A MASS DIFFUSION EFFECT IN GAS DYNAMICS EQUATIONS

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Abstract. In the current work we propose a theory for an additional mass diffusion effect in the conventional gas dynamics equations. We find that this effect appears as a homogenization time limit correction, when the deterministic interaction process of the real gas molecules is replaced with a simplified random interaction process for consistency with the Boltzmann equation. For the simplified random interaction processes represented by either a hard sphere random scattering model, or by a model which employs the Lennard-Jones potential for random molecular deflections, we compute the estimates of the corrective diffusion coefficient in the Euler, Navier-Stokes and Grad equations for some monatomic and polyatomic gases.

1. Introduction

Recently, there has been a profound interest in the extended fluid dynamics [7–9,15,16] and the underlying Boltzmann equation [14,28,36], which included an additional spatial diffusion term. A concept of the “volume velocity” was introduced in [7–9], which differed from the conventional mass velocity by a small flux term derived from Fick’s law. Similar additional terms to model the self-diffusion of mass were introduced in [15,16]. In [14,28,36], an ad hoc diffusion term was introduced directly into the Boltzmann equation. Also, in [21], it was demonstrated that an additional mass diffusion term in the Navier-Stokes equations provided a more accurate model for a supersonic shock wave.

In our recent work [1], we found that a simplified model of the gas molecule interactions based on the appropriately chosen random jump process is more consistent with the Boltzmann equation [10,11] than the deterministic multimolecular dynamics of a real gas based on a repelling potential (such as the Lennard-Jones potential [30]). We then speculated that a difference between the two models could manifest in the form of a corrective mass diffusion term with an empirically determined mass diffusion coefficient $D_\alpha$. Also, in [1] we tested the proposed mass diffusion model in the Couette microflow setting with the appropriately scaled near-wall viscosity [2] and fully recovered the basic moments of the benchmark Direct Simulation Monte Carlo (DSMC) [6,35] computation in the same setting, including the Knudsen layers, for the diffusive Navier-Stokes and regularized Grad equations. In the subsequent work [3] we tested the same diffusive model of [1] with the same viscosity scaling [2] in the Poiseuille microflow setting, and recovered the basic moments of the corresponding benchmark DSMC computation with...
high accuracy (about 1% relative error in the velocity, mass flow, temperature and pressure).

In the current work, we propose a more coherent theory for the mass diffusion effect in the gas dynamics equations, based on a diffusion correction of the simplified random molecule interaction process to match the dynamics of a realistic gas in the homogenization time limit [26,27,33,38]. For the corresponding simplified interaction model of the gas molecules based on randomly colliding hard spheres [12,17,22] and random deflections via the Lennard-Jones potential [23,24,30,39], we subsequently compute the estimates of the corrective mass diffusion coefficient $D_\alpha$ in the Euler, Navier-Stokes [5,18] and Grad [19,31,37] equations for some monatomic and polyatomic gases.

The manuscript is organized as follows. In Section 2 we review the multiscale time approach [26,27,33,38] for a general multiparticle interaction system [1], while also including an external acceleration (such as, for example, the planetary gravity) which may optionally affect the gas molecules. In Section 3 we introduce a multiparticle system with a simplified random molecular interaction process with an additional diffusion correction to ensure consistency with the realistic gas dynamics in the homogenization time limit. In Section 4 we review the random jump molecular interaction operator from [1] and the derivation of the corresponding diffusive Boltzmann equation, which now includes the optional external acceleration. In Sections 5, 6 and 7 we review, respectively, the diffusive Euler, Navier-Stokes and Grad equations, and compute the estimates of the corrective mass diffusion coefficients for neon, argon, krypton, xenon, nitrogen, oxygen, carbon dioxide and methane. We discuss the results of the work in Section 8.

2. Averaging and homogenization for a fast interaction dynamics

Here we review the homogenization formalism for a multiparticle gas system we introduced in [1], and equip it with an optional external acceleration term (which could be important in practical applications). The relevant theory can be found in [26,27,33,38].

Consider a general system of $K$ particles in an $N$-dimensional space, where the $i$-th particle has the coordinate $x_i$ and velocity $v_i$. For the whole system of particles, we concatenate their respective coordinate and velocity vectors into

$$X = (x_1, \ldots, x_K), \quad V = (v_1, \ldots, v_K).$$

For realistic gases, the first 3 components of each $x_i$ or $v_i$ refer to the translational movement of molecules, while the remaining $(N-3)$ components refer to rotational degrees of freedom, and thus are naturally periodic. In what is presented below, we assume that the translational coordinates are also periodic (that is, the 3-dimensional physical space is folded into a torus), to keep all $K$ molecules in a finite volume and avoid boundary effects at the same time.

We start with a general $(X(t), V(t))$-process, given by

$$\frac{dX}{dt} = V, \quad dV = A dt + d\mathcal{N}(t, X, V).$$

Above, $A$ is an external acceleration of the form

$$A = (a_1, \ldots, a_K).$$
where \( a_i \) is an individual external acceleration which acts on the \( i \)-th molecule. We assume that only the first 3 components of any \( a_i \) are nonzero (that is, the external acceleration may only act along the translational directions). Also, \( \mathcal{N} \) is a general, possibly random, stationary interaction process between the molecules. We assume that \( \mathcal{N} \) preserves the momentum \( m \) and energy \( \mathcal{E} \) of the form

\[
\begin{align*}
m &= \sum_{k=1}^{K} v_k, \quad \mathcal{E} = \frac{1}{2} \sum_{k=1}^{K} \|v_k\|^2 = \frac{1}{2} \|V\|^2,
\end{align*}
\]

where \( \| \cdot \| \) is the usual Euclidean norm. Note that for realistic gas interaction processes the energy does not have a purely kinetic form above, as it normally also includes the interaction potential (such as the Lennard-Jones potential \([30]\)). We will, however, assume that the gas is dilute, that is, the effective range of the potential is negligible in comparison with the average distance between the molecules, so that most of the time the energy indeed consists solely of its kinetic part in (2.3).

The corresponding Kolmogorov equation for the process in (2.1) is, subsequently, given by

\[
\frac{\partial F}{\partial t} + \nabla V \cdot (AF) = \mathcal{L}^* F,
\]

where \( \mathcal{L} \) is the infinitesimal generator of (2.1) with the external acceleration \( A \) set to zero. The general form of \( \mathcal{L} \) is given by

\[
\mathcal{L} = V \cdot \nabla X + \{ \text{velocity interaction} \},
\]

where the second term in the right-hand side is given through the properties of \( \mathcal{N} \) (and thus is undefined, for now). We will assume that any solution \((X(t), V(t))\) of (2.1) with \( A \) set to zero is ergodic and strongly mixing on the corresponding union of \( X \)-torus and \( V \)-sphere. Thus, both \( \mathcal{L} \) and its adjoint \( \mathcal{L}^* \) possess a one-dimensional null space of constant functions, such that, in the absence of the external acceleration \( A \), any starting state of \( F \) in (2.4) is forced by \( \mathcal{L}^* \) to relax, with time, towards the uniform invariant state on the \( X \)-torus and \( V \)-sphere.

