} \hat{=} \frac{1}{\varepsilon\,(\mathbf{y})} \left[\int_{\mathbf{v}\cdot\mathbf{n}\geq 0} S\,(\mathbf{y}, \mathbf{n})\, d\mathbf{n} \int_{\mathbf{v}'\cdot\mathbf{n}\leq 0} R(\mathbf{v}' \to \mathbf{v}, \mathbf{n}) |\mathbf{v}' \cdot \mathbf{n}| F' d\mathbf{v}' \right.$$

$$\left. - \int_{\mathbf{v}\cdot\mathbf{n}\leq 0} |\mathbf{v} \cdot \mathbf{n}|\, S\,(\mathbf{y}, \mathbf{n})\, F d\mathbf{n} \right] \tag{6}$$

The *E.R.V.* functions $\varepsilon(\mathbf{y})$ and $S(\mathbf{y}, \mathbf{n})$ are defined in A.1. They respectively denote the porosity and the specific area per solid angle. We can split $W(F)$ the same way as what is usually done for $Q(F, F)$, by discriminating between the loss and gain terms:

$$W^+(F) = \int_{\mathbf{v}\cdot\mathbf{n}\geq 0} S(\mathbf{y}, \mathbf{n}) d\mathbf{n} \int_{\mathbf{v}'\cdot\mathbf{n}\leq 0} R(\mathbf{v}' \to \mathbf{v}, \mathbf{n}) |\mathbf{v}' \cdot \mathbf{n}| F(\mathbf{y}, \mathbf{v}', t)\, d\mathbf{v}' \tag{7}$$

$$W^-(F) = \int_{\mathbf{v}\cdot\mathbf{n}\leq 0} |\mathbf{v} \cdot \mathbf{n}|\, S\,(\mathbf{y}, \mathbf{n})\, F\,(\mathbf{y}, \mathbf{v}, t)\, d\mathbf{n}$$

$W^+(F)$ counts the particles that gain the velocity $\mathbf{v}$ inside the *E.R.V* thanks to a collision with a wall while $W^-(F)$ counts the particles that lose the velocity $\mathbf{v}$ inside the *E.R.V.* because of a collision with a wall. By injecting now (4) into (6b), we can write down three particular homogenized scattering kernels (HSK) as follows:

$$\text{HRSK}: \quad W_R(F) = \begin{cases} \displaystyle\int_{\mathbf{v}\cdot\mathbf{n}\geq 0} S\,(\mathbf{y}, \mathbf{n})\, |\mathbf{r}_\mathbf{n}\,(\mathbf{v}) \cdot \mathbf{n}|\, F\,(\mathbf{r}_\mathbf{n}\,(\mathbf{v}))\, d\mathbf{n} \\ \quad \displaystyle - \int_{\mathbf{v}\cdot\mathbf{n}\leq 0} S\,(\mathbf{y}, \mathbf{n})\, |\mathbf{v} \cdot \mathbf{n}|\, F\,(\mathbf{v})\, d\mathbf{n} \\ \mathbf{r}_\mathbf{n}\,(\mathbf{v}) \;\hat{=}\; \mathbf{v} - 2\,(\mathbf{v} \cdot \mathbf{n})\, \mathbf{n} \end{cases}$$

$$\text{HDSK}: \quad W_D(F) = \begin{cases} \displaystyle\int_{\mathbf{v}\cdot\mathbf{n}\geq 0} S(\mathbf{y},\mathbf{n})\,|\mathbf{v}\cdot\mathbf{n}|\,g_W(\mathbf{v}) \left(\int_{\mathbf{v}'\cdot\mathbf{n}\leq 0} |\mathbf{v}'\cdot\mathbf{n}|\,F(\mathbf{v}')\,d\mathbf{v}' \right) d\mathbf{n} \\ \quad - \displaystyle\int_{\mathbf{v}\cdot\mathbf{n}\leq 0} S(\mathbf{y},\mathbf{n})\,|\mathbf{v}\cdot\mathbf{n}|\,F(\mathbf{v})\,d\mathbf{n} \\ g_W(\mathbf{v}) \hat{=} \dfrac{m^2}{2\pi\,(k_B T_w)^2} \exp\left(-\dfrac{m\mathbf{v}^2}{2k_B T_w}\right) \end{cases}$$

$$\text{HMSK}: \quad \exists \alpha \in [0,1], \quad W_M(F) = \alpha W_R(F) + (1-\alpha)\,W_D(F) \tag{8}$$

For any wall operator W, the new homogenized kinetic equation is then:

$$\frac{\partial F}{\partial t} + \mathbf{v}\cdot\nabla_{\mathbf{y}} F = \frac{Q(F,F)}{\varepsilon(\mathbf{y})} + \frac{W(F)}{\varepsilon(\mathbf{y})} \tag{9}$$

3. PART II: FROM KINETIC TO HYDRODYNAMICS

In this section we show how to exploit the kinetic Eq. (9) to obtain a hydrodynamic picture. Indeed, the transition from the statistical physics of gases to fluid dynamics has quite a long history and several methods have already been proposed to achieve it. Among them, the most popular are probably the ones derived by Grad[31] and Chapman–Enskog. In spite of this, one can find in Levermore[28] an alternative way to establish a hydrodynamic limit from a kinetic equation. This section consists in a straightforward application of his closure strategy. The main point of his theory rests on the demonstration of the equivalences between three mathematical properties attached to the kinetic operator $M(F)$. In the first part, we recall the vocabulary and the main tools of Levermore's strategy (LS). In the second part, we show that all the operators considered in the last section (9) satisfy the basic properties required by LS. The resulting hydrodynamic equations are then be presented in the third part.

3.1. The Levermore Strategy

For the rest of this section, we assume that F is a positive function which satisfies the following general kinetic equation:

$$\frac{\partial}{\partial t} F(\mathbf{y},\mathbf{v},t) + \mathbf{v}\nabla_{\mathbf{y}} F(\mathbf{y},\mathbf{v},t) = M(F)(\mathbf{y},\mathbf{v},t) \tag{10}$$

The mathematical study of the kinetic operator M usually requires the introduction of its kernel $Ker(M)$ and entropy density $\eta(F)$ defined as:

$$Ker(M) = \{\phi(\mathbf{v}), \quad \forall F \in D(M), \quad \langle M(F)\,\phi\rangle = 0\} \tag{11a}$$

$$\forall F \in D(M), \quad \langle M(F)\,\partial_F \eta(F)\rangle \leq 0 \tag{11b}$$

Here $D(M)$ is the domain of the operator M and the bracket notation stands for the integration over $\mathbf{v}$ in $\mathbf{R}^3$. We shall say that a kinetic operator M satisfies the Levermore equivalences (Ref. 28) whenever the following propositions are mathematically equivalent:

$$\begin{array}{ll} (i) & M(F) = 0 \\ (ii) & \langle M(F)\, \partial_F \eta(F) \rangle = 0 \\ (iii) & \partial_F \eta(F) \in Ker(M) \end{array} \tag{12}$$

The passage from the kinetic point of view to that of momentums is simply achieved by multiplying Eq. (10) with a set of well chosen functions (which can be either scalar, vector or tensor) only depending on the vector variable $\mathbf{v}$. We denote by T the classical vector transposition and suppose that k relevant functions (forming the basis of a suited linear space) have been chosen for the hydrodynamic description:

$$\mathbf{m}(\mathbf{v}) \hat{=} (m_1(\mathbf{v}), \ldots, m_k(\mathbf{v}))^T \tag{13}$$

A set of fluid dynamic equations is drawn from (10) by computing:

$$\frac{\partial}{\partial t} \langle \mathbf{m}(\mathbf{v})\, F \rangle + \nabla_{\mathbf{y}} \langle \mathbf{v}\mathbf{m}(\mathbf{v})\, F \rangle = \langle \mathbf{m}(\mathbf{v})\, M(F) \rangle \tag{14}$$

For the rest of the article, we shall adopt the notation $\langle \mathbf{m}(\mathbf{v})\, F \rangle = \boldsymbol{\rho}$. The so called closure problem is that of choosing the reasonable function F in order the second and third terms of (14) to be expressed as functions of the moment vector $\boldsymbol{\rho}$ itself. It is indeed a difficult methodological question to answer but Levermore[28] has given a systematic way to solve it, provided that the kinetic operator M satisfies the system of equivalences (12)

3.2. Application of the Levermore Strategy to the Homogenized Operators

We turn now on the practical computation of the kernels (11a), entropy densities (11b) and Levermore equivalences (12) for the operators (9) (up to $\varepsilon(\mathbf{y})$) using (8a) and (8c) and respectively denoted by M_R and M_M. We first demonstrate in the Appendix A.2:

$$Ker(M_R) = \{1, \mathbf{v}^2\} \tag{15a}$$

$$Ker(M_M) = \{1\} \tag{15b}$$

We also establish the following properties in the Appendix C:

$$\begin{array}{l} \eta_R(F) = F \ln(F) - F \text{ is an entropy density for } M_R(F) \\ \eta_M(F) = F \ln(F/g_W) - F + g_W \text{ is an entropy density for } M_M(F) \end{array} \tag{16}$$

We recall here that those results have been obtained under the symmetry assumption (A.19) for the function $S(\mathbf{y}, \mathbf{n})$. The entropy density (16b) is known as the relative entropy of f to g_W. We now finish the job by showing the last mathematical results in the Appendix D:

$$\begin{array}{llll} M_R(F), & Ker(M_R), & \eta_R(F) & \text{satisfy (12)} \\ M_M(F), & Ker(M_M), & \eta_M(F) & \text{satisfy (12)} \end{array} \tag{17}$$

Having justified the Levermore equivalences, we are now in position to apply his closure strategy. For a sake of simplicity we will now only work with the operator M_R. In practice, there are several basis functions (and corresponding admissible linear spaces) that can be chosen to close the system (14). For the operator M_R and the associated entropy density, one can find in Levermore[28] a comprehensive description of them. We only present here the so called Eulerian and Gaussian linear spaces. They read respectively as:

$$\begin{array}{l} \mathbf{E} = \{1, \mathbf{v}, \mathbf{v}^2\} \\ \mathbf{G} = \{1, \mathbf{v}, \mathbf{v} \otimes \mathbf{v}\} \end{array} \tag{18}$$

where $\otimes$ denotes the usual tensor product. Let us focus here on the linear space $\mathbf{E}$. The closure of the system (14) requires to choose F as (Ref. 28):

$$F(\mathbf{y}, \mathbf{v}, t) = \exp\left(a(\mathbf{y}, t) + \mathbf{b}(\mathbf{y}, t) \cdot \mathbf{v} + c(\mathbf{y}, t)\, \mathbf{v}^2\right) \tag{19}$$

The constrains of the moments $\langle \mathbf{m}(\mathbf{v})\, F \rangle = (\rho, \rho\mathbf{u}, \rho(\mathbf{u}^2 + 3k_b T/m))$ implies then:

$$F(\mathbf{y}, \mathbf{v}, t) = \frac{\rho(\mathbf{y}, t)}{(2\pi k_B T(\mathbf{y}, t)/m)^{3/2}} \exp\left(-\frac{m(\mathbf{v} - \mathbf{u}(\mathbf{y}, t))^2}{2k_B T(\mathbf{y}, t)}\right) \tag{20}$$

We are sure that for the function (20) the fluid dynamic Eq. (14) consist in a closed set of equations linking the usual moments $(\rho, \rho\mathbf{u}, T)$. Besides the function F at stake is the only one that minimizes the entropy per unit volume subjected to the constraints of the moments.

