Review of the Original Derivation of the Boltzmann Equation and its Extension to an Infinite-Range Potential

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1. INTRODUCTION

Consider a gas and its behavior.

Molecular size is very small in a gas dynamic scale. There are very many molecules in a volume of the gas dynamic scale.

The Boltzmann equation is the equation that describes the behavior of the gas in the limit of the above parameters under the condition that the Knudsen number is kept constant in the limiting process. The understanding that the real perfect gas is well described by the Boltzmann equation because the parameter is so large is the underlying assumption.

Here, its derivation is reviewed by paying attention to the gas dynamic and molecular scales.

2. The LIMITING PROCESS

Gas dynamic and molecular scales of length, speed, and time

Gas dynamic scales:

$$L,\ \ (2RT_0)^{1/2},\ \ t_0\,[= L/(2RT_0)^{1/2}].$$

Molecular scales:

$$d_M,\ \ (2RT_0)^{1/2},\ \ t_{\mathrm{mol}}\,[= d_M/(2RT_0)^{1/2}],$$

where the velocity sizes are of the same in the two scales.

In a gas we are interested in,

$$d_M/L \ll 1, \quad t_{\mathrm{mol}}/t_0 \ll 1, \quad \tilde{N} \gg 1,$$

where $\tilde{N}$ is the time average over t_0 of the molecules in the volume L^3 in space.

The gas-dynamic variables are defined at a point in the gas dynamic scales. It is not a point in the molecular scales, but is some volume. Let its sizes of length, velocity, and time be

$$L_\delta,\ \xi_\delta,\ \text{and}\ t_\delta.$$

They have to be so small as to satisfy the request of precision, but the volume has to contain so many molecules that the gas-dynamic variables are defined with fluctuations small enough.

$$\begin{aligned}&L_\delta/L \ll 1, \qquad d_M/L_\delta \ll 1,\\ &\xi_\delta/(2RT_0)^{1/2} \ll 1,\\ &t_\delta/t_0 \ll 1 \qquad t_{\text{mol}}/t_\delta \ll 1.\end{aligned}$$

The sizes of different δ variables (length, velocity, and time) are related because the ambiguity of one variable introduces the ambiguity of another variable.* That is,

$$\frac{L_\delta}{L} = \frac{\xi_\delta}{(2RT_0)^{1/2}} = \frac{t_\delta}{t_0}, \qquad \frac{t_{\text{mol}}}{t_\delta} = \frac{d_M}{L_\delta} \ll 1.$$

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*An error L_δ or $t_\delta \Rightarrow$ the error of velocity $\xi_\delta = (2RT_0)^{1/2}(L_\delta/L)$.

The information in the δ-scale domain at $(\boldsymbol{X}, \boldsymbol{\xi}, t)$ or $(\boldsymbol{X}, t) \Rightarrow$ the local variables are defined.

N_δ: the number of molecules in a volume L_δ^3 around $\boldsymbol{X}$.$\Rightarrow$

The time average $\overline{N}_\delta / L_\delta^3$ over time t_δ of N_δ / L_δ^3 = the number density around $(\boldsymbol{X}, t)$. $\overline{N}_\delta \gg \infty$

$\mathcal{F}_\delta$: the number of molecules in a volume $L_\delta^3 \xi_\delta^3$ around $(\boldsymbol{X}, \boldsymbol{\xi})$ in space and molecular velocity, which is required large $\Rightarrow$

The time average $m\overline{F}_\delta / L_\delta^3 \xi_\delta^3$ over time t_δ of $m\mathcal{F}_\delta / L_\delta^3 \xi_\delta^3 (\overline{\mathcal{F}}_\delta \gg 1)$. = the velocity distribution function $\bar{f}_\delta$ at $(\boldsymbol{X}, \boldsymbol{\xi}, t)$.

$\Rightarrow$the other GD variables defined by $\bar{f}_\delta$.