2.1. **Averaging for the fast interaction dynamics.** Let us rescale the dynamical system in (2.1) as follows:

\[
\frac{dX}{dt} = V, \quad \frac{dY}{dt} = \frac{1}{\varepsilon} V, \quad dV = Adt + d\mathcal{N}(t/\varepsilon, Y, V),
\]

where \( 0 < \varepsilon \ll 1 \) is a small constant scaling parameter. Here we assume that \( \mathcal{N} \) is the “fast” process (as compared to the external acceleration \( A \)), and we also introduce the “fast” coordinate process \( Y \), which formally replaces \( X \) (as the latter becomes the “slow” coordinate process). This rescaling is similar to what was done, for example, in Section 11.7.5 of \([33]\). Observe that the rescaled system in (2.6) is “backward-compatible” with the original one in (2.1) if one sets \( \varepsilon = 1 \). The corresponding rescaled Kolmogorov equation is then given by

\[
\frac{\partial F}{\partial t} + V \cdot \nabla_X F + \nabla V \cdot (AF) = \frac{1}{\varepsilon} \mathcal{L}^* F,
\]
where \( \mathcal{L}^* \) now depends on \( Y \), rather than on \( X \). We now expand \( F \) in powers of \( \varepsilon \) as
\[
F = F_0 + \varepsilon F_1 + \varepsilon^2 F_2 + \ldots,
\]
where each \( F_i \) does not depend on \( \varepsilon \). This yields, for the successive powers of \( \varepsilon \),
\[
\mathcal{L}^* F_0 = 0, \quad \frac{\partial F_0}{\partial t} + V \cdot \nabla_X F_0 + \nabla V \cdot (A F_0) = \mathcal{L}^* F_1.
\]
From the first identity above we find that \( F_0 \) is an invariant measure for the process \((Y, V)\) in the absence of the external acceleration \( A \). In particular, let
\[
F = \int F \, dY dV,
\]
then for any suitable \( \psi \) we have
\[
\int \psi F_0 \, dY dV = \bar{F}_0 \int \psi \, d\nu,
\]
where \( \nu \) is the uniform invariant probability measure on the \( Y \)-torus and on the constant momentum/energy sphere of \( V \). Then, integrating the second identity above over \( dY dV \), we find
\[
\frac{\partial \bar{F}_0}{\partial t} + \nabla_X \cdot (\bar{F}_0 U_0) = 0,
\]
where \( U_0 \) is the average velocity of the fast system:
\[
U_0 = \int V \, d\nu.
\]
Due to the fact that all particles are statistically identical when \( V \) is uniformly distributed on the constant momentum/energy sphere, \( U_0 \) consists of \( K \) identical vectors \( u_0 \):
\[
U_0 = (u_0, \ldots, u_0),
\]
and can be set to zero via an appropriate Galilean shift of the coordinate system in the \( N \)-dimensional space where the multimolecular system in (2.1) evolves.

2.2. Homogenization for the fast interaction dynamics. We are now going to set the average velocity \( u_0 \) of the fast system above to zero via an appropriate Galilean shift, which sets \( \partial F_0 / \partial t = 0 \) at the \( O(1) \) time scale, according to (2.12). This, however, simply means that the time derivative of \( F \) manifests on the longer time scale \( O(\varepsilon^{-1}) \) [33,38], so we rescale
\[
\frac{\partial F}{\partial t} \rightarrow \varepsilon \frac{\partial F}{\partial t}
\]
above in (2.7). In this situation, the expansion in (2.8) yields
\[
\mathcal{L}^* F_0 = 0, \quad \mathcal{L}^* F_1 = V \cdot \nabla_X F_0 + \nabla V \cdot (A F_0),
\]
\[
\frac{\partial F_0}{\partial t} + V \cdot \nabla_X F_1 + \nabla V \cdot (A F_1) = \mathcal{L}^* F_2.
\]
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Apparently, $F_0$ has the same meaning as above in the averaging case, and integrating the third equation in $dYdV$ yields

\begin{equation}
\frac{\partial F_0}{\partial t} + \nabla_x \cdot \left( \int V F_1 \, dYdV \right) = 0.
\end{equation}

To compute the integral above, let us define the process $\Phi(t, Y, V)$ as

\begin{equation}
\Phi(t, Y, V) = \int_0^t \mathbb{E} V(s) \, ds.
\end{equation}

where the notation $\mathbb{E} V(t)$ is a shorthand for

\begin{equation}
\mathbb{E} V(t) \overset{\text{def}}{=} \mathbb{E} [V(t) | Y(0) = Y, V(0) = V],
\end{equation}

where the velocity process $V(t)$ is generated by (2.1) with $A$ set to zero. Above, the expectation $\mathbb{E}$ is included in case $\mathcal{N}$ happens to be a random process. Now, by the definition of the generator $\mathcal{L}$,

\begin{equation}
\mathcal{L} \Phi(t, Y, V) = \lim_{h \to 0} \frac{\mathbb{E} \Phi(t, Y(h), V(h)) - \Phi(t, Y, V)}{h} = \mathbb{E} V(t) - V.
\end{equation}

For more details on the above identity, see, for example, Lemma 3.2.2 in [4]. Now, let us consider the integral of the form

\begin{equation}
\int V F_1 \, dYdV - \int \mathbb{E} V(t) F_1 \, dYdV = -\int \mathcal{L} \Phi(t, Y, V) F_1 \, dYdV =
\end{equation}

\begin{equation}
= -\int \Phi(t, Y, V) \mathcal{L}^* F_1 \, dYdV = -\int_0^t ds \int \mathbb{E} V(s) \left( V \cdot \nabla_x F_0 + \nabla_V \cdot (A F_0) \right) \, dYdV.
\end{equation}

Observe that the first term in the first line is what we need to compute, while the last identity depends entirely on the properties of the leading-order dynamics. Thus, in order to express the former in terms of the latter, we need to eliminate the second term in the first line, where $F_1$ depends on $Y$ and $V$ (but not on $V(t)$), and we are also at freedom to choose the time parameter $t$.

First, let us note that the integration over $dYdV$ above occurs over the $Y$-torus and $V$-sphere (with the latter now centered at zero momentum due to the choice of the coordinates). Thus, we can write

\begin{equation}
\int \mathbb{E} V(t) F_1 \, dYdV \sim \int \mathbb{E} V(t) F_1 \, d\nu,
\end{equation}

where $\nu$ is, as before, the uniform probability measure of the fast interaction dynamics, and the constant proportionality coefficient involves the surface areas of the $Y$-torus and $V$-sphere. Next, the strong mixing assumption for (2.1) (and, equivalently, (2.6)) yields

\begin{equation}
\lim_{t \to \infty} \int \mathbb{E} V(t) F_1 \, d\nu = 0,
\end{equation}

and, therefore,

\begin{equation}
\int V F_1 \, dYdV = -\int_0^\infty ds \int \mathbb{E} V(s) \left( V \cdot \nabla_x F_0 + \nabla_V \cdot (A F_0) \right) \, dYdV.
\end{equation}
The expression above is still practically intractable, a thus a further simplification is needed. As in [1], here we are going to assume that the statistics of the velocity process exhibit properties similar to Gaussian random processes. Namely, we are going to assume that the following analog of the regression theorem [34] holds for a suitable \( \psi(Y, V) \):

\[
\int \mathbb{E} V(s) \psi(Y, V) \, dYdV = \mathbf{C}(s) \mathbf{C}^{-1}(0) \int V \psi(Y, V) \, dYdV.
\]

Above, \( \mathbf{C}(t) \) is the velocity time autocorrelation function

\[
\mathbf{C}(t) = \int \mathbb{E} V(t) V^T \, dv.
\]

This assumption yields

\[
\int V F_1 \, dYdV = -\left( \int_0^\infty \mathbf{C}(s) \, ds \right) \mathbf{C}^{-1}(0) \int V \left( V \cdot \nabla_x F_0 + \nabla_V \cdot (A F_0) \right) \, dYdV.
\]

Now observe that

\[
\int V \left( V \cdot \nabla_x F_0 \right) \, dYdV = \nabla_x \cdot \int V V^T F_0 \, dYdV = \nabla_x \cdot \left( F_0 \int V V^T \, dv \right) = \nabla_x \cdot (F_0 \mathbf{C}(0)),
\]

\[
\int V \left( \nabla_V \cdot (A F_0) \right) \, dYdV = -\int I A F_0 \, dYdV = -\bar{F}_0 \int A \, dv = -\bar{F}_0 A_0,
\]

where \( \bar{A}_0 \) is the \( \nu \)-average of \( A \). Thus, we further obtain

\[
\int V F_1 \, dYdV = -\left( \int_0^\infty \mathbf{C}(s) \, ds \right) \mathbf{C}^{-1}(0) \left( \nabla_x \cdot (F_0 \mathbf{C}(0)) - F_0 \bar{A}_0 \right)
\]