3.3. The Euler Equations for a Gas in Porous Medium

The application of the closure procedure to M_R yields the following general equations:

$$\frac{\partial}{\partial t} \int_{\mathbf{v}} F(\mathbf{v}) + \nabla_{\mathbf{y}} \int_{\mathbf{v}} \mathbf{v} F(\mathbf{v}) = \left\langle \frac{M_R}{\varepsilon(\mathbf{y})}(F) \right\rangle \tag{21a}$$

$$\frac{\partial}{\partial t} \int_{\mathbf{v}} \mathbf{v} F(\mathbf{v}) + \nabla_{\mathbf{y}} \int_{\mathbf{v}} \mathbf{v} \otimes \mathbf{v} F(\mathbf{v}) = \left\langle \mathbf{v} \frac{M_R}{\varepsilon(\mathbf{y})}(F) \right\rangle \tag{21b}$$

$$\frac{\partial}{\partial t}\int_{\mathbf{v}}\frac{\mathbf{v}^2}{2}F(\mathbf{v})+\nabla_{\mathbf{y}}\int_{\mathbf{v}}\frac{\mathbf{v}^2\mathbf{v}}{2}F(\mathbf{v})=\left\langle\frac{\mathbf{v}^2}{2}\frac{M_R}{\varepsilon(\mathbf{y})}(F)\right\rangle \tag{21c}$$

where F is chosen as (20). As the functions 1 and $\mathbf{v}^2$ are in $Ker\ (M_R)$, the second members of (21a) and (21c) vanish. But as the Eulerian space $\mathbf{E}$ chosen for the closure procedure is not equal to $Ker\ (M_R)$, then $M_R(F)$ is not null according to the equivalences (12). As a consequence, since $\mathbf{v}$ is not in $Ker\ (M_R)$, the second member of (21b) does not vanish. Nevertheless, if we make $S(\mathbf{y}, \mathbf{n}) = 0$, then M_R reduces to the homogenized colision Boltzmann operator (HCBO) and we recover the Euler equations. We can see (21) as a natural continuous generalisation of them for a gas evolving in a porous structure. The second member of (21b) describes the action of the porous matrix on the gas dynamics. We naturally expect this force to be dissipative and null when the gas is at rest. The final system of equations reads as:

$$\frac{\partial}{\partial t}\rho+\nabla_{\mathbf{y}}\rho\mathbf{u}=0 \tag{22a}$$

$$\frac{\partial}{\partial t}\rho\mathbf{u}+\rho\mathbf{u}\nabla_{\mathbf{y}}\mathbf{u}+\nabla_{\mathbf{y}}P=\left\langle\frac{\mathbf{v}W_{\mathbf{R}}(F)}{\varepsilon(\mathbf{y})}\right\rangle \tag{22b}$$

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho\mathbf{u}^2+\frac{3}{2}\frac{\rho k_B T}{m}\right)+\nabla_{\mathbf{y}}\left(\frac{1}{2}\rho\mathbf{u}^2\mathbf{u}+\frac{5}{2}\frac{\rho k_B T}{m}\mathbf{u}\right)=0 \tag{22c}$$

where:

$$(\rho\mathbf{u}\nabla_{\mathbf{y}}\mathbf{u}+\nabla_{\mathbf{y}}P)\ \hat{=}\ \nabla_{\mathbf{y}}\int_{\mathbf{v}}\mathbf{v}\otimes\mathbf{v}F(\mathbf{v}) \tag{22d}$$

In writing down this set of equations, one must keep in mind that all the relevant "macroscopic values" (P, ρ, T, $\rho\mathbf{u}$) have been obtained as moments of the *pdf* F that does not make any distinction between pores and obstacles. As detailed in the Appendix A.1, $F(\mathbf{y}, \mathbf{v}, t)d\mathbf{y}d\mathbf{v}dt$ is the infinitesimal probability to find a particle at time t with the velocity $\mathbf{v}$ *anywhere in the* E.R.V (whose volume $d\mathbf{y}$ can be seen as the new infinetisimal volume at the macro-scale). Of course, we know in reality that the obstacles volume is not allowed for the particles. The consequence is that there is a need to make a clear distinction between what is traditionally named as the "intrinsic values" and what will be referred in the following as the "porous values." For instance, in (22a), the bulk mass ρ that appears in the conservation equation is not that of the gas, as well as the pressure P defined by (22d). The intrinsic pressure and mass rate of the gas P_i and ρ_i are obtained straightforward using:

$$P_i=\frac{P}{\varepsilon(\mathbf{y})},\quad \rho_i=\frac{\rho}{\varepsilon(\mathbf{y})} \tag{23}$$

As for the temperature T, it is indeed the same value, independently of the choice of the "porous" or "intrinsic" point of views. (22a) is of course the mass conservation. (22b) is the momentum equation for the gas in the porous media. At last (22c) describes the energy conservation. It is very clear indeed that this last equation would have been different if we had used HMSK rather than HRSK to model the interaction between wall and particles.

4. PART III: STUDY OF THE HYDRODYNAMIC FORCE

This section is devoted to the detailed study of the force appearing in the second member of (22b). In the first part, we establish the basic properties of this hydrodynamic force. In particular, we show that it can be linearized. As a consequence we will be in position, in the second part, to formally recover Darcy's law for gas transport in porous media. The attentive study of the so called permeability tensor will bring to light a new interpretation of the Klinkenberg's effect. Some numerical values computed through the theoretical expression of the kinetic Klinkenberg permeability will be compared to some ones that can be found in the literature. A brief discussion will then follow.

4.1. Detailed Study of the Hydrodynamic Force

Let's first recall the exact expression of the force (22b). Using the formula (B.5) with F given by (20) leads to:

$$\mathbf{F}(\mathbf{u}) \hat{=} \left(\frac{m}{2\pi k_B T}\right)^{3/2} \rho \int_{\mathbf{n}} \frac{S(\mathbf{y},\mathbf{n})}{2\varepsilon(\mathbf{y})} \mathbf{n} d\mathbf{n} \times \int_{\mathbf{v}} |\mathbf{v}\cdot\mathbf{n}|\, \mathbf{v}\cdot\mathbf{n} \left(\exp\left(-\frac{m(\mathbf{r}_{\mathbf{n}}(\mathbf{v})-\mathbf{u})^2}{2k_B T}\right) - \exp\left(-\frac{m(\mathbf{v}-\mathbf{u})^2}{2k_B T}\right)\right) d\mathbf{v} \tag{24}$$

In these notations we have dropped the $(\mathbf{y}, t)$ dependence of the variables $(\rho,\ \rho\mathbf{u},\ T)$. $\mathbf{F}(\mathbf{u})$ has the dimension of force per unit volume. It depends simultaneously on $(\rho,\ \mathbf{u},\ T)$ but the main difficulty remains its non linearity in $\mathbf{u}$. Even if the Eq. (22b) associated with (24) seems to be very far from Darcy's law, an easy set of computations will recover it. We demonstrate in the Appendix E the two following results:

$$(\forall \mathbf{u},\ \mathbf{F}(-\mathbf{u}) = -\mathbf{F}(\mathbf{u})), \tag{25a}$$

$$(\forall \mathbf{u},\ \mathbf{F}(\mathbf{u})\cdot\mathbf{u} \leq 0) \tag{25b}$$

(25a) is a property of symmetry that is *in fine* directly linked to the assumption of the symmetry property of $S(\mathbf{y}, \mathbf{n})$. It implies $\mathbf{F}(\mathbf{0}) = \mathbf{0}$. This property appears to be quite natural: physically, the porous matrix hampers the gas to flow in the medium and the structure can be seen as a set of passive obstacles the molecules have to go round to continue their paths. When the gas is at rest however, the porous medium is a kind of special vessel in which the particles are evolving, and except for the pressure, no other force is applied to the gas. Following the above ideas, we mainly expect $\mathbf{F}(\mathbf{u})$ to be dissipative when $\mathbf{u} \neq 0$, which is assured by (25b). We demonstrate in Appendix A.6 that:

$$\forall \mathbf{u}, \quad \|\mathbf{u}\| \ll \sqrt{\frac{k_B T}{m}}, \quad \mathbf{F}(\mathbf{u}) \approx -\left[\frac{4}{\sqrt{6\pi}} \frac{\rho\sigma}{\varepsilon(\mathbf{y})\, m} \mu(T) \int_{\mathbf{n}} S(\mathbf{y}, \mathbf{n})\, \mathbf{n} \otimes \mathbf{n} d\mathbf{n}\right] : \mathbf{u} \tag{26}$$

where : denotes the matrix/vector product and $\otimes$ the usual tensor product. Equation (26) expresses that $\mathbf{F}(\mathbf{u})$ has a reasonable linear approximation whenever the velocity $\mathbf{u}$ is small compared to the thermal velocity associated to the temperature T, which occurs genera lly in nano-metric and even micrometric porous structures. If we write now the Eq. (22b) by using all the relevant approximations and notations, it becomes:

$$\frac{\partial}{\partial t} \rho \mathbf{u} + \rho \mathbf{u} \nabla_{\mathbf{y}} \mathbf{u} + \nabla_{\mathbf{y}} P = -\mathbf{M} : \mathbf{u} \tag{27}$$

where the matrix $\mathbf{M}$ is the one calculated in the Appendix F. Let's consider a steady regime for which the inertial effects are negligible. If the porosity $\varepsilon(\mathbf{y})$ does not depend on the space variable $\mathbf{y}$, then (27) becomes $\mathbf{u} = -\varepsilon \mathbf{M}^{-1} : \nabla_{\mathbf{y}} P_i$ and we formally recover the Darcy's law in for which the permeability tensor is given by $\mathbf{K} = \mu(T)\, \varepsilon \mathbf{M}^{-1}$.