In the following, we discuss the equation that describes the behavior of $m\overline{\mathcal{F}}_\delta/L_\delta^3\xi_\delta^3$ in the limit

$$L_\delta/L \to 0, \quad \xi_\delta/(2RT_0)^{1/2} \to 0, \quad t_\delta/t_0 \to 0,$$

$$d_M/L_\delta \to 0, \quad t_{\mathrm{mol}}/t_\delta \to 0, \quad \overline{N}_\delta \to \infty.$$

We add the condition that the Knudsen number is invariant in the limiting process,*

$$(\overline{N}_{\delta 0}/L_\delta^3)d_M^2 L = \overline{N}_{\delta 0}(d_M/L_\delta)^2(L/L_\delta) = C_L,$$

$$0 < C_L < \infty,$$

This limit will be called the gas-dynamic limit or the GD limit.

From the invariant Knudsen number condition, $\overline{N}_{\delta 0}$ is determined by L_δ/L and d_M/L. They are the independent limiting parameters.

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*$(\overline{N}_{\delta 0}/L_\delta^3)d_M^2 L$: the number of collision of a molecules when it moves over the distance L. Thus, $1/(\overline{N}_{\delta 0}/L_\delta^3)d_M^2\,(= L/C_L)$: mean free path ℓ, $1/(\overline{N}_{\delta 0}/L_\delta^3)d_M^2(2RT_0)^{1/2}\,[= L/C_L(2RT_0)^{1/2}]$: mean free time t_f, and $(\overline{N}_{\delta 0}/L_\delta^3)d_M^2 L$: the inverse of the Knudsen number. Then, $L_\delta/\ell = C_L L_\delta/L \ll 1$ and $t_\delta/t_f = C_L(t_\delta/t_0) \ll 1$,

In the GD limit,

$\overline{N}_\delta d_M^3/L_\delta^3 = \overline{N}_\delta (d_M/L_\delta)^3 \to 0$ (the perfect gas),

From the condition $\overline{N}_\delta \to \infty$,

$$(d_M/L)(L/L_\delta)^{3/2} \to 0.$$

The local gas dynamic variables in the GD limit are defined as, for example,

$$m\overline{\mathcal{F}}_\delta/L_\delta^3\xi_\delta^3 \to f(X_i, \xi_i, t), \quad m\overline{N}_\delta/L_\delta^3 \to \rho(X_i, t),$$

where f and ρ are the velocity distribution function and density of the gas.

Other relations of parameters:

The average distance D_{sp} between the neighboring molecules is the order of $L_\delta/N_\delta^{1/3}$. Thus,

$$D_{\text{sp}}/L_\delta \to 0.$$

From the perfect gas condition, $\overline{N}_\delta (d_M/L_\delta)^3 \to 0$,

$$d_M/D_{\text{sp}} \to 0.$$

Note on the sizes of d_M and the potential U:

The representative distance interacting between molecules for which the velocities of each molecule is subject to a finite change in a short time t_δ is taken d_M. Thus, we choose*

$$U(d_M) = 2\alpha_{\text{pot}} mRT_0.$$

Let the potential be given. Then, with a function $\tilde{U}(x)$ [$\tilde{U}(1)$] and a constant $\mathcal{U}_0$, the potential is expressed as

$$U(r) = m\mathcal{U}_0\tilde{U}(r/d_M).$$

where $\mathcal{U}_0 = 2\alpha_{\text{pot}}RT_0$. $\mathcal{U}_0/2RT_0$ is of the order of unity.

*The minimum distance d_{min} is given by

$$U(d_{\text{dim}}) = \frac{1}{4}m(\boldsymbol{\xi}_1 - \boldsymbol{\xi}_0)^2,$$

where m is the mass of a molecule.