Even in this simplified form, the velocity autocorrelation function \( \mathbf{C}(t) \) and its inverse are \( KN \times KN \) matrices, and thus are still computationally intractable. Thus, as in [1], we make yet another simplifying assumption:

\[
\mathbf{C}(0) = \theta_0 I, \quad \left( \int_0^\infty \mathbf{C}(s) \, ds \right) \mathbf{C}^{-1}(0) = \tau_0 I.
\]

This can be justified by recalling that all particles in the fast interaction process are statistically identical, and that their number is large enough to make them statistically decorrelated (even though, strictly speaking, they are not independent since they reside on a common constant energy sphere). The quantities \( \theta_0 \) (temperature) and \( \tau_0 \) (decorrelation time) are thus given by

\[
\theta_0 = \frac{1}{KN} \int \|V\|^2 \, dv, \quad \tau_0 = \frac{1}{KN \theta_0} \int_0^\infty ds \int \mathbb{E} V(s) \cdot V(0) \, dv.
\]

The latter simplification finally yields a tractable homogenization time limit

\[
\frac{\partial F_0}{\partial t} = \nabla_x \cdot \left( \frac{1}{\tau_0} (\nabla_x (\theta_0 F_0) - \bar{A}_0 F_0) \right).
\]
3. A DIFFUSION CORRECTION FOR SIMPLIFIED INTERACTION PROCESSES

Let us assume that the interaction process $\mathcal{N}$ in (2.1) was that of a realistic gas, and that it can be approximated by a different, simplified interaction process $\mathcal{N}_s$, with the corresponding simplified molecular dynamics equations accordingly given by

\begin{equation}
\frac{dX}{dt} = V, \quad dV = Adt + d\mathcal{N}_s(t, X, V).
\end{equation}

We will assume that the simplified interaction process $\mathcal{N}_s$ also preserves the momentum and energy in (2.3) and has the same invariant uniform probability measure $\nu$ on the sphere of constant momentum and energy, so that the momentum and energy (and, therefore, the fast temperature $\theta_0$) of $\mathcal{N}_s$ match those of $\mathcal{N}$. As before, we choose a suitable coordinate system via an appropriate Galilean shift so that the momenta of both $\mathcal{N}$ and $\mathcal{N}_s$ equal zero.

Observe that while the system in (3.1) is a valid approximation of (2.1) in the averaging time limit (that is, on the $O(1)$ time scale), their corresponding homogenization time limits differ due to the difference in the velocity autocorrelations. Here we propose a more accurate modification of the simplified interaction system in (3.1), which is consistent with (2.1) in the homogenization time limit.

Let us first look at the following two rescaled systems:

\begin{equation}
\frac{dY}{dt} = V, \quad dV = \varepsilon Adt + d\mathcal{N}(t, Y, V),
\end{equation}

\begin{equation}
\frac{dY}{dt} = V, \quad dV = \varepsilon Adt + d\mathcal{N}_s(t, Y, V).
\end{equation}

Observe that these two processes are the analogs of (2.6), except that the time scale of $\mathcal{N}$ and $\mathcal{N}_s$ was not accelerated, but rather the one of the external acceleration $A$ was slowed down instead. Let $\tau_\varepsilon$ refer to the decorrelation time of (3.2a), and let $\tau_{s,\varepsilon}$ be the same for (3.2b). The temperature $\theta_\varepsilon$ and the averaged acceleration $\bar{A}_\varepsilon$ will refer to the simplified system in (3.2b). Clearly, with $\varepsilon$ set to zero we arrive to the limiting quantities $\theta_0$ and $\tau_0$ of the previous section for both realistic and simplified systems; on the other hand, setting $\varepsilon = 1$ yields the corresponding temperature and decorrelation times of (2.1) and (3.1) (and in this case we drop the subscript, that is, $\theta_1 = \theta$, $\bar{A}_1 = \bar{A}$, $\tau_1 = \tau$, and $\tau_{s,1} = \tau_s$).

Now, consider the following Itô stochastic differential equation, which is also based on the simplified fast interaction operator $\mathcal{N}_s$:

\begin{equation}
\text{d}X = (V + \theta \nabla_X (\tau - \tau_s) + (\tau - \tau_s)\bar{A})dt + \sqrt{2\theta(\tau - \tau_s)d\mathcal{W}(t)},
\end{equation}

\begin{equation}
\text{d}V = Adt + d\mathcal{N}_s(t, X, V),
\end{equation}

where $\mathcal{W}(t)$ is a $KN$-dimensional Wiener process, while $\theta$, $\bar{A}$, $\tau$ and $\tau_s$ are those of (3.2a) and (3.2b), with $\varepsilon = 1$ as described above. We are now going to show that, when rescaled in the same manner as above in (2.6), the system in (3.3) has the same homogenization
limit as the one in the realistic system (2.1), despite the fact that the interactions of particles are governed by the simplified process $\mathcal{N}_s$, rather than by the realistic process $\mathcal{N}$. Indeed, with the same rescaling as in (2.6), we have

\begin{equation}
(3.4a) \quad dX = \left( V + \epsilon \theta \nabla_X (\tau_\epsilon - \tau_{s,\epsilon}) + \epsilon (\tau_\epsilon - \tau_{s,\epsilon}) A_\epsilon \right) dt + \sqrt{2 \epsilon t \epsilon} (\tau_\epsilon - \tau_{s,\epsilon}) dW(t),
\end{equation}

\begin{equation}
(3.4b) \quad dY = \left( \frac{1}{\epsilon} V + \epsilon \nabla_Y (\tau_\epsilon - \tau_{s,\epsilon}) + (\tau_\epsilon - \tau_{s,\epsilon}) A_\epsilon \right) dt + \sqrt{2 \epsilon t \epsilon} (\tau_\epsilon - \tau_{s,\epsilon}) dW(t),
\end{equation}

\begin{equation}
(3.4c) \quad dV = A dt + d\mathcal{N}_s(t/\epsilon, Y, V).
\end{equation}

Observe that the velocity autocorrelation times of $\mathcal{N}(t/\epsilon)$ and $\mathcal{N}_s(t/\epsilon)$ scale as $O(\epsilon)$, which necessitates multiplying both $\tau_\epsilon$ and $\tau_{s,\epsilon}$ by $\epsilon$ above. Taking into account (2.15), for the corresponding Kolmogorov equation we have

\begin{equation}
(3.5) \quad \frac{\epsilon}{t} \frac{dF}{dt} + V \cdot \nabla_X F + \nabla_Y \cdot (AF) - \epsilon \nabla_X \cdot ((\tau_\epsilon - \tau_{s,\epsilon}) (\nabla_X (\theta F) - A_\epsilon F)) - \nabla_Y \cdot ((\tau_\epsilon - \tau_{s,\epsilon}) (\nabla_Y (\theta F) - A_\epsilon F)) = \frac{1}{\epsilon} L_s^* F.
\end{equation}

This yields, in the corresponding orders of $\epsilon$,

\begin{equation}
(3.6a) \quad L_s^* F_0 = 0,
\end{equation}

\begin{equation}
(3.6b) \quad L_s^* F_1 = V \cdot \nabla_X F_0 + \nabla_Y \cdot (AF_0) - \nabla_Y \cdot ((\tau_0 - \tau_{s,0}) (\nabla_Y (\theta F_0) - A_0 F_0)),
\end{equation}

\begin{equation}
(3.6c) \quad \frac{dF_0}{dt} + V \cdot \nabla_X F_0 + \nabla_Y \cdot (AF_1) - \nabla_Y \cdot ((\tau_0 - \tau_{s,0}) (\nabla_Y (\theta F_0) - A_0 F_0)) - \nabla_Y \cdot ((\tau_0 - \tau_{s,0}) (\nabla_Y (\theta F_1) - A_0 F_1)) = L_s^* F_2.
\end{equation}