4.2. The Klinkenberg Effect

The last relation and (26) enable to compute the following permeability tensor:

$$\mathbf{K} = \varepsilon(\mathbf{y}) \frac{\sqrt{6\pi}}{4} \frac{\varepsilon(\mathbf{y})\, m}{\rho(\mathbf{y})\, \sigma} \left[\int_{\mathbf{n}} S(\mathbf{y}, \mathbf{n})\, \mathbf{n} \otimes \mathbf{n} d\mathbf{n}\right]^{-1} \tag{28}$$

As we can see, (28) shows that permeability not only depends of the geometry (because of the specific area per solid angle $S(\mathbf{y}, \mathbf{n})$ and the porosity $\varepsilon(\mathbf{y})$), but also involves another characteristic length:

$$l \hat{=} \frac{\sqrt{6\pi}}{4} \frac{\varepsilon m}{\rho \sigma} = \frac{\sqrt{6\pi}}{4} \lambda \tag{29}$$

where λ is the mean free path of the particles. The linear dependency of $\mathbf{K}$ with λ could be surprising since the classical theory only retains geometrical factors. In practice however, λ can be linked to the intrinsic pressure and let some hope to recover the Klinkenberg tensor. At low values, the ideal gas law is valid and $\mathbf{K}$ reads then as:

$$\mathbf{K} = \varepsilon \frac{\sqrt{6\pi}}{4} \frac{k_B T}{P_i \sigma} \left[\int_{\mathbf{n}} S(\mathbf{y}, \mathbf{n}) \, \mathbf{n} \otimes \mathbf{n} d\mathbf{n} \right]^{-1} \tag{30}$$

This expression suggests that the permeability is directly proportional to the inverse of the fluid pressure P_i. Nevertheless this is not what is commonly retained as the correct form of the Klinkenberg correction. Generally the latter reads as (see (1)):

$$\mathbf{K} = K_\infty \left(1 + \frac{B}{P_i} \right) \mathbf{I} \tag{31}$$

where $\mathbf{I}$ denotes the identity matrix. As we can see the permeability is rather an affine than a linear function of the inverse pressure. Equation (31) suggests indeed that the behaviour of the system is not the same depending on the value of the intrinsic gas pressure. For low values $1 \ll B/P_i$ and we recover the expression (28) for an isotropic porous media:

$$K_\infty B \mathbf{I} = \frac{\sqrt{6\pi}}{4} \frac{k_B T}{P_i \sigma} \frac{2\varepsilon}{S(\mathbf{y})} \mathbf{I} \tag{32}$$

Nevertheless, when the pressure increases, the ideal gas law is not valid anymore and we must use some correction. If we only retain the so called co-volume effects in the Van Der Waals equation (i.e. the so called co-volume state equation), we have:

$$\frac{m\varepsilon}{\rho} = \frac{m}{\rho_i} = b \left(1 + \frac{k_B T}{b P_i} \right) \tag{33}$$

where b denotes the co-volume of the particles. For an isotropic porous medium, the expression of the permeability tensor reads as:

$$\mathbf{K} = \frac{\sqrt{6\pi}}{4} \frac{2b\varepsilon}{\sigma S(\mathbf{y})} \left(1 + \frac{k_B T}{b P_i} \right) \mathbf{I} \tag{34}$$

and we recover the exact form of the Klinkenberg tensor in which the non local dependency on the mean pressure has however turned into a local dependency on the gas one. Moreover we obtain the explicit expressions for the constants involved in (31).

4.2.1. Numerical Aspects

The fist problem occurring with (34) is the fact that the so called "intrinsic" or "liquid" permeability K_∞ appearing in (31) is not supposed to change with the nature of the gas evolving in the porous structure. This is not yielded by (34) in so far as:

$$K_\infty = \frac{\sqrt{6\pi}}{4}\frac{2b\varepsilon}{\sigma S(\mathbf{y})} \tag{35}$$

Yet, we are going to see that the variations of K_∞ with the nature of the gas are not that significant. As a first approximation, let's consider $b = 4/3\pi R^3$, $\sigma = \pi R^2$ where R denotes here (and only here) the radius of the particles. Then, we have:

$$K_\infty = \frac{\sqrt{6\pi}}{2S(\mathbf{y})}\varepsilon\frac{4}{3}\sqrt[3]{\frac{3b}{4\pi}} = C(\mathbf{y})\sqrt[3]{b} \tag{36}$$

A short list of values for b (in m^3) and $\sqrt[3]{b}$ (in m) is presented in Fig. 2 for different gases. The figures do not change a lot with the nature of the involved "molecules" and, as a consequence, K_∞ can appear as being practically independent of it.

4.2.2. Comparisons with the Experiments of Wu et al. (32)

In their article, Wu *et al.*[32] carried out a set of experimental data destined to the indirect calculation of the Klinkenberg constant B introduced in (1). Let's briefly describe how they proceeded. A steady-state N_2 gas flows is conducted at ambient temperature in a porous cylindrical column (of length L) by keeping a pressure difference $(P_0 - P_L)$ between the inlet (indexed by 0) and the outlet (indexed by L). At the bottom of the column, the nitrogen mass flow rate q_m is

Gas	*co-volume b*	*b cubic root*
Air	*6,04651E-29*	***3,92496E-10***
CO2	*7,09302E-29*	***4,13946E-10***
N2	*6,39535E-29*	***3,99903E-10***
H2	*4,40199E-29*	***3,53088E-10***
H2O	*5,04983E-29*	***3,69623E-10***
NH3	*6,19601E-29*	***3,95704E-10***
He	*3,88704E-29*	***3,38745E-10***
CCl2F2	*1,65781E-28*	***5,49344E-10***

Fig. 2. Variation of co-volume cubic root with the nature of the gas.

measured. The following quantity is then calculated:

$$Y = \frac{q_m \mu L}{\beta (P_0 - P_L)}, \quad \beta \hat{=} \frac{M_g}{RT} \tag{37}$$

with M_g being the molecular mass of the nitrogen N_2, R the universal gas constant, T the temperature and μ the dynamical viscosity. Y is then related to K_∞ and B *by using a model accounting for the mass flow rate in the porous sample*. In their computations, the authors came to the conclusion that:

$$Y \approx B K_\infty + \left(\frac{P_0 + P_L}{2} \right) K_\infty \tag{38}$$

Using the result (38), they plotted Y versus $(P_0 + P_L)/2$ thus determining the constants B and K_∞ by a linear regression. Their analysis was based on the fact that the gas pressure P satisfies the following quadratic equation derived from the steady mass conservation equation:

$$\frac{\partial}{\partial x} \left((P + B) \frac{\partial P}{\partial x} \right) = 0 \tag{39}$$

However, *in this theory*, using the system (22) with the approximation (26) and the assumption of constant *E.R.V.* geometry inside the column leads to $\Delta P = 0$ where Δ denotes the classical Laplace operator. It is then easy to deduce that P decreases linearly from inlet to outlet and to establish with a little computation that $Y = B K_\infty$ is independent of the experimental pressures, unlikely to what has been obtained by Wu *et al*. In spite of this, we defend here that the measures reported by Wu *et al.* are only slowly varying with the mean pressure (Fig. 3: more precisely, the relative variations of Y range from 1 to a maximum of 10 per cent). As a consequence, $Y = B K_\infty$ can be regarded as a possible interpretation of their experimental results with a pretty good agreement.

The theoretical expression (34) leads to calculate for N_2 the following value for B:

$$B_{N_2} (T = 293\,\mathrm{K}) \approx 64.4 \times 10^6\,\mathrm{Pa} \tag{40}$$

This differs by a factor 30 or 40 from the value obtained by Wu *et al*. that is calculated to lie between 1×10^6 and 2×10^6 Pa, depending on the sample that is used. Nevertheless, this can be explained by the fact that the equations modelling the gas flow in the porous medium are not the same in this theory and the one developed by Wu *et al*. In particular, in this paper, the Klinkenberg constant B is supposed to be given by the very nature of the gas. It permits then to calculate K_∞ by using $Y = B K_\infty$. In Wu *et al.* paper, both B and K_∞ are unknown and (38) is used to provide indirect experimental values.

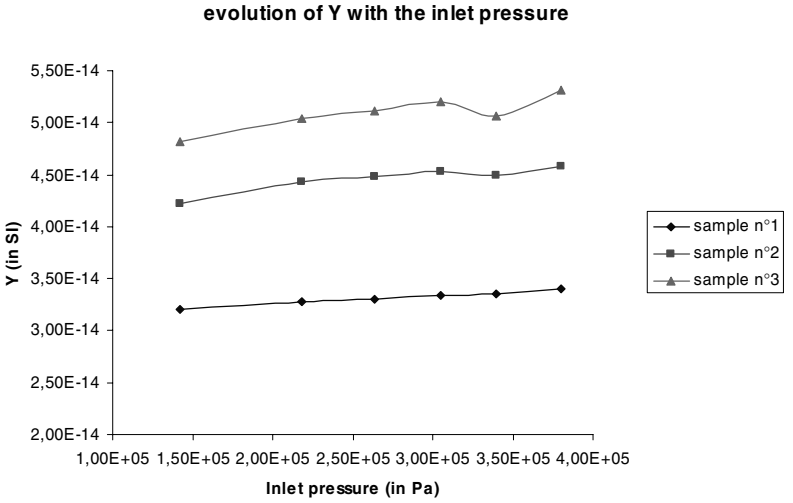

Fig. 3. Slow evolution of Y versus the inlet pressure, taken from Wu *et al.*

4.3. Discussion

4.3.1. Different Interpretations of the Klinkenberg Effect

One of the key points related to the study of gas flows in porous media lies in the computation of the permeability tensor. If we consider the porous matrix as a set of obstacles hampering the gas to flow, then, at the macroscopic scale, it becomes correct to model the action of the porous on the fluid as a force $\mathbf{F}(\mathbf{u})$ locally depending on the filtration velocity $\mathbf{u}$ and related to some functions defined in the *E.R.V.* (see Ref. 24). The steady and non inertial momentum Eq. (22b) then yields the following "implicit" Darcy's law:

$$\mathbf{F}(\mathbf{u}) + \nabla_{\mathbf{y}} P = 0 \tag{41}$$

When $\mathbf{F}$ can be linearized, (41) reads then as:

$$\mathbf{u} = -\frac{\mathbf{K}}{\mu} : \nabla_{\mathbf{y}} P \tag{42}$$

And the general formalism of Darcy is recovered. The central problem of course remains that of modelling $\mathbf{F}(\mathbf{u})$. Equivalently, in the linear regime, the matter has turned into that of computing the permeability tensor $\mathbf{K}$. Basically, the expression of $\mathbf{K}$ depends on the primary "micro-scale" at stake. For high values of the mean pore size (roughly corresponding to $Kn < 0.01$) it seems natural to compute $\mathbf{K}$ from a homogenization procedure applied to NSE. The permeability appears thus to depend only on the (often intricate) geometry of the *E.R.V.* and the interaction

between fluid and walls. The question then collapses into that of finding the accurate relation linking **K** with the geometry and the boundary conditions. *In such a formalism, the Klinkenberg effect appears to result from a slipping effect at the walls*. But of course, as the mean pore size decreases, the basic assumption of the NSE validity breaks down. For gases, the alternative consists in obtaining a continuum equation in the porous medium thanks to the application of some hydrodynamic closure to CBE. The principal stake lies then in the computation of the wall particle/interaction and its addition to CBE. The theory of the Dusty Gas Model, though a little artificial, provided an original framework to achieve it. However the computation of numerous *ad hoc* constants to make the *E.R.V.* geometry appears in the statistics of the so called heavy particles has no rigorous grounds. The framework chosen for this study seems to be more faithful to the geometry than the Dusty Gas Model as demonstrated in the part I. *In our derivation however, the Klinkenberg effect has been recovered by introducing the so called co-volume state equation. The co-volume effects impose a lower limit to the permeability linked to the limit of the gas density for high pressures*. One of the problems between this interpretation and the one deriving from the NSE homogenization is that they apparently differ whereas they potentially cover the same flows regimes. As a consequence we believe here that some formal work remains to be done in order to bridge them.