3. OUTLINE OF THE DERIVATION OF THE LIMITING EQUATION FOR A FINITE-RANGE POTENTIAL

The velocity distribution function

$$f(\boldsymbol{X},\boldsymbol{\xi},t)=\lim_{\mathrm{GD}} m\overline{F}_\delta/L_\delta^3\xi_\delta^3,$$

The total mass of the molecules in $\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi}$

$$\mathrm{d}M=f\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi}.$$

Before the limit, $\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi}$ contains all $V_\delta(\boldsymbol{X},\boldsymbol{\xi})$.

$$\overline{N}_{\delta 0}=\overline{\mathcal{F}}_{\delta 0}[(2RT_0)^{1/2}/\xi_\delta]^3=\overline{\mathcal{F}}_{\delta 0}(L/L_\delta)^3.$$

$$\Rightarrow \overline{\mathcal{F}}_{\delta 0}=C_L(L_\delta/L)^4(L_\delta/d_M)^2.$$

$$\overline{\mathcal{F}}_{\delta 0}\to\infty\Rightarrow(d_M/L_\delta)/(L_\delta/L)^2\to 0.$$

$$\overline{\mathcal{F}}_{\delta 0}\to\infty\Rightarrow\overline{N}_{\delta 0}(L_\delta/L)^3\to\infty.$$

The motion of a molecule without interaction with the other molecules:

$$m\mathrm{d}\xi_i/\mathrm{d}t = mF_i, \quad \mathrm{d}X_i/\mathrm{d}t = \xi_i,$$

where mF_i is the external force with the intermolecular potential excluded.[*] The solution is expressed as

$$\boldsymbol{X}(t) = \boldsymbol{X}(t; \boldsymbol{X}_0, \boldsymbol{\xi}_0, t_0),\ \boldsymbol{\xi}(t) = \boldsymbol{\xi}(t; \boldsymbol{X}_0, \boldsymbol{\xi}_0, t_0),$$

$$(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_t = \left| \frac{D(\boldsymbol{X}, \boldsymbol{\xi})}{D(\boldsymbol{X}_0, \boldsymbol{\xi}_0)} \right| (\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_{t_0}.$$

$$(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_{t+\Delta t} = \left(1 + \frac{\partial F_i}{\partial \xi_i}\Delta t \right) (\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_t + o(\Delta t).$$

[*] More generally, the part of the intermolecular force that introduces a force with variation in the gas-dynamic scales is included in mF_i.

$$
\begin{aligned}
(\mathsf{d}M)_t &= f(\boldsymbol{X},\boldsymbol{\xi},t)(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_t,\\
(\mathsf{d}M)_{t+\Delta t} &= f(\boldsymbol{X}+\boldsymbol{\xi}\Delta t,\boldsymbol{\xi}+\boldsymbol{F}\Delta t,t+\Delta t)\\
&\quad\times\left(1+\frac{\partial F_i}{\partial \xi_i}\Delta t\right)(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_t+o(\Delta t)
\end{aligned}
$$

$$
\begin{aligned}
&(\mathsf{d}M)_{t+\mathsf{d}t}-(\mathsf{d}M)_t\\
&\quad=\left(\frac{\partial f}{\partial t}+\xi_i\frac{\partial f}{\partial X_i}+\frac{\partial F_i f}{\partial \xi_i}\right)\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi}\mathsf{d}t,
\end{aligned}
$$

If there is no interaction between molecules,

$$
\frac{\partial f}{\partial t}+\xi_i\frac{\partial f}{\partial X_i}+\frac{\partial F_i f}{\partial \xi_i}=0.
$$

⇒ Discussion of inter-molecular interaction along $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_t$

A) While traveling in the floating $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_\tau$ $(t \leq \tau < t + \mathrm{d}t)$, some molecule happens to come close to another, to interact with it, and their velocities are subject to changes of the order of $(2RT_0)^{1/2}$. The molecule in $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_\tau$ goes out immediately from $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_\tau$. $\Rightarrow$ The number (or total mass) of molecules in $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_t$ that will collide in $\mathrm{d}t =$ the number of the molecules that leave the floating $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_{t\to t+\mathrm{d}t}$ in $\mathrm{d}t$.