This leads to $F_0$ having the same meaning as before (a uniform invariant measure in $Y$ and on the constant momentum/energy sphere of $V$), which means that the $Y$-derivative of $F_0$ (and, therefore, $\theta_0$ and $\tau_0 - \tau_{s,0}$) is zero, which sets the second identity above to

\begin{equation}
(3.7) \quad L_s^* F_1 = V \cdot \nabla_X F_0 + \nabla_Y \cdot (AF_0).
\end{equation}

As before, integrating the third equation in $dY dV$ yields

\begin{equation}
(3.8) \quad \frac{dF_0}{dt} + \int V \cdot \nabla_X F_1 dY dV - \nabla_X \cdot ((\tau_0 - \tau_{s,0}) (\nabla_X (\theta F_0) - A_0 F_0)) = 0.
\end{equation}

Comparing the above equation with what was derived in the previous section, it becomes clear that, under the same assumptions, the integral above is given by

\begin{equation}
(3.9) \quad \int V \cdot \nabla_X F_1 dY dV = -\nabla_X (\tau_{s,0} (\nabla_X (F_0 \theta_0) - A_0 F_0)).
\end{equation}

Substituting (3.9) into (3.8), we arrive at

\begin{equation}
(3.10) \quad \frac{dF_0}{dt} = \nabla_X (\tau_0 (\nabla_X (\theta_0 F_0) - A_0 F_0)),
\end{equation}

where we remember that the non-lagged long-term statistics of $\mathcal{N}$ and $\mathcal{N}_s$ are identical due to their identical invariant measures.
4. The pairwise random interaction operator and the Boltzmann equation

In [1], we found that the Boltzmann equation can be obtained directly from a pairwise random interaction operator which preserves the momentum and energy of interactions of each pair of molecules. Here we briefly recall its derivation and show how the Boltzmann equation can be obtained, together with the corresponding fluid dynamics equations. Note that the molecules of a real gas do not interact in this manner. The reason why we consider such an operator is that for a realistic interaction (i.e. via the Lennard-Jones potential [30]) the subsequent formal derivation of the Boltzmann equation is not readily available, and thus we have to resort to a simplification.

Let the simplified molecular interaction process in (3.2b) with $\epsilon = 0$ be given by the velocity random jump generator $L_s$ of the following form:

$$L_s\psi = V \cdot \nabla X \psi + \int G(X', V'|X, V)(\psi(X', V') - \psi(X, V))dX'dV',$$

where the form of the conditional probability $G$ for the random jump process $N_s$ is to be specified below. This simplified process is known as the Lévy-type Feller process [4], and the form of its generator above is established by Courrège's theorem [13]. Despite its simplicity, the random jump generator in (4.1) can statistically describe a wide variety of molecular deflections via an appropriate choice of the conditional probability $G$.

In what follows, $G$ is chosen to be such that the jumps, generated by it, are reversible (that is, $G(X', V'|X, V) = G(X, V|X', V')$). Thus, the approximate system in (3.3) together with the generator in (4.1) yields the following Kolmogorov equation:

$$\frac{\partial F}{\partial t} + V \cdot \nabla X F + \nabla V \cdot (AF) = \nabla X \cdot ((\tau - \tau_s)(\nabla X (\theta F) - \bar{A}F)) +$$

$$+ \int G(X', V'|X, V)(F(X', V') - F(X, V))dX'dV'.$$

Next, following [1], we specify $G$ in the form of pairwise random interactions of all particles, under the condition that the coordinates (both translational and rotational) of all molecules do not change during the jump:

$$G(X', V'|X, V) = \frac{6}{\pi \sigma^3 V_{rot}}\delta(X' - X) \cdot$$

$$\sum_{i=1, \ldots, K-1 \atop j=i+1, \ldots, K} \left( g(v'_i, v'_j|v_i, v_j) \chi_\sigma \left( \|x_i^3 - x_j^3\| \right) \prod_{k \neq i \atop k \neq j} \delta(v'_k - v_k) \right).$$

Above, $x_i^3$ denotes the 3-dimensional translational coordinate vector of $i$-th molecule, and $\chi_\sigma$ is the following indicator function:

$$\chi_\sigma(x) = \begin{cases} 1, & 0 \leq x \leq \sigma, \\ 0, & x > \sigma. \end{cases}$$

As we can see, each $i,j$-pair of particles is permitted to interact via a two-particle conditional jump measure $g$ (which is to be prescribed below) whenever the 3-dimensional translational distance between them is within $\sigma$, and when they do, all other particles
(enumerated via \( k \)) retain their original velocities. Thus, the interaction range parameter \( \sigma \) can be interpreted as a diameter of a gas molecule. The reciprocal of the volume of the ball of diameter \( \sigma \) is included in the constant normalization factor of \( G \). The rotational components of \( x_i \) are not used at all in the simplified interaction model, and the reciprocal of the volume \( V_{\text{rot}} \) of the space of the rotational coordinates of a single molecule is also included in the constant normalization factor of \( G \). In addition to that, we will assume that the velocity decorrelation time \( \tau \) of the real gas also does not depend, to any non-negligible extent, on the rotational components of \( X \), and thus we can restrict ourselves to the solutions \( F \) of (4.2) which do not depend on any rotational components of \( X \). For now, however, we will proceed with the full \( N \)-dimensional notations for the coordinate vectors, while keeping in mind that the rotational components of the coordinate vectors are not really present (that is, all their spatial derivatives are zero, while the integrals can be factored out as constants).

At this point, we are ready to formally derive the Boltzmann equation. First, we assume that \( F \) is invariant under an arbitrary particle re-enumeration (that is, the particles are statistically indistinguishable). Second, let us denote the marginals

\[
f^{(2)} = \int F \, dx_3 \ldots dx_K \, dv_3 \ldots dv_K, \quad f = \int f^{(2)} \, dx_2 \, dv_2.
\]

Then, integrating (4.2) over all particles but one, we obtain

\[
\frac{\partial f}{\partial t} + v \cdot \nabla_x f + \nabla_v \cdot (af) = \nabla_x \cdot \left( (\tau - \tau_s) (\nabla_x (\theta f) - \bar{a} f) \right) +
\]

\[
+ (K - 1) \frac{6}{\pi \sigma^3} \int g(v', w' | v, w) \chi_\sigma \left( \| x^3 - y^3 \| \right) \times
\]

\[
\times \left( f^{(2)}(x, v', y, w') - f^{(2)}(x, v, y, w) \right) \, dv' \, dw' \, dy^3 \, dw,
\]

where \( V_{\text{rot}} \) was cancelled due to the integration over the rotational coordinates. Also, \( a \) is the acceleration vector (which, as we agreed above, contains only translational nonzero components) acting on a particle at the location \( x \) and moving with the velocity \( v \), while \( \bar{a} \) is its respective average over the invariant measure of the fast interaction process.