4.3.2. The Difficulty to Measure Permeability

The measures of the permeability are always obtained through the resolution of some inverse problems involving an important part of modelling. More precisely, most of the time, Darcy's law is injected in the mass conservation as follows:

$$\frac{\partial}{\partial t}\left(\varepsilon\left(\mathbf{y}\right)\rho_i\left(T\right)\right) - \nabla_{\mathbf{y}}\left(\varepsilon\left(\mathbf{y}\right)\rho_i\left(T\right)\frac{\mathbf{K}}{\mu\left(T\right)}\nabla_y\left(\varepsilon\left(\mathbf{y}\right)P_i\right)\right) = 0 \qquad (43)$$

Depending on the assumptions on the form of **K**, on the validity of the ideal gas law or on the fact that the **y** dependency can be dropped for a few geometrical values (in **K** or ε), a new basic steady or unsteady equation is obtained which can be different depending on the modelling. For example, in the region of the Klinkenberg effect, Wu *et al.*[32] have obtained (39) while we have computed ($\Delta P = 0$). Gross and Sherer[5] computed a more complex equation in a porous aerogel sample linking a strain measured in the medium to some relaxation time attached to an equation on the pressure derived from (43). Here again, a lot of assumptions are made on the physical values involved in their experiment without any real possibility to feed back the hypothesis to the obtained results. In short, *as the measure of* **K** *depends* both on the experiment modelling (of course) and *on the assumptions made for the particular form of* **K**, it is very difficult to pick up results in the literature in order to verify the validity of our theory. The simplest

we found was performed by Wu *et al.* and in spite of the apparent limitation it conveys we believe that it tends to confirm the Klinkenberg interpretation we proposed in this paper.

5. CONCLUSION

In spite of its pretty long history (at least since 1941) and the interest that has been constantly attached to it, we believe that the Klinkenberg effect can still offer some stimulating discussions in the framework of porous media modelling. In fact, the numerous values that have been given to the Klinkenberg constant B (which are rather ranging on a logarithmic scale,[20] the local or non local dependency on the pressure retained to model the Klinkenberg effect, the different ways it has been interpreted (by often invoking rarefaction and slipping effects, but also sometimes a dependency on geometrical parameters (see Ref. 7), and the approaches that were chosen to model it (homogenization procedures applied to NSE[20] or Chapman–Enskog developments starting from the Dusty Gas Model[27] seem to prove that the question is still not over. In such a situation indeed, the purpose of this article was to bring new ideas in the debate. Actually, there are two major conclusions that can be drawn from the developments we have led. The first one establishes that the Klinkenberg constant only depends on the nature of the gas (by the means of the particles co-volume b) and is directly proportional to the temperature T. The second one brings to light a new interpretation of the Klinkenberg effect in terms of local gas state equations. At low pressures, the ideal gas law is valid and the bulk mass is then linear with the inverse of the pressure. At high pressures however, the bulk mass tends to reach limit only depending on the co-volume and we recover some "intrinsic" permeability. To obtain these results, we have mixed up four different ingredients. The first one consisted in modifying the classical Boltzmann equation by making appear a source term modelling the action of the porous structure on the particles. In a second step, we applied a regularizing procedure inspired by the Averaging Scale Method to the resulting equation thus obtaining a so-called homogenized kinetic Boltzmann equation (HCBE). In a third stage this equation was treated within the framework of the Levermore Strategy (LS) for which it was necessary to compute the relevant kernels, entropy densities and Levermore equivalences. At last, the use of the co-volume gas state equation permits us to formally recover the Klinkenberg permeability. Unfortunately for our theory, we were not able to find numerous experiments in the literature to confirm or contradict our results. The works performed by Wu *et al.*[32] in spite of a slight variation of the Klinkenberg constant B that is not predicted by our theory, enable to think however that there are good chances for our model to be sensible. To confirm the expression we have established for B:

$$B = \frac{k_B T}{b} \tag{44}$$

it would be of a major interest to carry out flow experiments with varying gas *and* porous temperatures (in order to avoid thermal phenomena) so as to observe the predicted dependency (44). Unfortunately, we were not able to find such systematic data in the literature. Besides, from the theoretical point of view, it would be very interesting to extend the derivation we have performed using the pure specular scattering kernel (8a) for the Maxwellian one (8c). In practice, this will not change the Klinkenberg factor B but will rather provide a correction on the "intrinsic" permeability K_∞. Another interesting continuations could also be found either in the derivation of the hydrodynamic limit by closing the kinetic equation in the Gaussian linear space $\mathbf{G}$ or in computing a BGK approximation of HBCO (see Ref. 28). In these cases, we believe that the resulting fluid dynamic descriptions will lead in getting the so-called Darcy Brinkman equations and will provided a new framework for the study of thermal effects and diffusion in porous media. To finish with the perspectives opened by this work, it seems pretty clear for us that all the formalism we have developed in this paper could be extended to a mixture of gases leading to the corresponding macroscopic equations for gas mixture in porous media.

APPENDIX A: A REGULARIZED BOLTZMANN EQUATION FOR PARTICLES EVOLVING IN A POROUS MEDIUM

The following developments are devoted to the getting and the regularization of the Boltzmann equation presented in (2). The basic tool used to achieve the last goal essentially consists in making the convolution product of (2) with some regular test function. We mainly expect this operation to yield a new kinetic equation whose handling is easier than the original one. We shall see that the success of this procedure rests on a simplifying assumption concerning the local behaviour of the *pdf* in the support of the test function. This hypothesis will be referred as the *small deviations assumption* in the rest of the paper. The remainder of this appendix is organized as follows. In the first part, we show how to model the source term $B(f)$. In the second part we regularize Eq. (2). This will lead us to explicit the regularizing function and to compute the regularization of the Boltzmann operator $Q(f, f)$ and the wall operator $B(f)$.

A.1. Modelling the Action of the Walls on the Particles in the Boltzmann Equation

To get the contribution of the walls to the evolution of $f(\mathbf{x}, \mathbf{v}, t)$ we have to count the infinitesimal number of particles $\mathrm{d}N$ that gain or lose the velocity $\mathbf{v}$ in the volume $d\mathbf{x}$ during dt because of a collision with a wall. By definition, this infinitesimal number is equal to $B(f)d\mathbf{x}d\mathbf{v}dt$. Let $\mathbf{n}(\mathbf{x})$ be the normal to the wall (denoted by Γ) at $\mathbf{x}$ and pointing from obstacles to pores. $d\sigma(\mathbf{x}) = \delta(\mathbf{x} \in \Gamma)d\mathbf{x}$

(where δ denotes the Dirac symbol) is the infinitesimal surface of obstacles within $d\mathbf{x}$. If $\mathbf{v} \cdot \mathbf{n}(\mathbf{x}) \leq 0$, then particles having the velocity $\mathbf{v}$ are moving to the wall and they lose their velocities because of a collision with the wall between t and $t + dt$. $B(f)$ acts then as a sink term and an elementary count of the lost of these molecules leads to:

$$\begin{aligned} dN \hat{=} B(f)d\mathbf{x}d\mathbf{v}dt &= -f(\mathbf{x}, \mathbf{v}, t)\, d\mathbf{v}\, |\mathbf{v} \cdot \mathbf{n}(\mathbf{x})|\, dtds \\ &= -f(\mathbf{x}, \mathbf{v}, t)\, d\mathbf{v}\, |\mathbf{v} \cdot \mathbf{n}(\mathbf{x})|\, dt\delta(\mathbf{x} \in \Gamma)\, d\mathbf{x} \end{aligned} \tag{A.1}$$

If $\mathbf{v} \cdot \mathbf{n}(\mathbf{x}) \geq 0$, then particles are going away from the wall, meaning that they have just taken a collision that has made them gain the velocity $\mathbf{v}$. $B(f)$ acts then as a source term and the same elementary count of the molecules leads to:

$$\begin{aligned} dN \hat{=} B(f)d\mathbf{x}d\mathbf{v}dt &= f(\mathbf{x}, \mathbf{v}, t)\, d\mathbf{v}\, |\mathbf{v} \cdot \mathbf{n}(x)|\, dtds \\ &= f(\mathbf{x}, \mathbf{v}, t)\, d\mathbf{v}\, |\mathbf{v} \cdot \mathbf{n}(\mathbf{x})|\, dt\delta(\mathbf{x} \in \Gamma)\, d\mathbf{x} \end{aligned} \tag{A.2}$$

So, whatever is the sign of $\mathbf{v} \cdot \mathbf{n}(\mathbf{x})$, the new Boltzmann equation reads as:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f = Q(f, f) + f(\mathbf{x}, \mathbf{v}, t)\, \mathbf{v} \cdot \mathbf{n}(\mathbf{x})\, \delta(\mathbf{x} \in \Gamma) \tag{A.3}$$

A.2. The Regularization Function

The most important problem with (A.3) is the presence of the Dirac term in its right hand side. To get round this difficulty and handle (A.3) more easily, a mathematical simplification procedure consists in regularizing it by making its convolution product with a regular test function (meaning of class C^∞ with compact support). This function however has to be chosen while keeping in mind that the values obtained after the convolution product must have a reasonable physical meaning. This can be achieved by considering the E.R.V. (elementary representative volume) function ψ. Its support (referred as the E.R.V.) strictly contains the ball of radius R which volume is denoted V_R. We assume besides that there is some tiny parameter $\varepsilon > 0$ satisfying:

$$\forall \mathbf{x}, \quad \|\mathbf{x}\| \geq R + \varepsilon, \quad \psi(\mathbf{x}) = 0 \tag{A.4}$$

We also suppose that ψ is of class C^∞, positive and constant in the ball of radius R such that:

$$\int_{\|\mathbf{x}\| \leq R} \psi(\mathbf{x})\, d\mathbf{x} = 1 \tag{A.5}$$

To finish with, we suppose that there exists some $\eta > 0$ which can be chosen as close as 0 as we want such that for any function of interest g considered in this

article we have:

$$\int_{\mathbf{R}^3} g(\mathbf{x})\,\psi(\mathbf{x}) = \int_{\|\mathbf{x}\|\le R} g(\mathbf{x})\,\psi(\mathbf{x}) + \delta(g), \quad |\delta(g)| \le \eta \tag{A.6}$$

If $f(\mathbf{x}, \mathbf{v}, t)d\mathbf{x}d\mathbf{v}$ is the probability to find a particle between $\mathbf{x}$ and $\mathbf{x} + d\mathbf{x}$ with a velocity lying between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$, then $(f * \psi)(\mathbf{y})d\mathbf{v}V_R$ is the probability to find a particle with a velocity lying between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$ *anywhere* inside the ball of radius R which centre is $\mathbf{y}$ and which will be denoted by $B(\mathbf{y}, R)$ till the end of the study. We are now ready to turn to the regularizing procedure.