B) Two molecules with velocities $\boldsymbol{\xi}'$ and $\boldsymbol{\xi}'_*$ in $(\mathbf{d}\boldsymbol{X})_{t_*}$ happen to interact at $t_*(t \leq t_* < t + \mathrm{d}t)$ and to get the velocities $\boldsymbol{\xi}$ and $\boldsymbol{\xi}_*$, where $\boldsymbol{\xi}_*$ is not specified. Then, the first molecule enters $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_{t_*}$ and proceed to $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_{t+\mathrm{d}t}$.$\Rightarrow$ The number (or total mass) of molecules in $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_{t+\mathrm{d}t}$ that collided in the past $\mathrm{d}t =$ the number of molecules that enter the floating $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_{t\to t+\mathrm{d}t}$ in $\mathrm{d}t$.

For glancing weak interaction, the molecule $\boldsymbol{\xi}$ will not go out from $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_\tau$, but it is counted in B and canceled out. Thus, the net increase of mass in $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_{t\to t+\mathrm{d}t}$ by collision is given by the difference of B and A.

From the preceding discussion, the variation is given by

$$\frac{\partial f}{\partial t} + \xi_i \frac{\partial f}{\partial X_i} + \frac{\partial F_i f}{\partial \xi_i} = J_G - J_L.$$

where

$J_L \mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi}\mathrm{d}t$: the total mass of molecules in $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_t$ that will collide in time $\mathrm{d}t$, and

$J_G \mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi}\mathrm{d}t$: the total mass of molecules in $(\mathbf{d}\boldsymbol{X}\mathbf{d}\boldsymbol{\xi})_{t+\mathrm{d}t}$ that collided in the past time $\mathrm{d}t$.

For the correct evaluation of the variation of f, $J_G - J_L$ has to be evaluated as a combination so as to cancel the contributions of weak interactions in J_G and J_L.

The collision has to be considered at the level of molecular scale d_M. We are considering the molecules in V_δ, and count the collision among molecules in V_δ $[V_\delta(\boldsymbol{X},\boldsymbol{\xi}) = L_\delta^3 \xi_\delta^3]$.

$\mathcal{A}_n(\mathsf{X}_n, \boldsymbol{\xi}_n)$: the arrangement of molecules $(\mathsf{X}_m, \boldsymbol{\xi}_m)$'s in $L_\delta^3(\boldsymbol{X})$ around the molecule $(\mathsf{X}_n, \boldsymbol{\xi}_n)$ in $V_\delta(\boldsymbol{X}, \boldsymbol{\xi})$.

$\mathcal{C}[\mathcal{A}_n(\mathsf{X}_n, \boldsymbol{\xi}_n)]$: the rate of the collision of the molecule at $(\mathsf{X}_n, \boldsymbol{\xi}_n)$.

$$\mathcal{C}[\mathcal{A}_n(\mathsf{X}_n, \boldsymbol{\xi}_n)] \ \to \textstyle\sum_n \ \mathcal{C}[\mathcal{A}_n(\mathsf{X}_n, \boldsymbol{\xi}_n)]$$

$$\text{time average over } t_\delta \to \overline{\sum_n \mathcal{C}[\mathcal{A}_n(\mathsf{X}_n, \boldsymbol{\xi}_n)]}$$

the number of collisions of the molecules in $V_\delta(\boldsymbol{X}, \boldsymbol{\xi})$ that will occur in time dt (the desired result). No information of $\mathcal{A}_n(\mathsf{X}_n, \boldsymbol{\xi}_n)$ without the particle dynamics (molecular dynamics).

What is required here is the total number of collision of the molecules in V_δ in a short time dt. This can be carried out by changing the process of calculation.

$$\begin{aligned}\sum_n \mathcal{A}_n(\mathsf{X}_n &\to \mathsf{X}, \boldsymbol{\xi}_n) \to \overline{\sum_n \mathcal{A}_n(\mathsf{X}_n \to \mathsf{X}, \boldsymbol{\xi}_n)} \\ &\to \mathcal{C}[\overline{\sum_n \mathcal{A}_n(\mathsf{X}_n \to \mathsf{X}, \boldsymbol{\xi}_n)}]\end{aligned}$$