We now assume that the variations of \( F \) are negligible on the scale of the interaction range \( \sigma \), so that the integration over \( y^3 \) can be replaced by multiplication by the volume of a 3-dimensional ball of diameter \( \sigma \), which simplifies the equation above to

\[
\frac{\partial f}{\partial t} + v \cdot \nabla_x f + \nabla_v \cdot (af) = \nabla_x \cdot \left( (\tau - \tau_s) (\nabla_x (\theta f) - \bar{a} f) \right) +
\]

\[
+ (K - 1) \int g(v', w' | v, w) \left( f^{(2)}(v', w') - f^{(2)}(v, w) \right) \, dv' \, dw' \, dw.
\]

At this point, a standard argument is to assume that \( f^{(2)}(v, w) \) approximately factorizes into the product \( f(v) f(w) \),

\[
f^{(2)}(v, w) \approx f(v) f(w),
\]
which yields

\[
\frac{\partial f}{\partial t} + v \cdot \nabla_x f + \nabla_v \cdot (af) = \nabla_x \cdot (\tau - \tau_s) (\nabla_x (\theta f) - \bar{a} f) + \\
+ (K-1) \int g(v', w'|v, w) \left( f(v')f(w') - f(v)f(w) \right) dv' dw' dw.
\]

By construction, the density \( f \) is the single-molecule marginal of the full probability density \( F \), and thus is normalized to one. However, in order to obtain the standard gas dynamics equations, it is necessary for the full integral of \( f \) over the velocities and coordinates to yield the total mass of the system of molecules. Thus, denoting by \( m \) the mass of a single molecule, we renormalize \( f \) by the total mass \( Km \) of the system as

\[
f \rightarrow Km f.
\]

In order to replace the renormalized density in the Boltzmann equation, we need to include the factor \((Km)^{-1}\) in front of the collision term, since the latter is quadratic in \( f \). As a result, we arrive at the following general form of the Boltzmann equation:

\[
\frac{\partial f}{\partial t} + v \cdot \nabla_x f + \nabla_v \cdot (af) = \nabla_x \cdot (\tau - \tau_s) (\nabla_x (\theta f) - \bar{a} f) + \\
+ \frac{K-1}{Km} \int g(v', w'|v, w) \left( f(v')f(w') - f(v)f(w) \right) dv' dw' dw.
\]

Note that at this stage the momentum and energy conservation laws are yet to be taken into account, by imposing appropriate constraints on the conditional jump measure \( g \).

In order to prescribe \( g \), we need to recall that the interactions between two particles must preserve their momentum and energy, that is, the following identities should be in effect:

\[
v'_i + v'_j = v_i + v_j, \quad \|v'_i\|^2 + \|v'_j\|^2 = \|v_i\|^2 + \|v_j\|^2.
\]

Let us denote by \( n \) the unit vector pointing along the difference in outgoing velocities \( v' \) and \( w' \):

\[
n = \frac{v' - w'}{\|v' - w'\|}.
\]

Now, observe that the momentum and energy conservation constraints in (4.12) imply the following relations between the incident and outgoing pairs of velocities:

\[
v' = \frac{v + w}{2} + \frac{\|v - w\|}{2} n, \quad w' = \frac{v + w}{2} - \frac{\|v - w\|}{2} n.
\]

For realistic particles which move deterministically, the vector \( n \) is obviously not arbitrary and depends on how the particles are positioned with respect to each other prior to the interaction. However, in our artificial random jump generator above, the direction \( n \) is a random parameter, since \( g \) does not have any information about the coordinates of the interacting particles. In addition, observe that under the momentum and energy conservation constraints, the norm of the difference \( \|v - w\| \) is an invariant,

\[
\|v' - w'\| = \|v - w\|,
\]
and thus the integration over $d\nu' dw'$ is equivalent to the integration over $|v - w| dn$:

\[(4.16)\]

\[
\frac{K - 1}{K} g(v', w'|v, w) d\nu' dw' \sim \sigma^2 b(v', w'|v, w) |v - w| dn.
\]

Above, $\sigma^2$ is the collision cross section, and the interaction kernel $b$ specifies the random distribution properties of particle scattering within the limits permitted by the momentum and energy conservation constraints in (4.12). Also, we discard the ratio $(K - 1)/K$, since it approaches 1 in the case of many molecules. As a result, we finally arrive at the diffusive Boltzmann equation \[(1)\]:

\[(4.17a)\]

\[
\frac{\partial f}{\partial t} + v \cdot \nabla_x f + \nabla_v \cdot (af) = C(f) + \nabla_x \cdot (\langle \tau - \tau_s \rangle (\nabla_x (\theta f) - \bar{a} f)),
\]

\[(4.17b)\]

\[
C(f) = \frac{\sigma^2}{m} \int b(v', w'|v, w) |v - w| (f(v')f(w') - f(v)f(w)) d\nu' dw,
\]

where $v'$ and $w'$ are the functions of $v$, $w$ and $n$, given in (4.14). Note that the collision operator $C(f)$ in general employs the full $N$-dimensional velocity vectors, with both translational and rotational components (only the rotational components of the coordinate vectors are discarded in the presented random collision model). Further simplifications of (4.17b) can potentially be made for particular applications (for example, the computation of the theoretical diffusion coefficient of a random deflection model does not require the rotational components of the velocity deflection angle \[(23)\]), however, such direct computations are beyond the scope of the present work.

There is a variety of choices for $b$ \[(10–12)\]. In the simplest case of monatomic molecules ($N = 3$) it can be assumed that particles statistically deflect from each other as if they were hard spheres of diameter $\sigma$. Then, $b$ depends only on the angle $\phi$ between the directions of differences in incoming and outgoing velocities. This case is very well studied in the literature (see, for example, \[(10, 11, 18, 19)\] and references therein). In more elaborate deflection models \[(12, 23, 24)\], such as those employing the Lennard-Jones potential \[(30)\], the interaction kernel $b$ also takes into account the relative speed $|v - w|$ of the colliding molecules, in addition to the deflection angle. Note that these forms of $b$ are automatically consistent with the reversibility condition which we imposed earlier on $G$.

At this point, we have to use the single-particle distribution $f$ to express $\theta$ and $\tau$, rather than the full distribution $F$. However, it is fairly straightforward under the previous assumption of statistical identity of the particles. First, let us denote the density $\rho$, normalized distribution $\tilde{f}$, and its moment $\langle \psi \rangle$, for a suitable $\psi(v)$, as

\[(4.18)\]

\[
\rho = \int f dv, \quad \tilde{f} = \frac{f}{\rho}, \quad \langle \psi \rangle = \int \psi \tilde{f} dv,
\]

respectively. Then, we express the average acceleration $\bar{a}$ and velocity $u$ as

\[(4.19)\]

\[
\bar{a} = \langle a \rangle, \quad u = \langle v \rangle,
\]
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where the latter is, by assumption, the same for (2.1) and (3.1), since those are presumed to be identical in the averaging time limit. With this, we express \( \theta \) and \( \tau \) as

\[
\theta = \frac{1}{N} \langle \| v - u \|^2 \rangle, \quad \tau = \frac{1}{N \theta} \int_0^\infty \langle (E v(s) - u) \cdot (v(0) - u) \rangle \, ds.
\]

Now let us recall that the conventional \( \rho \)-weighted diffusion coefficient \( D \) is given by

\[
D = \frac{1}{N} \int_0^\infty ds \int (E v(s) - u) \cdot (v(0) - u) f \, dv = \rho \theta \tau.
\]

Denoting the pressure \( p \) as the product of the density and temperature,

\[
p = \rho \theta,
\]

we can express the decorrelation time \( \tau \) as

\[
\tau = \frac{D}{p}, \quad \tau_s = \frac{D_s}{p},
\]

where the pressures of the realistic and simplified systems are presumed to be identical due to \( p \) being the product of non-lagged statistical quantities \( \rho \) and \( \theta \). Also, for convenience, we follow the notations in [1] and denote the difference between \( D \) and \( D_s \) as a corrective diffusion coefficient \( D_\alpha \):

\[
D_\alpha = D - D_s.
\]

In what is to follow, we show that \( D_\alpha \) is proportional to the diffusion coefficient \( D \) of the realistic gas interaction process \( N \) of (2.1), that is,

\[
D_\alpha = \alpha D, \quad \alpha = \frac{D - D_s}{D} > 0.
\]

In [1] and [3], the diffusion coefficient \( D_\alpha \) (and, therefore, the proportionality coefficient \( \alpha \)) were set empirically via numerical simulations. In what is to follow, we compute the formulas for the estimates of \( \alpha \) and \( D_\alpha \) based on the known properties of the system. Finally, the Boltzmann equation can be written via \( D_\alpha \) as

\[
\frac{\partial f}{\partial t} + v \cdot \nabla_x f + \nabla_v \cdot (af) = C(f) + \nabla_x \cdot (D_\alpha \nabla_x \tilde{f}) + \nabla_x \cdot \left( \frac{D_\alpha}{p} (\nabla_x p - \rho \langle a \rangle) \tilde{f} \right).
\]

Observe that the expression \( \nabla_x p - \rho \langle a \rangle \) in the right-hand side above is zero when the hydrostatic balance is achieved.