A.3. The Small Deviations Assumption

The main point of the regularization problem consists in computing some partial differential equation for the regular function $F(\mathbf{y}) \hat{=} [f * \psi](\mathbf{y})$ where f denotes the single particle probability density function extended in the whole space $\mathbf{R}^3$ and regarded as a distribution. Of course, we now that its value is 0 in the obstacle volume Λ and strictly positive in the pore volume Ω. As convolution and differentiation commute, we can compute the convolution product of the left hand side of (2) conveniently:

$$\left(\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f\right) * \psi = \frac{\partial F}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{y}} F \tag{A.7}$$

But to write an equation for F, we have to express the convolution product of the right hand side of (3) in term of F. To achieve that, let us now introduce the assumption of the small deviations. It consists in writing:

$$\begin{cases} \forall \mathbf{x} \in B(\mathbf{y}, R), & f(\mathbf{x}, \mathbf{v}, t) = \chi(\mathbf{x})[g(\mathbf{v}, t) + h(\mathbf{x}, \mathbf{v}, t)] \\ \forall \mathbf{x} \in B(\mathbf{y}, R), & h(\mathbf{x}, \mathbf{v}, t) \ll g(\mathbf{v}, t) \end{cases} \tag{A.8}$$

Here $\chi(\mathbf{x})$ is the characteristic function of Ω. Basically it is believed that the homogenization procedure will be all the more relevant that the *pdf* f we are working with does not have significant variations inside the E.R.V. This is indeed a routine assumption of any up-scaling method and it is justified by the fact that we are only interested in studying the slow variations of f. This is going to help us for the homogenization of the left hand side of (A.3). Let us begin with the operator $Q(f, f)$. We quickly recall here that the latter reads as:

$$Q(f, f) = \int_{\mathbf{n}} \int_{\mathbf{v}_1} b(|(\mathbf{v}_1 - \mathbf{v}) \cdot \mathbf{n}|) \times \left[f(\mathbf{v}_1^*, \mathbf{x}, t)\, f^*(\mathbf{v}^*, \mathbf{x}, t) - f(\mathbf{v}_1, \mathbf{x}, t)\, f(\mathbf{v}, \mathbf{x}, t)\right] \tag{A.9}$$

where the star notation refers to velocities after binary collisions. Since $f = 0$ in Λ, the particular form of ψ leads to compute:

$$Q(f, f) * \psi = \frac{1}{V_R} \int\limits_{\Omega \cap B(\mathbf{y}, R)} Q(f, f)\, d\mathbf{x} \tag{A.10}$$

We naturally defines the porosity of the E.R.V. as being:

$$\varepsilon(\mathbf{y}) \hat{=} \frac{V(\Omega \cap B(\mathbf{y}, R))}{V_R} \tag{A.11}$$

Using (A.8), (A.10) leads quickly to:

$$Q(f, f) * \psi = \frac{Q(F, F)}{\varepsilon(\mathbf{y})} \tag{A.12}$$

Let us now turn to the homogenization of the Dirac term. The small deviation assumptions leads to:

$$[\mathbf{v} \cdot \mathbf{n}(\mathbf{x})\, f(\mathbf{x}, \mathbf{v}, t)\, \delta(\mathbf{x} \in \Gamma)] * \psi = \frac{1}{V_R} \int\limits_{\Gamma \cap B(\mathbf{y}, R)} g(\mathbf{v})\, \mathbf{v} \cdot \mathbf{n}(\mathbf{x})\, d\sigma(\mathbf{x}) \tag{A.13}$$

The domain of integration $\Gamma \cap B(\mathbf{y}, R)$ is now divided in two complementary sets Γ^+ and Γ^-:

$$\begin{aligned} \Gamma \cap B(\mathbf{y}, R) = [\{\mathbf{x} \in \Gamma \cap B(\mathbf{y}, R), \mathbf{v} \cdot \mathbf{n}(\mathbf{x}) \leq 0\} = \Gamma^-] \\ \cup [\{\mathbf{x} \in \Gamma \cap B(\mathbf{y}, R), \mathbf{v} \cdot \mathbf{n}(\mathbf{x}) > 0\} = \Gamma^+] \end{aligned} \tag{A.14}$$

We exploit this separation to get:

$$\begin{aligned} &\frac{1}{V_R} \left[\int\limits_{\Gamma \cap B(\mathbf{y}, R)} g(\mathbf{v})\, \mathbf{v} \cdot \mathbf{n}(\mathbf{x})\, d\sigma(\mathbf{x}) \right] \\ &\quad = \frac{1}{V_R} \left[\int\limits_{\Gamma^-} g(\mathbf{v})\, \mathbf{v} \cdot \mathbf{n}(\mathbf{x})\, d\sigma(\mathbf{x}) \quad + \int\limits_{\Gamma^+} g(\mathbf{v})\, \mathbf{v} \cdot \mathbf{n}(\mathbf{x})\, d\sigma(\mathbf{x}) \right] \end{aligned} \tag{A.15}$$

But using now the particle/wall collision models (4) we compute easily

$$\begin{aligned} &\frac{1}{V_R} \left[\int\limits_{\Gamma^+} g(\mathbf{v})\, \mathbf{v} \cdot \mathbf{n}(\mathbf{x})\, d\sigma(\mathbf{x}) \right] \\ &\quad = -\frac{1}{V_R} \left[\int\limits_{\Gamma^+} d\sigma(\mathbf{x}) \int\limits_{\mathbf{v}' \cdot \mathbf{n} \leq 0} g(\mathbf{v}', t) R(\mathbf{v}' \to \mathbf{v}, \mathbf{x}, \mathbf{n}) \mathbf{v}' \cdot \mathbf{n}(\mathbf{x})\, d\mathbf{v}' \right] \end{aligned} \tag{A.16}$$

The equality (A.15) can now be rewritten:

$$\frac{1}{V_R}\left[\int\limits_{\Gamma\cap B(\mathbf{y},R)} g(\mathbf{v})\,\mathbf{v}\cdot\mathbf{n}(\mathbf{x})\,d\sigma(\mathbf{x})\right]$$
$$= \frac{1}{V_R}\left[\int\limits_{\Gamma^-} g(\mathbf{v})\,\mathbf{v}\cdot\mathbf{n}(\mathbf{x})\,d\sigma(\mathbf{x})\right.$$
$$\left.-\int\limits_{\Gamma^+} d\sigma(\mathbf{x}) \int\limits_{\mathbf{v}'.\mathbf{n}\le 0} g(\mathbf{v}')\,R(\mathbf{v}'\to\mathbf{v})\mathbf{v}'\cdot\mathbf{n}(\mathbf{x})\,d\mathbf{v}'\right]$$

By ordering the integration in the last expression we get:

$$\frac{1}{V_R}\left[\int\limits_{\Gamma\cap B(\mathbf{y},R)} g(\mathbf{v})\,\mathbf{v}\cdot\mathbf{n}(\mathbf{x})\,d\sigma(\mathbf{x})\right]$$
$$= \frac{1}{V_R}\left[g(\mathbf{v})\,\mathbf{v}\cdot\int\limits_{\Gamma^-}\mathbf{n}(\mathbf{x})\,d\sigma(\mathbf{x}) - \int\limits_{\Gamma^+} d\sigma(\mathbf{x})\,\mathbf{n}(\mathbf{x})\right.$$
$$\left.\cdot\int\limits_{\mathbf{v}'.\mathbf{n}\le 0} g(\mathbf{v}')R(\mathbf{v}'\to\mathbf{v})\mathbf{v}'d\mathbf{v}'\right]$$

Let's define the function $S(\mathbf{y},\mathbf{n})$ by:

$$\int\limits_{\Gamma\cap B(\mathbf{y},R)} \frac{d\sigma(\mathbf{x})}{V_R}\mathbf{n}(\mathbf{x}) \hat{=} \int\limits_{\mathbf{n}} S(\mathbf{y},\mathbf{n})\,\mathbf{n}d\mathbf{n} \tag{A.17}$$

Then using (A.10), (A.13) becomes:

$$\frac{1}{V_R}\int\limits_{\Gamma\cap B(\mathbf{y},R)} g(\mathbf{v})\,\mathbf{v}\cdot\mathbf{n}(\mathbf{x})\,d\sigma(\mathbf{x}) = \int\limits_{\mathbf{v}\cdot\mathbf{n}\ge 0} S(\mathbf{y},\mathbf{n})\,d\mathbf{n}\int\limits_{\mathbf{v}'.\mathbf{n}\le 0}\frac{F'(\mathbf{y})}{\varepsilon(\mathbf{y})}R(\mathbf{v}'\to\mathbf{v},\mathbf{n})|\mathbf{v}'\cdot\mathbf{n}|d\mathbf{v}'$$
$$-\int\limits_{\mathbf{v}\cdot\mathbf{n}\le 0}|\mathbf{v}\cdot\mathbf{n}|\,S(\mathbf{y},\mathbf{n})\,\frac{F(\mathbf{y})}{\varepsilon(\mathbf{y})}d\mathbf{n}$$

A.3. Physical Interpretation

The definition (A.17) introduces a new function $S(\mathbf{y}, \mathbf{n})$. As for the porosity $\varepsilon(\mathbf{y})$, this function is defined inside the E.R.V. Its physical dimension is that of a surface per volume and solid angle. More precisely, the quantity:

$$S(\mathbf{y}) \hat{=} \int_{\mathbf{n}} S(\mathbf{y}, \mathbf{n})\, d\mathbf{n} \tag{A.18}$$

is the total amount of surface of obstacles inside the *E.R.V.* divided by its volume V_R. Following the usual denotation used in porous media, this value will be referred as the specific area. For the rest of the article, we assume that the function $S(\mathbf{y}, \mathbf{n})$ has the following property of symmetry:

$$\forall \mathbf{n}, \quad S(\mathbf{y}, -\mathbf{n}) = S(\mathbf{y}, \mathbf{n}) \tag{A.19}$$

It means that for a given direction $\mathbf{n}$, there is inside the *E.R.V.* as much area which normal points in the direction $\mathbf{n}$ as area which normal points in the direction $-\mathbf{n}$. This includes of course the isotropic case, but also numerous other symmetrical distributions of obstacles in the *E.R.V.* The interest of this assumption will be discussed a bit further.