$$\widehat{\mathcal{A}}_\delta = \overline{\sum_n \mathcal{A}_n(\mathsf{X}_n \to \mathsf{X}, \boldsymbol{\xi}_n)}/\overline{\mathcal{F}}_\delta :$$

the average number of molecules around a molecule in $V_\delta(\boldsymbol{X}, \boldsymbol{\xi})$. Then,

$$\mathcal{C}[\overline{\sum_n \mathcal{A}_n(\mathsf{X}_n \to \mathsf{X}, \boldsymbol{\xi}_n)}] = \mathcal{C}[\widehat{\mathcal{A}}_\delta \overline{\mathcal{F}}_\delta].$$

$$m\widehat{\mathcal{A}}_\delta \to f^\diamond(\mathsf{X}_*, \boldsymbol{\xi}_*; \boldsymbol{X}, \boldsymbol{\xi}) \text{ (GD limit)}$$

$f^\diamond(\mathsf{X}_*, \boldsymbol{\xi}_*; \boldsymbol{X}, \boldsymbol{\xi})\mathrm{d}\mathsf{X}_*\mathrm{d}\boldsymbol{\xi}_*$ is the average total mass of molecules in $\mathrm{d}\mathsf{X}_*\mathrm{d}\boldsymbol{\xi}_*$ around a molecule at $(\mathsf{X}, \boldsymbol{\xi}_n)$.

(1) slowly varying assumption: $f^\diamond$ is independent of X_*.
(2) molecular chaos assumption: $f^\diamond$ is independent of $\boldsymbol{\xi}$.

$$\Rightarrow f^\diamond(\mathsf{X}_*, \boldsymbol{\xi}_*; \boldsymbol{X}, \boldsymbol{\xi}) = f(\boldsymbol{X}, \boldsymbol{\xi}_*).$$

$$J(f,f) =$$

$$\hat{d}_m^2 \frac{d_M^2}{2m} \int_{\text{all}\, \boldsymbol{e},\, \text{all}\, \boldsymbol{\xi}_*} |(\boldsymbol{\xi} - \boldsymbol{\xi}_*)\boldsymbol{e}|(f' f'_* - f f_*) \mathrm{d}\Omega(\boldsymbol{e}) \mathbf{d}\boldsymbol{\xi}_*,$$

$$\theta_c - \theta_e =$$

$$\hat{d}_m \sin\theta_e \int_{\hat{r}_c}^{\hat{d}_m} \hat{r}^{-2} \left(1 - \frac{4\mathcal{U}_0 \tilde{U}(\hat{r})}{(\boldsymbol{\xi}_* - \boldsymbol{\xi})^2} - \frac{\hat{d}_m^2 \sin^2\theta_e}{\hat{r}^2}\right)^{-\frac{1}{2}} \mathrm{d}\hat{r},$$

$$1 - \frac{4\mathcal{U}_0 \tilde{U}(\hat{r})}{(\boldsymbol{\xi}_* - \boldsymbol{\xi})^2} - \frac{\hat{d}_m^2 \sin^2\theta_e}{\hat{r}^2} = 0, \qquad \hat{d}_m = \frac{d_m}{d_M},$$

$$J(f,f) =$$

$$\frac{d_M^2}{m} \int_{\text{all}\, \boldsymbol{\xi}_*} \int_0^{2\pi} \int_0^{\hat{d}_m} |\boldsymbol{\xi}_* - \boldsymbol{\xi}|(f' f'_* - f f_*) \hat{b} \mathrm{d}\hat{b} \mathrm{d}\varphi \mathbf{d}\boldsymbol{\xi}_*.$$

$$\theta_c = \arcsin \frac{\hat{b}}{\hat{d}_m}$$

$$+\hat{b} \int_{\hat{r}_c}^{\hat{d}_m} \hat{r}^{-2} \left(1 - \frac{4\mathcal{U}_0 \tilde{U}(\hat{r})}{(\boldsymbol{\xi}_* - \boldsymbol{\xi})^2} - \frac{\hat{b}^2}{\hat{r}^2}\right)^{-1/2} \mathrm{d}\hat{r},$$

$$1 - \frac{4\mathcal{U}_0 \tilde{U}(\hat{r})}{(\boldsymbol{\xi}_* - \boldsymbol{\xi})^2} - \frac{\hat{b}^2}{\hat{r}^2} = 0, \qquad \hat{b} = \frac{b}{d_M}.$$