In what follows, we recognize the fact that the previously estimated values of the diffusion coefficient for different gases, either in the case of the relatively simple hard sphere collision model \([10,11,18,19]\), or in the case of the more sophisticated Lennard-Jones random deflection model \([12,23,24]\), are all based on the general collision operator of the form (4.17b), which in the presented theory corresponds to the simplified random gas process \( N_s \). Because of this fact, there is no need for us to carry out any additional computations to estimate the corrective diffusion coefficient \( D_\alpha \) for gases which were already studied in the aforementioned works; the theoretical values of the diffusion coefficient \( D_s \) for a given simplified random deflection model can be found in \([12,23,24]\), whereas the values of the diffusion coefficient \( D \) of the corresponding real gas can be
looked up in the works where the direct laboratory measurements have been completed, such as [25, 39].

5. The Euler equations

For a suitable $\psi(v)$, let us denote its collision moment as

\[(5.1) \quad \langle \psi \rangle_{C(f)} = \int \psi C(f) dv.\]

Then, integrating the Boltzmann equation in (4.26) against $\psi dv$, we obtain

\[(5.2) \quad \frac{\partial (\rho \langle \psi \rangle)}{\partial t} + \nabla \cdot (\rho \langle \psi v \rangle) = \rho \langle (a \cdot \nabla) \psi \rangle + \langle \psi \rangle_{C(f)} +
\]

\[+ \nabla \cdot (D_a \nabla \langle \psi \rangle) + \nabla \cdot \left( \frac{D_a}{p} (\nabla p - \rho \langle a \rangle) \langle \psi \rangle \right),\]

where we integrated the term with the external acceleration $a$ by parts. In what follows, we will for simplicity assume that $a$ does not depend on the particle velocity $v$, that is,

\[(5.3) \quad a = a(x), \quad \langle a \rangle = a, \quad \langle (a \cdot \nabla) \psi \rangle = a \cdot \langle \nabla \psi \rangle.\]

If necessary, what is presented below can be recalculated for a $v$-dependent $a$.

Observe that, due to mass, momentum and energy conservation, the following collision moments are zero:

\[(5.4) \quad \langle 1 \rangle_{C(f)} = 0, \quad \langle v \rangle_{C(f)} = 0, \quad \langle \|v\|^2 \rangle_{C(f)} = 0.\]

Denoting the energy

\[(5.5) \quad E = \frac{1}{2} \langle \|v\|^2 \rangle = \frac{1}{2} (\|u\|^2 + N\theta),\]

we obtain, correspondingly, the mass, momentum and energy transport equations:

\[(5.6a) \quad \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = \nabla \cdot \left( \frac{D_a}{p} (\nabla p - \rho a) \right),\]

\[+ \nabla \cdot (\rho \langle vv^T \rangle) = \rho a + \nabla \cdot (D_a \nabla u) + \nabla \cdot \left( \frac{D_a}{p} (\nabla p - \rho a) u^T \right),\]

\[(5.6c) \quad \frac{\partial (\rho E)}{\partial t} + \frac{1}{2} \nabla \cdot (\rho \langle \|v\|^2 v \rangle) = \rho u \cdot a + \nabla \cdot (D_a \nabla E) + \nabla \cdot \left( \frac{D_a}{p} (\nabla p - \rho a) E \right).\]

The higher-order moments in the advection terms can be expressed as

\[(5.7) \quad \langle vv^T \rangle = uu^T + T, \quad \frac{1}{2} \langle \|v\|^2 v \rangle = Eu + Tu + q,\]

where the temperature tensor $T$ and heat flux $q$ are given by the velocity-centered moments

\[(5.8) \quad T = \langle (v - u)(v - u)^T \rangle, \quad q = \frac{1}{2} \langle \|v - u\|^2 (v - u) \rangle.\]
In the conventional Euler equations \([5.18]\), \(T\) and \(q\) are set to

\[
T_E = \theta I, \quad q_E = 0,
\]

and thus the equations in \((5.6)\) become fully closed with respect to \(\rho, u\) and \(E\). In the current set-up, however, the identities in \((5.9)\) require a suitable justification, which, in turn, should be based on the properties of the simplified interaction process \(N'_s\).

Let us, for convenience, denote the stress \(S\) as the difference between \(T\) and \(\theta I\):

\[
S = T - \theta I, \quad S_E = 0,
\]

where the second identity follows immediately from \((5.9)\). Observe that for \(\varepsilon = 0\) the solution of \((3.2b)\) should eventually settle at the uniformly distributed dynamics on the constant momentum-energy sphere due to strong mixing. Clearly, when the dimension of the sphere is large enough (so that the single-particle marginal distributions are Gaussian \([1]\)), both the stress \(S\) in \((5.10)\) and heat flux \(q\) in \((5.8)\) become zero. At the same time, the rate at which \(S\) and \(q\) approach zero is determined by the rate of interactions in the simplified process \(N'_s\) (the more interactions occur per unit of time, the faster \(S\) and \(q\) approach zero). Thus, a consistent way in the present framework to set \(S\) and \(q\) of the approximate fast interaction process \(N'_s\) in \((3.3)\) much closer to zero than their realistic counterparts of \(N\) is to “accelerate” \(N'_s\) by the time rescaling \(N'_s(t) \rightarrow N'_s(t/\delta)\) for some constant \(0 < \delta \ll 1\). In this case, by adjusting \(\delta\), the stress \(S\) and heat flux \(q\) of \((3.3)\) can be damped to zero as fast as necessary, so that one would be able to discard them in comparison with the realistic stress and heat flux of \((2.1)\).

However, the same time rescaling of \(N'_s\) also scales its corresponding diffusion coefficient \(D_s\) by the same constant parameter \(\delta\) as above, as \(D_s\) is given by the correlation time integral \((4.21)\). In this situation, the diffusion coefficient \(D_s\) of the simplified process \(N'_s\) should also become negligible in comparison with the realistic diffusion coefficient \(D\). Therefore, the following identities follow from \((4.24)\) and \((4.25)\) for the Euler equations:

\[
\alpha = \frac{D - D_s}{D} = 1, \quad \text{or} \quad D_\alpha = D.
\]

Thus, the Euler equations assume the form

\[
\begin{align*}
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) &= \nabla \cdot \left( \frac{D}{p} \left( \nabla p - \rho a \right) \right), \\
\frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho uu^T + \theta I) &= \rho a + \nabla \cdot (D \nabla u) + \nabla \cdot \left( \frac{D}{p} \left( \nabla p - \rho a \right) u^T \right), \\
\frac{\partial (\rho E)}{\partial t} + \nabla \cdot (\rho(E + \theta) u) &= \rho u \cdot a + \nabla \cdot (D \nabla E) + \nabla \cdot \left( \frac{D}{p} \left( \nabla p - \rho a \right) E \right).
\end{align*}
\]

Formally, the Euler equations above are derived for the full \(N\)-dimensional dynamics, which involve translational and rotational (if any) components of the average velocity vector \(u\). However, observe that the all components of \(u\) beyond translational can be discarded from the equations. Indeed, the rotational components of \(u\) never enter the advection terms due to the corresponding zero spatial derivatives, as \(f\) does not depend
on them. Also, they do not enter the external acceleration term because the corresponding components of \( \mathbf{a} \) are also zero. Thus, the Euler equations above in (5.12) remain valid if the average velocity vector \( \mathbf{u} \), the external acceleration vector \( \mathbf{a} \), and the spatial differentiation operator \( \nabla \) are all truncated to the first 3 translational components.

Observe that the additional diffusion terms, which are present in the right-hand side of (5.12) (and absent from the conventional Euler equations \([5,18]\)) are nonvanishing, since it is impossible for the diffusion coefficient \( D \) of a realistic gas to be zero as long as there is a free flight between consecutive molecular collisions (which is a requirement for a dilute gas \([10,11,19]\)). Thus, the conventional Euler equations \([5,18]\) do not appear to be a valid approximation for a realistic gas on a time scale longer than \( O(1) \), and the corrected equations in (5.12) should be used instead. In Tables 1 and 2 we show the measured diffusion coefficients for some gases.