APPENDIX B: COMPUTING LOCALLY CONSERVED QUANTITIES FOR M_R AND M_M

In this part we compute the set of all conserved quantities for both M_R and M_M. The demonstration begins with the following lemma:

Lemma 1.

$$Ker(M_R) \subset Ker(Q) \cap Ker(W_R) \quad and \quad Ker(M_M) \subset Ker(Q) \cap Ker(W_M) \tag{B.1}$$

These two results are mainly based on the linearity of $W_R(F)$ and $W_M(F)$ with respect to their arguments as well as the bi-linearity of $Q(F, F)$. We shall make the calculations for the operator M_R, but they work identically for M_M. So let ϕ be in $Ker(M_R)$. We have $\forall F, \langle M_R(F)\phi\rangle = 0$. By a consequence we can write $\forall G, \forall \lambda > 0, \langle M_R((1+\lambda)G)\phi\rangle = 0$. Now we expand the term $M_R((1+\lambda)G)$. It is easy to check that:

$$\begin{aligned} M_R((1+\lambda)G) &\hat{=} Q((1+\lambda)G, (1+\lambda)G) + W_R((1+\lambda)G) \\ &= (1+\lambda)^2 Q(G, G) + (1+\lambda) W_R(G) \end{aligned} \tag{B.2}$$

By ordering terms with the decreasing powers of λ we get:

$$M_R((1+\lambda)G) = \lambda^2[Q(G,G)] + \lambda[2Q(G,G) + W_R(G)] + [W_R(G) + Q(G,G)] \tag{B.3}$$

Using now relations (B.2) and (B.3), we compute:

$$\forall G, \quad \forall \lambda > 0 \quad \lambda^2 \langle [Q(G,G)]\phi\rangle + \lambda\langle [2Q(G,G) + W_R(G)]\phi\rangle + \langle [W_R(G) + Q(G,G)]\phi\rangle = 0 \tag{B.4}$$

As the polynomial is null, so are every coefficients, and we prove the Lemma 1. It is well known that $Ker(Q) = \langle 1, \mathbf{v}, \mathbf{v}^2\rangle$ (see for instance Ref. 28) and we only have to find which functions among $1, \mathbf{v}, \mathbf{v}^2$ are either in $Ker(W_R)$ or in $Ker(W_M)$. Let's begin with the operator W_R. We first show the following result:

Lemma 2.

$$(1, \mathbf{v}^2) \in Ker(W_R) \quad and \quad \mathbf{v} \notin Ker(W_R)$$

When the symmetry assumption (A.19) holds we have clearly:

$$\langle W_R(F)\phi\rangle = \int_{\mathbf{n}} \frac{S(\mathbf{y},\mathbf{n})}{2}\left[\int_{\mathbf{v}} |\mathbf{v}\cdot\mathbf{n}|[F(r_{\mathbf{n}}(\mathbf{v})) - F(\mathbf{v})]\phi(\mathbf{v})\,d\mathbf{v}\right] d\mathbf{n} \tag{B.5}$$

It is possible to make a change of variable $\mathbf{v} \to r_{\mathbf{n}}(\mathbf{v}) \hat{=} \mathbf{v} - 2(\mathbf{v}\cdot\mathbf{n})\mathbf{n}$ in the inner integral (B.5) and rewrite it as:

$$\langle W_R(F)\phi\rangle = \int_{\mathbf{n}} \frac{S(\mathbf{y},\mathbf{n})}{2}\left[\int_{\mathbf{v}} |r_{\mathbf{n}}(\mathbf{v})\cdot\mathbf{n}|[F(\mathbf{v}) - F(r_{\mathbf{n}}(\mathbf{v}))]\phi(r_{\mathbf{n}}(\mathbf{v}))\,d\mathbf{v}\right] d\mathbf{n} \tag{B.6}$$

By making the half sum of (B.5) and (B.6) we obtain:

$$\langle W_R(F)\phi\rangle = \int_{\mathbf{n}} \frac{S(\mathbf{y},\mathbf{n})}{4}\left[\int_{\mathbf{v}} |\mathbf{v}\cdot\mathbf{n}|[F(r_{\mathbf{n}}(\mathbf{v})) - F(\mathbf{v})][\phi(\mathbf{v}) - \phi(r_{\mathbf{n}}(\mathbf{v}))]\,d\mathbf{v}\right] d\mathbf{n} \tag{B.7}$$

It is then easy to check that for $\phi(\mathbf{u}) = 1, \phi(\mathbf{u}) = \mathbf{u}^2$ we have $\forall F, \langle W_R(F)\phi\rangle = 0$ whereas this is obviously not true for$\phi(\mathbf{u}) = \mathbf{u}$. We have then proved Lemma 2. Now let's characterize the kernel of M_M operator. More precisely, let's argue the:

Lemma 3.

$$1 \in Ker\,(W_R) \quad \text{and} \quad \mathbf{v}, \mathbf{v}^2 \notin Ker\,(W_R)$$

The demonstration is in fact a little more difficult than the former one but it is basically grounded on the same techniques. We recall first that for $1 > \alpha > 0$ we have denoted:

$$W_M(F) = \alpha W_R(F) + (1-\alpha) W_D(F) \tag{B.8}$$

where W_R is the purely specular scattering kernel and W_D the purely diffusive scattering kernel. Let's recall the form of the operator W_D:

$$\begin{cases} W_D(F) = \displaystyle\int_{\mathbf{v}\cdot\mathbf{n}\geq 0} S(\mathbf{y},\mathbf{n}) \left(\int_{\mathbf{v}'.\mathbf{n}\leq 0} R_D(\mathbf{v}' \to \mathbf{v}) |\mathbf{v}'\cdot\mathbf{n}| F(\mathbf{v}') d\mathbf{v}' \right) d\mathbf{n} \\ \qquad\qquad - \displaystyle\int_{\mathbf{v}\cdot\mathbf{n}\leq 0} S(\mathbf{y},\mathbf{n}) |\mathbf{v}\cdot\mathbf{n}| F(\mathbf{v}) d\mathbf{n} \\ R_D\left(\mathbf{v}' \to \mathbf{v}\right) = H(\mathbf{v}\cdot\mathbf{n}) \dfrac{m^2 \mathbf{v}\cdot\mathbf{n}}{2\pi (k_B T_w)^2} \exp\left(-\dfrac{m\mathbf{v}^2}{2k_B T_w}\right) \hat{=} H(\mathbf{v}\cdot\mathbf{n}) |\mathbf{v}\cdot\mathbf{n}| g_W(\mathbf{v}) \end{cases} \tag{B.9}$$

In these notations, $H(x)$ is referring to the Heavyside function. To simplify the handling of the latter expression, let's define:

$$\begin{cases} W_D^+(F) \hat{=} \displaystyle\int_{\mathbf{v}\cdot\mathbf{n}\geq 0} S(\mathbf{y},\mathbf{n}) |\mathbf{v}\cdot\mathbf{n}| g_W(\mathbf{v}) \left(\int_{\mathbf{v}'\cdot\mathbf{n}\leq 0} |\mathbf{v}'\cdot\mathbf{n}| F(\mathbf{v}') d\mathbf{v}' \right) d\mathbf{n}. \\ W_D^-(F) \hat{=} \displaystyle\int_{\mathbf{v}\cdot\mathbf{n}\leq 0} S(\mathbf{y},\mathbf{n}) |\mathbf{v}\cdot\mathbf{n}| F(\mathbf{v}) d\mathbf{n} \end{cases} \tag{B.10}$$

We recognize the so called incoming and outgoing contributions. It is worth noting that: $\int_{\mathbf{v}'} H(\mathbf{v}'\cdot\mathbf{n}) |\mathbf{v}'\cdot\mathbf{n}| g_W(\mathbf{v}') = 1$ so $W_D^-(F)$ can be rewritten as:

$$W_D^-(F) = \int_{\mathbf{v}'} \int_{\mathbf{v}\cdot\mathbf{n}\leq 0} S(\mathbf{y},\mathbf{n}) |\mathbf{v}\cdot\mathbf{n}| F(\mathbf{v}) H(\mathbf{v}'\cdot\mathbf{n}) |\mathbf{v}'\cdot\mathbf{n}| g_W(\mathbf{v}') d\mathbf{v}' d\mathbf{n} \tag{B.11}$$

If one multiplies $W_D^-(F)$ by a test function ϕ and integrate for $\mathbf{v} \in \mathbf{R}^3$ he gets:

$$\begin{aligned} \left\langle W_D^-(F)\phi \right\rangle = \int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' \int_{\mathbf{n}} dn S(\mathbf{y},\mathbf{n}) H(-\mathbf{v}\cdot\mathbf{n}) |\mathbf{v}\cdot\mathbf{n}| \\ \times F(\mathbf{v}) \phi(\mathbf{v}) H\left(\mathbf{v}'\cdot\mathbf{n}\right) \left|\mathbf{v}'\cdot\mathbf{n}\right| g_w\left(\mathbf{v}'\right) \end{aligned} \tag{B.12}$$

Doing the same thing with $W_D^+(F)$ one has:

$$\langle W_{\mathbf{D}}^+(F)\phi\rangle = \int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' \int_{\mathbf{n}} d\mathbf{n} S(\mathbf{y},\mathbf{n}) F(\mathbf{v}) \times H(-\mathbf{v}\cdot\mathbf{n})|\mathbf{v}\cdot\mathbf{n}|\phi(\mathbf{v}')H(\mathbf{v}'\cdot\mathbf{n})|\mathbf{v}'\cdot\mathbf{n}|g_w(\mathbf{v}') \quad \text{(B.13)}$$

If we make the difference between the last two terms, we obtain:

$$\langle W_{\mathbf{D}}(F)\phi\rangle = \int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' \int_{\mathbf{n}} d\mathbf{n} S(\mathbf{y},\mathbf{n}) H(\mathbf{v}\cdot\mathbf{n})|\mathbf{v}\cdot\mathbf{n}|g_w(\mathbf{v}) \times H(-\mathbf{v}'\cdot\mathbf{n})|\mathbf{v}'\cdot\mathbf{n}|F(\mathbf{v}')(\phi(\mathbf{v})-\phi(\mathbf{v}')) \quad \text{(B.14)}$$

It immediately appears now that $\phi(\mathbf{u}) = 1$ belongs to the kernel of W_D. As it also belongs to the kernel of W_R, it is then in the kernel of W_M. Nevertheless, since $\mathbf{v}$ and $\mathbf{v}'$ are totally independent variables, there are no special reasons why $\langle W_{\mathbf{D}}(F)\phi\rangle$ should be null for other general forms of ϕ. So neither $\phi(\mathbf{u}) = \mathbf{u}$ nor $\phi(\mathbf{u}) = \mathbf{u}^2$ are in the kernel of W_D and by consequence in $Ker(W_M)$. The physical meaning of this result is indeed quite obvious: a diffusive wall re-emits particles at a given temperature, which signifies that their energies differ before and after the collision. So except for the case when the gas and the wall have the same temperatures, the mean energy of the particles is not conserved any more. In order to simplify further studies of the Maxwellian scattering kernel, we denote:

$$\chi(\mathbf{v},\mathbf{v}') = \int_{\mathbf{n}} S(\mathbf{y},\mathbf{n})H(\mathbf{v}\cdot\mathbf{n})|\mathbf{v}\cdot\mathbf{n}|H(-\mathbf{v}'\cdot\mathbf{n})|\mathbf{v}'\cdot\mathbf{n}|d\mathbf{n} \quad \text{(B.15)}$$

With assumption (A.19), one can easily check that

$$\forall(\mathbf{v},\mathbf{v}'), \quad \chi(\mathbf{v},\mathbf{v}') = \chi(\mathbf{v}',\mathbf{v}). \quad \text{(B.16)}$$

APPENDIX C: COMPUTING ENTROPY DENSITIES FOR M_R AND M_M

In this section, we compute the entropy densities for the operators M_R and M_M. We first show the following result:

Proposition 1. *$\eta_R(F) = F\ln(F) - F$ is an entropy density for $M_R(F)$.*

We know that $\eta_R(F)$ is already an entropy density for $Q(F, F)$ (see Ref. 28). So, if such is the case for $W_R(F)$, the proposition is demonstrated. We recall here that the symmetry hypothesis (A.19) has been assumed. By applying now formula

(B.7) with $\phi(\mathbf{u}) = \ln(F(\mathbf{u}))$, we compute:

$$\langle W_R(F)\,\partial_F \eta_R(F)\rangle = \int_{\mathbf{n}} \frac{S(\mathbf{y},\mathbf{n})}{4}\left[\int_{\mathbf{v}} |\mathbf{v}\cdot\mathbf{n}|\,[F(r_{\mathbf{n}}(\mathbf{v})) - F(\mathbf{v})]\,[\ln F(\mathbf{v}) - \ln F(r_{\mathbf{n}}(\mathbf{v}))]\,d\mathbf{v}\right] d\mathbf{n} \tag{C.1}$$