In the evaluation of J_L and J_G, the collision rate is obtained with the information of the state of the gas before collision. The J_G can also be obtained with the information of the state after collision under the molecular chaos assumption. Then, $J_G = J_L$, and the equation for f is reduced to

$$\frac{\partial f}{\partial t} + \xi_i \frac{\partial f}{\partial X_i} + \frac{\partial F_i f}{\partial \xi_i} = 0.$$

The molecules just collided are correlated. Thus, the molecular chaos assumption is not appropriate for the pair. After one mean free time, the majority of the molecules collided once. This does not mean that the molecular chaos state is destroyed. $\overline{N}_\delta$ molecules are in L_δ^3, and $\overline{N}_\delta(\overline{N}_\delta - 1)/2$ pairs molecules are there.⇒ Almost all the pairs have not collided or are not correlated. ⇒ For the next collision, the chaos assumption can be applied.⇒ Next Page

Molecular chaos assumption applies up to n mean free time, and thus the Boltzmann equation is valid to that time, where

$$\frac{\overline{N}_\delta}{\overline{N}_\delta(\overline{N}_\delta - 1)} \times n \ll 1,$$

It is no longer valid where

$\dfrac{N^*}{N^*(N^* - 1)} \times n$ is more than order of unity.

Effect of triple collision

The collision frequency of binary collision

$$O[C_L(2RT_0)^{1/2}/L].$$

When the density of the gas is doubled, the frequency of binary collision is doubled,[*] but the increase of the frequency of the triple collision is $C_L(d_M/L)$ times of that of binary collision. Thus, it is negligible.

[*] By the definition of C_L, it is doubled.

4. EQUATION FOR AN INFINITE-RANGE POTENTIAL

Infinite range potential $U(r)$ is expressed in the form

$$U(r) = m\mathcal{U}_0 \tilde{U}(r/d_M),$$

where $\tilde{U}(x)$ is assumed here to be bounded as

$$\left|\partial\tilde{U}(x)/\partial x\right| < C_{\tilde{U}} x^{-\alpha} \quad (\alpha > 3) \text{ for large } x.$$

The cutoff potential is defined by

$$\begin{aligned} U_{d_m}(r) &= U(r) \quad (r \leq d_m), \\ &= 0 \qquad\quad (r > d_m). \end{aligned}$$

Correspondingly,

$$\begin{aligned} \tilde{U}_{d_m}(x) &= \tilde{U}(x) \quad (x \leq d_m/d_M), \\ &= 0 \qquad\quad (x > d_m/d_M). \end{aligned}$$

With this $\tilde{U}_{d_m}(x)$,

$$U_{d_m}(r) = m\mathcal{U}_0 \tilde{U}_{d_m}(r/d_M).$$

Choose d_m in the following way:

$$\begin{aligned}&d_m/L_\delta \to 0, \quad d_M/d_m \to 0,\\ &\overline{N}_{\delta 0}(d_m/L_\delta)^3 \to 0, \text{ [or } d_m/D_{\text{sp}} \to 0].\end{aligned}$$

A gas of molecule of size d_m satisfies the perfect gas condition. The size d_m is to be consistent with the condition that the Knudsen number is invariant in the limiting process. For this, d_m/d_M has to satisfy the condition*

$$\left(\frac{d_m}{d_M}\right)\left(\frac{d_M}{L}\right)^{1/3} \to 0.$$

Take the above limit of the collision integral for a finite range potential U_{d_m}. After confirming that the contribution of grazing collision is negligible (J-C. Jiang, T-P.Liu, Y.S.), we have

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*$\overline{N}_{\delta 0}(d_m/L_\delta)^3 = C_L d_m^3/d_M^2 L = C_L(d_m/d_M)^3 d_M/L$.