6. The Navier-Stokes equations

Unlike the Euler equations above, the Navier-Stokes equations \([5,18]\) appear when the moment transport equations in (5.6) contain appropriately parameterized expressions for the stress \( \mathbf{S} \) and heat flux \( \mathbf{q} \), given by the Newton and Fourier laws:

\[
\begin{align*}
\mathbf{S}_{NS} &= \frac{\mu}{\rho} \left( \frac{2}{N} (\nabla \cdot \mathbf{u}) \mathbf{l} - \nabla \mathbf{u} - (\nabla \mathbf{u})^T \right), \\
\mathbf{q}_{NS} &= -\frac{N + 2 \mu}{2 \Pr} \nabla \theta.
\end{align*}
\]

Just as the Euler equations, the Navier-Stokes equations formally contain the velocity moments for all degrees of freedom, however, they can be restricted to the translational components of \( \mathbf{u} \), \( \mathbf{S} \) and \( \mathbf{q} \) using the same reasoning as for the Euler equations.

Above in (6.1), the parameter \( \Pr \) is the Prandtl number, and the coefficient \( \mu \) is the viscosity, given, in the absence of a long-range interaction potential and under the assumption of statistical equivalency of the velocity components, by the following correlation integral \([20,29,40]\):

\[
\mu = \frac{1}{\theta} \int_0^\infty ds \int \mathbb{E} \left[ (v(s) - u)(v'(s) - u') \right] (v(0) - u)(v'(0) - u') f dv.
\]

Here, \( v \) and \( v' \) are two different, but otherwise arbitrary, molecular velocity components, while \( u \) and \( u' \) are their respective averages. It is clear that a time-rescaling of the simplified interaction process \( \mathbf{N}_s \) adjusts both its diffusion coefficient \( D_s \) and its viscosity \( \mu_s \) by the same factor (since both are time autocorrelation functions). Recall that the Schmidt number \( Sc \) of a gas is given by the quotient of the viscosity \( \mu \) and the mass diffusion coefficient \( D \):

\[
Sc = \frac{\mu}{D}.
\]

Clearly, the Schmidt number \( Sc_s \) of the simplified interaction process \( \mathbf{N}_s \) is invariant under the time rescaling of the latter.

In what follows, we construct the Navier-Stokes equations by choosing the appropriate time rescaling for \( \mathbf{N}_s \) so that the viscosity of the simplified interaction process \( \mathbf{N}_s \)
matches that of \( \mathcal{N} \). The corrective diffusion coefficient \( D_\alpha \) is then chosen to simultaneously equalize the diffusion rates of the realistic and approximate gas systems. More precisely, let us assume that the activity of the collision kernel \( b \) in (4.16) is normalized so that \( \mu_s = \mu \), where the latter is the experimentally measured autocorrelation function (6.2) for a given real gas. Then, we can compute the corresponding diffusion coefficients, \( D_s \) and \( D \), by expressing them via the corresponding Schmidt numbers:

\[
D = \frac{\mu}{Sc}, \quad D_s = \frac{\mu}{Sc_s} = \frac{Sc}{Sc_s}D.
\]

Subsequently, from (4.24) and (4.25) we can express \( \alpha \) and \( D_\alpha \) as

\[
\alpha = \frac{D - D_s}{D} = 1 - \frac{Sc}{Sc_s}, \quad D_\alpha = \left(1 - \frac{Sc}{Sc_s}\right)D = \left(\frac{1}{Sc} - \frac{1}{Sc_s}\right)\mu.
\]

As we can see, the corrective diffusion coefficient \( D_\alpha \) is expressed via the viscosity of the real gas, and the Schmidt numbers of the real and simplified gas processes. The Schmidt number of a real gas can be determined as a quotient of the measured viscosity and mass diffusion coefficient, while the one of a simplified process \( \mathcal{N}_s \) can, in some cases, be evaluated from the properties of \( \mathcal{N}_s \). In particular, the Schmidt number of a random hard sphere deflection process has been computed explicitly \([12, 17, 22]\) under the same assumptions as were used above for the derivation of the Boltzmann equation in (4.26) (that is, statistical independence and identical distribution of molecules):

\[
Sc_{HS} = \frac{5}{6}.
\]

The diffusion properties and the corresponding Schmidt numbers of real gases are also an extensively studied subject, and the relevant data is readily available \([25, 32]\). In Table 1 we show the measured viscosity, Schmidt number, diffusion coefficient, and the corresponding coefficients \( \alpha_{HS} \) and \( D_{\alpha,HS} \) (the latter two computed from (6.5) and (6.6)) for neon, argon, krypton and xenon.
Table 2. The diffusive properties of some monatomic and polyatomic gases at 25°C (except for argon at 22°C) based on the Lennard-Jones potential [30] model. The data is taken from [23,24,39]. The units of the mass diffusion coefficient are [kg (m s)$^{-1}$]. The coefficient $\alpha_{LJ}$ and the corrective diffusion $D_{\alpha,LJ}$ are computed from (6.5).

| Gas | $D$ | $D_{LJ}/D$ | $\alpha_{LJ}$ | $D_{\alpha,LJ}$ |
|-----|-----|-------------|---------------|----------------|
| Ne  | $4.3 \cdot 10^{-5}$ | 0.977 | $2.33 \cdot 10^{-2}$ | $9.9 \cdot 10^{-7}$ |
| Ar  | $2.9 \cdot 10^{-5}$ | 0.989 | $1.11 \cdot 10^{-2}$ | $3.3 \cdot 10^{-7}$ |
| N$_2$ | $2.4 \cdot 10^{-5}$ | 0.958 | $4.25 \cdot 10^{-2}$ | $10^{-6}$ |
| O$_2$ | $3 \cdot 10^{-5}$ | 0.888 | 0.112 | $3.4 \cdot 10^{-6}$ |
| CO$_2$ | $2 \cdot 10^{-5}$ | 0.965 | $3.54 \cdot 10^{-2}$ | $7.2 \cdot 10^{-7}$ |
| CH$_4$ | $1.6 \cdot 10^{-5}$ | 0.895 | 0.104 | $1.6 \cdot 10^{-6}$ |

In the Lennard-Jones random deflection model (which was adapted for monatomic as well as polyatomic gases [23,24,39]), the collision parameters are also chosen so that the resulting model viscosity coefficients match the measured values, and thus we can estimate the corresponding coefficients $\alpha_{LJ}$ and $D_{\alpha,LJ}$ from the difference between the measured diffusion coefficient $D$ and its Lennard-Jones estimate $D_{LJ}$ via (6.5). In this case, both the theoretical estimated [23,24] and measured [39] diffusion coefficients are provided directly, and thus there is no need to express them via the viscosity and Schmidt numbers. We show the corresponding computed coefficients $\alpha_{LJ}$ and $D_{\alpha,LJ}$ in Table 2 for neon, argon, nitrogen, oxygen, carbon dioxide and methane. Observe that the Lennard-Jones coefficients $\alpha_{LJ}$ and $D_{\alpha,LJ}$ in Table 2 for neon and argon are much smaller than their hard sphere counterparts $\alpha_{HS}$ and $D_{\alpha,HS}$ in Table 1. This is likely due to the fact that the Lennard-Jones random deflection model for the monatomic gases is more accurate than the hard sphere random collision model, and subsequently necessitates a smaller diffusion correction.