And the result is proved since $\forall (x, y) \in R^{+*}, (x - y)(\ln(y) - \ln(x)) \leq 0$. Let's return to the notations (B.9). Then we can prove the following result:

Proposition 2. *$\eta_M(F) = F\ln(F/g_W) - F + g_W$ is an entropy density for $M_M(F)$.*

As for the study of M_M conserved maps, the demonstration will be a bit more difficult for this operator than for M_R. Our first task begins with demonstrating that $\eta_M(F)$ is an entropy density for $Q(F, F)$. Using the classical star notations, we recall here (Ref. 28):

$$\langle Q(F,F)\phi\rangle = \frac{1}{4}\int_{\mathbf{v}}\int_{\mathbf{v}_1}\int_{\mathbf{n}} b(|(\mathbf{v}_1 - \mathbf{v})\cdot\mathbf{n}|)[F_1^* F^* - F_1 F] \times (\phi_1 + \phi - \phi_1^* - \phi^*)d\mathbf{v}_1 d\mathbf{n} d\mathbf{v} \tag{C.2}$$

For g_W defined by (B.9), one can verify the following equality:

$$\forall(\mathbf{v}, \mathbf{v}_1), \quad g(\mathbf{v}_1^*)g_w(\mathbf{v}^*) = g_w(\mathbf{v}_1)g_w(\mathbf{v}) \tag{C.3}$$

The star notations stand for velocities after conservative binary collisions. Now if we apply formula (C.2) with $\phi = \partial_F \eta_M(F) = \ln(F/g_W)$, we obtain:

$$\langle Q(F,F)\partial_F \eta_M(F)\rangle = \frac{1}{4}\int_{\mathbf{v}}\int_{\mathbf{v}_1}\int_{\mathbf{n}} b(|(\mathbf{v}_1 - \mathbf{v})\cdot\mathbf{n}|)[F_1^* F^* - F_1 F] \times (\ln(F_1 F) - \ln(F_1^* F^*))d\mathbf{v}_1 d\mathbf{n} d\mathbf{v} \tag{C.4}$$

So we have quickly $\langle Q(F,F)\,\partial_F \eta_M(F)\rangle \leq 0$ and the first step has been taken. Now let's prove that $\eta_M(F)$ is also an entropy density for $W_R(F)$. Here again, the function g_W satisfies $g_w(\mathbf{v}) = g_w(r_{\mathbf{n}}(\mathbf{v}))$; so if we apply (B.7) with $\phi = \partial_F \eta_M(F) = \ln(F/g_W)$ we obtain equality (C.1) and $\eta_M(F)$ is an entropy density for $W_R(F)$. It remains then the most difficult to show, that $\eta_M(F)$ is an entropy density for $W_D(F)$. Using (B.14) with notation (B.15), we can write for any test

function ϕ:

$$\langle W_{\mathbf{D}}(F)\phi\rangle = \int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' g_w(\mathbf{v})F(\mathbf{v}')\chi(\mathbf{v},\mathbf{v}')(\phi(\mathbf{v})-\phi(\mathbf{v}')) \tag{C.5}$$

Now, if we compute (C.5) for $\phi = \partial_F \eta_M(F) = \ln(F/g_W)$ we get:

$$\langle W_{\mathbf{D}}(F)\partial_F \eta_M(F)\rangle = \int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' g_w(\mathbf{v})F(\mathbf{v}')\chi(\mathbf{v},\mathbf{v}') \left(\ln\left(\frac{g_w(\mathbf{v}')\,F(\mathbf{v})}{g_w(\mathbf{v})\,F(\mathbf{v}')}\right)\right) \tag{C.6}$$

Using now the symmetry of the function $\chi(\mathbf{v},\mathbf{v}')$ (B.16), it clearly appears:

$$\int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' g_w(\mathbf{v}')F(\mathbf{v})\chi(\mathbf{v}',\mathbf{v}) = \int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' g_w(\mathbf{v})F(\mathbf{v}')\chi(\mathbf{v}',\mathbf{v}) = M \tag{C.7}$$

Hence it is obvious that:

$$\begin{aligned}\langle W_{\mathbf{D}}(F)\,\partial_F \eta_D(F)\rangle = M \int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' \frac{g_w(\mathbf{v})\,F(\mathbf{v}')\,\chi(\mathbf{v},\mathbf{v}')}{M} \\ \times \left(\ln\left(\frac{g_w(\mathbf{v}')\,F(\mathbf{v})\,\chi(\mathbf{v},\mathbf{v}')\,M}{g_w(\mathbf{v})\,F(\mathbf{v}')\,\chi(\mathbf{v},\mathbf{v}')\,M}\right)\right)\end{aligned} \tag{C.8}$$

Let's note then:

$$p(\mathbf{v},\mathbf{v}') = \frac{g_w(\mathbf{v})\,F(\mathbf{v}')\,\chi(\mathbf{v},\mathbf{v}')}{M}; \quad q(\mathbf{v},\mathbf{v}') = \frac{g_w(\mathbf{v}')\,F(\mathbf{v})\,\chi(\mathbf{v},\mathbf{v}')}{M} \tag{C.9}$$

So $p(\mathbf{v},\mathbf{v}')$ and $q(\mathbf{v},\mathbf{v}')$ are both normalized probability density functions on the space$\mathbf{V}\times\mathbf{V}'$. It is possible to calculate their Kullback Information defined by:

$$K(p:q) = \int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' p(\mathbf{v},\mathbf{v}') \left(\ln\left(\frac{p(\mathbf{v},\mathbf{v}')}{q(\mathbf{v},\mathbf{v}')}\right)\right) \tag{C.10}$$

But it is a well known result that $K(p{:}q)$ is always positive so:

$$\begin{aligned}\langle W_{\mathbf{D}}(F)\,\partial_F \eta_M(F)\rangle &= -M \int_{\mathbf{v}} d\mathbf{v} \int_{\mathbf{v}'} d\mathbf{v}' p(\mathbf{v},\mathbf{v}') \left(\ln\left(\frac{p(\mathbf{v},\mathbf{v}')}{q(\mathbf{v},\mathbf{v}')}\right)\right) \\ &= -MK(p:q) \le 0\end{aligned} \tag{C.11}$$

APPENDIX D: ASSERTING LEVERMORE'S EQUIVALENCES

After the preliminary results shown in Appendices B and C, we are now in position of proving the system of Levermore's equivalences for the operators M_R and M_M. First we show:

Proposition 3. *M_R satisfies (12) for $Ker(M_R) = \langle 1, \mathbf{v}^2 \rangle$ and $\eta_R(F) = F \ln(F) - F$*

(1) First it is trivial to demonstrate that

$$M_R(F) = 0 \Rightarrow \langle M_R(F)\, \partial_F \eta_R(F) \rangle = 0 \tag{D.1}$$

(2) Assume that $\langle M_R(F)\, \partial_F \eta_R(F) \rangle = 0$. As $\eta_R(F)$ is an entropy density both for $Q(F, F)$ and $W_R(F)$ (see Appendix C), it implies:

$$\begin{cases} \langle Q(F, F)\, \partial_F \eta_R(F) \rangle = 0 \\ \langle W_R(F)\, \partial_F \eta_R(F) \rangle = 0 \end{cases} \tag{D.2}$$

From (2.1) we draw (see Ref. 28): $\exists (\mathbf{a}, \mathbf{b}, c)\,, \partial_F \eta_R(F) = \mathbf{a} + \mathbf{b} \cdot \mathbf{v} + c\mathbf{v}^2$. Now using (2.2), and (C.2) we have:

$$\langle W_R(F)\, \partial_F \eta_R(F) \rangle = \int_n \frac{S(\mathbf{y}, \mathbf{n})}{4} \times \left[\int_{\mathbf{v}} |\mathbf{v} \cdot \mathbf{n}| \left[F(r_{\mathbf{n}}(\mathbf{v})) - F(\mathbf{v}) \right] \left[\ln F(\mathbf{v}) - \ln F(r_{\mathbf{n}}(\mathbf{v})) \right] d\mathbf{v} \right] d\mathbf{n} = 0 \tag{D.3}$$

As the function to integrate is always negative, the integral is null if and only if the latter is always null. We get from these results: $\forall \mathbf{v}, \mathbf{n}\ \ln F(\mathbf{v}) - \ln F(r_{\mathbf{n}}(\mathbf{v})) = 0 = \mathbf{b} \cdot (\mathbf{v} - r_{\mathbf{n}}(\mathbf{v}))$, which implies $\mathbf{b} = \mathbf{0}$ and then $\langle M_R(F)\, \partial_F \eta_R(F) \rangle = 0 \Rightarrow \partial_F \eta_R(F) \in Ker(M_R)$.

(3) Assume now that $\partial_F \eta_R(F) \in Ker(M_R)$. Then we have $F(\mathbf{v}) = A \exp\left(-m\mathbf{v}^2 / 2k_B T\right)$. It is well known that $Q(F, F)$ vanishes for such F. As $\mathbf{v} \to r_{\mathbf{n}}(\mathbf{v})$ is isometric for each $\mathbf{n}$, it is easy to verify that $M_R(F)$ also vanishes for such F. So $\partial_F \eta_R(F) \in Ker(M_R) \Rightarrow M_R(F) = 0$ and the loop is achieved. In this demonstration indeed, the key point rests on the fact that $\eta_R(F)$ is an entropy density both for $Q(F, F)$ and $W_R(F)$. By using the same kind of demonstration, we can prove Levermore's equivalences for M_M:

Proposition 4. *M_M satisfies the system (12) for $Ker(M_M) = \langle 1 \rangle$ and for the entropy density $\eta_M(F) = F \ln(F/g_W) - F + g_W$*

As in Proposition 1, the key point of the demonstration will be the fact that $\eta_D(F)$ is an entropy density for $Q(F, F)$, $W_R(F)$ and $W_D(F)$.