Previously in [1,3], we used the following empirically chosen values of $D_{\alpha}$ for argon at normal conditions: $4 \cdot 10^{-6}$ in [1] (chosen to match the temperature profile of the DSMC [6,35] Couette flow for the Navier-Stokes equations), and $10^{-6}$ in [3] (chosen to match the velocity profile of the DSMC Poiseuille flow for the Navier-Stokes equations). Observe that, even though the Navier-Stokes equations were matched to a DSMC computation rather than the actual deterministic gas, those empirical values of $D_{\alpha}$ were not too far from the theoretical estimates of $2.4 \cdot 10^{-6}$ (hard sphere) and $3.3 \cdot 10^{-7}$ (Lennard-Jones) for argon that we show in Tables 1 and 2. For nitrogen, the Lennard-Jones value of $10^{-6}$ in Table 2 coincidentally matches our empirical choice in [3].

7. The Grad equations

The matching viscosity approximation in (6.5), used above for the Navier-Stokes equations, can be naturally extended onto the Grad [19,31] and regularized Grad [1,37] equations. The transport equations for the mass, momentum and energy in (5.6) are complemented by the additional transport equations for the stress and heat flux, which
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are derived by integrating the Boltzmann equation in (4.26) against the second and third velocity moments, and subtracting the transport equations for lower-order moments in appropriate combinations:

\[
\begin{align*}
(7.1a) \quad \frac{\partial (\rho S)}{\partial t} + \nabla \cdot (\rho (u \otimes S + Q)) + \left( P + P^T - \frac{2}{N} \text{tr}(P) I \right) &= -\frac{\rho p}{\mu} S + \nabla \cdot (D_\alpha \nabla \otimes S) + \nabla \cdot \left( \frac{D_\alpha}{p} (\nabla p - \rho a) \otimes S \right), \\
(7.1b) \quad \frac{\partial (\rho q)}{\partial t} + \nabla \cdot (\rho (u q T)) + \nabla \cdot (P^2 T^2 - T^2 \nabla \cdot P^2 - \nabla \cdot (\rho S^2) + \rho (\nabla u)^T q + \\
+ \frac{2}{N + 2} \rho \left[ \nabla u + (\nabla u)^T + (\nabla \cdot u) I \right] q + \rho Q : (\nabla u) + \nabla \cdot (\rho R) = \quad = -\rho p \frac{\rho p}{\mu} q + \nabla \cdot (D_\alpha \nabla q) + \nabla \cdot \left( \frac{D_\alpha}{p} (\nabla p - \rho a) q^T \right), 
\end{align*}
\]

where

\[
(7.2a) \quad P = \left( \rho T - D_\alpha (\nabla u)^T \right) \nabla u + \frac{2}{N + 2} \nabla (\rho q),
\]

\[
(7.2b) \quad T_2 = T + \frac{N}{2} \beta I, \quad P_2 = \rho T - 2D_\alpha \nabla u.
\]

Observe that the equations in (5.6) and (7.1) are not closed with respect to the matrix \( R \) and the 3-rank tensor \( Q \) above. Above, both the rank-3 tensor \( Q \) and the matrix \( R \) equal zero for the Grad equations [19,31], while for the regularized Grad equations [1,37] these are set to

\[
(7.3a) \quad Q_{\text{reg}} = \tilde{Q} + \tilde{Q}^T + \tilde{Q}^{TT},
\]

\[
(7.3b) \quad R_{\text{reg}} = \tilde{R} + \tilde{R}^T + \left( \tilde{R} - \frac{2}{N} \text{tr}(\tilde{R}) \right) I,
\]

where the notations \( \tilde{Q}, \tilde{R} \) and \( \tilde{R} \) read

\[
(7.4a) \quad \rho \tilde{Q} = -\frac{\mu}{\rho p} \left[ \nabla S - \frac{2}{N + 2} \beta I \right] - \frac{1}{p} \left( \nabla \cdot (\rho S) - \frac{2}{N + 2} \beta \right) \nabla \cdot (\rho S) \right) + \\
+ \frac{2}{(N + 2) \beta} \left( q \otimes \left( \nabla u + (\nabla u)^T \right) - \frac{2}{N + 2} \beta \right) \nabla \cdot \left( \nabla u + (\nabla u)^T + (\nabla \cdot u) I \right) q \right],
\]

\[
(7.4b) \quad \rho \tilde{R} = -\frac{2\mu}{\rho p} \left[ \frac{N + 2}{N} \beta \nabla \cdot \frac{\beta}{\theta} + \frac{2}{N} \left( \nabla \cdot q + S : (\nabla u) - \frac{1}{p} \beta \nabla \cdot (\rho S) \right) \right],
\]
(7.4c) $\rho \vec{R} = -\frac{\mu}{Pr^R} \left[ S \left( \nabla u + (\nabla u)^T \right) + \frac{N+4}{N+2} \left( \frac{\nabla (\theta q)}{\theta} - \frac{1}{p} \nabla \cdot (\rho S) q^T \right) - \left( \frac{2}{N} \nabla \cdot u + \frac{N+4}{2N\theta} \left( \frac{1}{\rho} \nabla \cdot (\rho q) + S : (\nabla u) \right) \right) S \right].$

Above, the constants $Pr^Q$, $Pr^R$ and $Pr^R$ are the third- and fourth-order moment Prandtl numbers, which, for a hard sphere collision approximation in the case of $N = 3$ [37], are equal to

(7.5) $Pr^Q_{HS} = \frac{3}{2}, \quad Pr^R_{HS} = \frac{2}{3}, \quad Pr^R_{HS} = \frac{7}{6}.$

As it seems, there are currently no estimates of $Pr^Q$, $Pr^R$ and $Pr^R$ for any other collision models, and, in particular, we used the hard sphere values above for nitrogen in [1, 3], which still provided reasonable accuracy of the results of numerical simulations. The value of the corrective diffusion coefficient $D_\alpha$ remains the same as before for the Navier-Stokes equations in (6.5), and thus the approximations from Tables 1 and 2 can be used for the listed gases.

8. Summary

Above we proposed a theory for the mass diffusion effect in gas transport equations, which is based on a diffusion correction for the dynamics of a simplified process of gas molecule interaction to match the realistic gas dynamics in the homogenization time scale limit [26, 27, 33, 38]. We computed the estimates of the corrective mass diffusion coefficient in the Euler, Navier-Stokes and Grad equations for neon, argon, krypton and xenon under the assumption that the corresponding simplified interaction model of the gas molecules is that of randomly colliding hard spheres, based on the experimental data from [25]. We also computed the estimates of the corrective mass diffusion coefficient for neon, argon, nitrogen, oxygen, carbon dioxide and methane for the Lennard-Jones random deflection model of simplified interactions, based on the theoretical estimates [23, 24] and experimental data [39]. We observed that the available experimental data seems to support the proposed theory, and that the empirical values of the corrective diffusion coefficient we used for argon and nitrogen in the preceding works [1, 3] were not too different from the corresponding theoretical estimates we computed above.

Note that the formula for the corrective diffusion coefficient, proposed above, is formally valid only when the Schmidt number of the realistic gas is smaller than that of the chosen simplified interaction process (otherwise, the diffusion term in the Boltzmann equation (4.26) becomes negative). This condition, in turn, requires that, for the same stress damping rate, the velocity time series of the real gas exhibit longer autocorrelation times than those of the simplified random interaction process. The available experimental data [39] suggests that this condition indeed holds for various gases, both monatomic and polyatomic, across a wide range of temperature values. However, we are not currently aware of a related theoretical result which indicates that the autocorrelation functions of a random jump process necessarily decay faster than those of a deterministic deflection process upon which the jump kernel is constructed, given that
their stress correlation functions decay at equal rate. It would be interesting to see if such result can be theoretically obtained, either in general, or at least for some particular examples of multimolecular deflection processes.

It is likely that a similar diffusion correction approach can also be adopted for more complicated particle dynamics, such as, for example, electrically charged (ionized) particles and plasma, where the long-range Coulomb interaction potential is present in addition to the Lennard-Jones potential. Observe that the proposed theory relies only on the measured diffusion coefficient and viscosity of a real particle system, and a suitable random kernel of the deflection approximation for a given potential, for which the integrals of relevant autocorrelation functions can be evaluated (even if approximately). Thus, a similar diffusion correction formalism could likely apply to the corresponding transport equations.

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