APPENDIX E: SHOWING THAT *F*(U) IS ODD AND DISSIPATIVE

In this Appendix, we demonstrate the following properties:

Proposition 5.

$$\begin{cases} \mathbf{F}(-\mathbf{u}) = -\mathbf{F}(\mathbf{u}) \\ \forall \mathbf{u}, \quad \mathbf{F}(\mathbf{u}) \cdot \mathbf{u} \leq 0 \end{cases}$$

The above results are in good agreement with what is expected from the hydrodynamic drag force, traditionally refers as the pressure drag in porous media. The demonstration rests on a set of calculations we are going to present now. The first part of this proposition can be proved easily:

$$\begin{cases} \mathbf{F}(-\mathbf{u}) = \dfrac{\rho}{(2\pi k_B T/m)^{3/2}} \displaystyle\int_{\mathbf{n}} \frac{S(\mathbf{y},\mathbf{n})}{4\varepsilon(\mathbf{y})} \mathbf{n} d\mathbf{n} \int_{\mathbf{v}} |\mathbf{v}\cdot\mathbf{n}|(\mathbf{v}\cdot\mathbf{n}) \\ \qquad\qquad \times \left[\exp\left(-\dfrac{m(\mathbf{r}_{\mathbf{n}}(\mathbf{v})+\mathbf{u})^2}{2k_B T} \right) - \exp\left(-\dfrac{m(\mathbf{v}+\mathbf{u})^2}{2k_B T} \right) \right] d\mathbf{v} \\ \mathbf{r}_{\mathbf{n}}(\mathbf{v}) \;\hat{=}\; \mathbf{v} - 2(\mathbf{v}\cdot\mathbf{n})\mathbf{n} \end{cases}$$

And it only remains to make the change of variable $\mathbf{v} \to -\mathbf{v}$ in the integral. So let us continue with the expression of $\mathbf{F}(\mathbf{u}) \cdot \mathbf{u}$:

$$\begin{cases} \mathbf{F}(\mathbf{u}) \cdot \mathbf{u} = \dfrac{\rho}{(2\pi k_B T/m)^{3/2}} \displaystyle\int_{\mathbf{n}} \frac{S(\mathbf{y},\mathbf{n})}{4\varepsilon(\mathbf{y})} \mathbf{u}\cdot\mathbf{n} d\mathbf{n} \\ \quad \times \displaystyle\int_{\mathbf{v}} |\mathbf{v}\cdot\mathbf{n}|\, \mathbf{v}\cdot\mathbf{n} \left[\exp\left(-\dfrac{m(\mathbf{r}_{\mathbf{n}}(\mathbf{v})-\mathbf{u})^2}{2k_B T} \right) - \exp\left(-\dfrac{m(\mathbf{v}-\mathbf{u})^2}{2k_B T} \right) \right] d\mathbf{v} \end{cases}$$

As we first integrate in $\mathbf{v}$ when $\mathbf{n}$ has been chosen, it is convenient to work with an orthonormal basis $(\mathbf{s}, \mathbf{t}, \mathbf{n})$ in the phase space $\mathbf{V}$. With such a choice, any vector $\mathbf{v}$ can be decomposed as $\mathbf{v} = v_s\mathbf{s} + v_t\mathbf{t} + v_n\mathbf{n}$. From this it is very clear that $\mathbf{r}_{\mathbf{n}}(\mathbf{v}) \cdot \mathbf{t} = \mathbf{v} \cdot \mathbf{t} = v_t$, $\mathbf{r}_{\mathbf{n}}(\mathbf{v}) \cdot \mathbf{s} = \mathbf{v} \cdot \mathbf{s} = v_s$, $\mathbf{r}_{\mathbf{n}}(\mathbf{v}) \cdot \mathbf{n} = -\mathbf{v} \cdot \mathbf{n} = -v_n$. Thus the sign of $\mathbf{F}(\mathbf{u}) \cdot \mathbf{u}$ is given by the sign of the function $J(\mathbf{u}, \mathbf{n})$ defined as:

$$\begin{cases} J(\mathbf{u},\mathbf{n}) \hat{=} u_n \displaystyle\int_{v_n} |v_n|\, v_n \left[\exp\left(-\dfrac{m(v_n+u_n)^2}{2k_B T} \right) - \exp\left(-\dfrac{m(v_n-u_n)^2}{2k_B T} \right) \right] dv_n \end{cases} \tag{E.1}$$

And it is a simple exercise to show that:

$$J(\mathbf{u},\mathbf{n}) = -8u_n^2\frac{k_BT}{m}\exp\left(-\frac{mu_n^2}{2k_BT}\right) + 2\left(\frac{k_BT}{m}+u_n^2\right)u_n\int_{u_n}^{-u_n}\exp\left(-\frac{mv_n^2}{2k_BT}\right)dv_n \leq 0 \tag{E.2}$$

APPENDIX F: COMPUTING AN APPROXIMATION OF THE PRESSURE DRAG

This very important appendix is devoted to the demonstration of the following result:

Proposition 6.

$$\forall\mathbf{u},\quad \|\mathbf{u}\| \ll \sqrt{\frac{k_BT}{m}},\quad F(\mathbf{u}) \approx -\left[\frac{4}{\sqrt{6\pi}}\frac{\rho\sigma}{\varepsilon(\mathbf{y})m}\mu(T)\int_{\mathbf{n}} S(\mathbf{y},\mathbf{n})\,\mathbf{n}\otimes\mathbf{n}d\mathbf{n}\right]:\mathbf{u}$$

Here again, the proof lies in the calculations. Since $\mathbf{F}(\mathbf{0})=\mathbf{0}$, it is clear that:

$$\mathbf{F}(\mathbf{u}) \underset{\mathbf{u}\to 0}{=} \mathbf{M}:\mathbf{u},\quad \mathbf{M} \hat{=} \left.\frac{\partial\mathbf{F}}{\partial\mathbf{u}}\right|_{\mathbf{u}=0} \tag{F.1}$$

To compute the matrix $\mathbf{M}$, let's calculate:

$$Du_i \hat{=} \frac{\partial}{\partial u_i}\left[\frac{\rho}{(2\pi k_BT/m)^{3/2}}\int_{\mathbf{n}}\frac{S(\mathbf{y},\mathbf{n})}{2\varepsilon(\mathbf{y})}\mathbf{n}d\mathbf{n}\int_{\mathbf{v}}|\mathbf{v}\cdot\mathbf{n}|(\mathbf{v}\cdot\mathbf{n}) \times\left(\exp\left(-\frac{m(\mathbf{r_n}(\mathbf{v})-\mathbf{u})^2}{2k_BT}\right)-\exp\left(-\frac{m(\mathbf{v}-\mathbf{u})^2}{2k_BT}\right)\right)d\mathbf{v}\right]\Bigg|_{\mathbf{u}=0} \tag{F.2}$$

Knowing that:

$$\begin{cases}\dfrac{\partial}{\partial u_i}\left[\exp\left(-\dfrac{m(\mathbf{v}-\mathbf{u})^2}{2k_BT}\right)\right]\Bigg|_{\mathbf{u}=0} = \dfrac{mv_i}{k_BT}\exp\left(-\dfrac{m(\mathbf{v})^2}{2k_BT}\right)\\ \dfrac{\partial}{\partial u_i}\left[\exp\left(-\dfrac{m(\mathbf{r_n}(\mathbf{v})-\mathbf{u})^2}{2k_BT}\right)\right]\Bigg|_{\mathbf{u}=0} = \dfrac{m(\mathbf{r_n}(\mathbf{v}))_i}{k_BT}\exp\left(-\dfrac{m(\mathbf{r_n}(\mathbf{v}))^2}{2k_BT}\right)\end{cases} \tag{F.3}$$

We get:

$$Du_i = \left[\frac{\rho}{(2\pi k_B T/m)^{3/2}} \int_{\mathbf{n}} \frac{S(\mathbf{y},\mathbf{n})}{2\varepsilon(\mathbf{y})} \mathbf{n} d\mathbf{n} \right.$$
$$\left. \times \int_{\mathbf{v}} \frac{m\,|\mathbf{v}\cdot\mathbf{n}|\,(\mathbf{v}\cdot\mathbf{n})}{k_B T} \left((\mathbf{r}_{\mathbf{n}}(\mathbf{v}))_i - \mathbf{v}_i\right) \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right) d\mathbf{v} \right] \quad \text{(F.4)}$$

But we can remark that $(\mathbf{r}_{\mathbf{n}}(\mathbf{v}))_i - v_i = (\mathbf{r}_{\mathbf{n}}(\mathbf{v}) - \mathbf{v}) \cdot \mathbf{e}_i = -2(\mathbf{v}\cdot\mathbf{n})\,\mathbf{n}\cdot\mathbf{e}_i = -2(\mathbf{v}\cdot\mathbf{n})\,n_i$ so:

$$Du_i = \left[-\frac{\rho}{(2\pi k_B T/m)^{3/2}} \int_{\mathbf{n}} \frac{S(\mathbf{y},\mathbf{n})}{\varepsilon(y)} \mathbf{n} n_i d\mathbf{n} \right.$$
$$\left. \times \int_{\mathbf{v}} \frac{m\,|\mathbf{v}\cdot\mathbf{n}|\,(\mathbf{v}\cdot\mathbf{n})^2}{k_B T} \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right) d\mathbf{v} \right] \quad \text{(F.5)}$$

But we have:

$$\int_{\mathbf{v}} \frac{m\,|\mathbf{v}\cdot\mathbf{n}|\,(\mathbf{v}\cdot\mathbf{n})^2}{k_B T} \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right) d\mathbf{v}$$
$$= \frac{m}{k_B T} \frac{2\pi k_B T}{m} 2 \int_0^{+\infty} v_n^3 \exp\left(-\frac{m v_n^2}{2k_B T}\right) dv_n \quad \text{(F.6)}$$

where $\int_0^{+\infty} v_n^3 \exp\left(-\frac{m v_n^2}{2k_B T}\right) dv_n = 2\frac{k_B^2 T^2}{m^2}$ and we finally obtain:

$$\mathbf{M} = \left[-\sqrt{\frac{8}{\pi}} \frac{\rho}{\varepsilon(\mathbf{y})} \sqrt{\frac{k_B T}{m}} \int_{\mathbf{n}} S(\mathbf{y},\mathbf{n})\,\mathbf{n}\otimes\mathbf{n} d\mathbf{n} \right]$$
$$= -\sqrt{\frac{8}{3\pi}} \frac{\rho\sigma}{\varepsilon(\mathbf{y})\,m} \frac{\sqrt{3mk_B T}}{\sigma} \int_{\mathbf{n}} S(\mathbf{y},\mathbf{n})\,\mathbf{n}\otimes\mathbf{n} d\mathbf{n} \quad \text{(F.7)}$$

If one then introduces the gas dynamical viscosity $\mu(T) = \sqrt{3mk_B T}/\sigma$ he recovers Proposition 1. It only remains now to explain why the approximation given by Proposition 1 is correct for $\|\mathbf{u}\| << \sqrt{k_B T/m}$. Indeed this is linked to the expansion of the force $\mathbf{F}(\mathbf{u})$ in power series of $\mathbf{u}$. Since $\forall \mathbf{u}$, $\mathbf{F}(-\mathbf{u}) = -\mathbf{F}(\mathbf{u})$, the odd terms appear alone in the expansion of $\mathbf{F}(\mathbf{u})$. But clearly, any odd partial derivative

of $\mathbf{F}$ in $\mathbf{0}$ reads as:

$$\left.\frac{\partial^{2p+1}\mathbf{F}}{\partial\mathbf{u}^{2p+1}}\right|_{\mathbf{u}=0} = c\sqrt{\frac{k_B T}{m}}\left(\frac{k_B T}{m}\right)^{p}\mathbf{N} \tag{F.8}$$

where c is some constant and $\mathbf{N}$ is a tensor of order $2p+1$ of order 0 in $\mathbf{u}$. Formally:

$$\frac{\|\mathbf{F}(\mathbf{u})\|}{\|\mathbf{M}\mathbf{u}\|} = \left(1 + \sum_{p=0}^{\infty}\alpha_p\left(\frac{m\,\|\mathbf{u}\|^2}{k_B T}\right)^{p}\right) \tag{F.9}$$

In porous media, the fluid velocity is often very much smaller than a thermal velocity so that the approximation claimed in Proposition 1 is largely satisfied.

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