$$(d_m/d_M)^3(d_M/L) \to 0.$$

Let $d_M/L_\delta = (L_\delta/L)^\beta$ and $(d_m/d_M) = (L/L_\delta)^\gamma$ ($\beta > 0$, $\gamma > 0$). Then, $\gamma < (\beta+1)/3$.

$$J(f,f) = \frac{d_M^2}{m} \int \int \int_0^\infty |\boldsymbol{\xi} - \boldsymbol{\xi}_*| (f' f'_* - f f_*) \widehat{b} \mathrm{d} \widehat{b} \mathrm{d} \varphi \mathrm{d} \boldsymbol{\xi}_*,$$

$$\theta_c = \int_0^{y_c} \frac{1}{\left(1 - \frac{4\mathcal{U}_0 \tilde{U}(\widehat{b}/y)}{(\boldsymbol{\xi} - \boldsymbol{\xi}_*)^2} - y^2\right)^{1/2}} \mathrm{d}y,$$

where y_c is the smallest solution of the equation

$$1 - \frac{4\mathcal{U}_0 \tilde{U}(\widehat{b}/y)}{(\boldsymbol{\xi} - \boldsymbol{\xi}_*)^2} - y^2 = 0.$$

The parameter d_M^2/m is rewritten as $C_L/\rho L$, and $(\boldsymbol{\xi} - \boldsymbol{\xi}_*)^2$ is of the order of $2RT_0$ for most of the pairs of molecules. Therefore, the parameters in θ_c (thus, $\boldsymbol{\xi}'$, $\boldsymbol{\xi}'_*$) is expressed with those in the gas dynamic scale.

The other contribution of the intermolecular force

Consider the interactions between molecules, one in a volume L_δ^3 and the others outside L_δ^3. Take a molecule at $\boldsymbol{X}(t)$ in L_δ^3. The force acting on it is

$$m\boldsymbol{F}^{L_\delta} = -\sum_{\boldsymbol{X}_0 \text{ with } r>L_\delta} \frac{\boldsymbol{X}-\boldsymbol{X}_0}{r}\frac{\partial U}{\partial r},$$

where $r = |\boldsymbol{X}-\boldsymbol{X}_0|$.

We consider the time average $m\overline{\boldsymbol{F}}^{L_\delta}$ over t_δ of the force $m\boldsymbol{F}^{L_\delta}$. The time average $\overline{N}_\delta/L_\delta^3$ of the number density of molecules in a volume L_δ^3 is assumed to be bounded as

$$\overline{N}_\delta/L_\delta^3 < C_\rho\left(\overline{N}_{\delta 0}/L_\delta^3\right),$$

over the whole space. Then, domain $r \geq L_\delta$ is subdivided into shells

$$L_\delta k \leq r < L_\delta(k+1) \quad (k = 1, 2, 3\cdots).$$

Note:

Time average is along the particle. The time average of the density

$$\overline{N}_{\delta}/L_{\delta}^{3} < C_{\rho}\left(\overline{N}_{\delta 0}/L_{\delta}^{3}\right),$$

is along the particle. In the gas-dynamic state, where the local variables can be defined, there is no need to pay attention to the difference.

From the contribution to the force in the shells, the force is bounded as

$$\begin{aligned}|\overline{\boldsymbol{F}}^{L_\delta}| &< \frac{4}{3}\pi C_{\tilde{U}} C_\rho \left(\frac{\overline{N}_\delta^3}{L_\delta^3}\right) \mathcal{U}_0 d_M^{\alpha-1} L_\delta^3 \\ &\qquad \times \sum_{k=1}^{\infty} \frac{[(k+1)^3 - k^3]}{(L_\delta k)^\alpha} \\ &= \frac{C_F \mathcal{U}_0 C_L}{L} \left(\frac{d_M}{L_\delta}\right)^{\alpha-3},\end{aligned}$$

where

$$C_F = \frac{4}{3}\pi C_{\tilde{U}} C_\rho \sum_{k=1}^{\infty} \frac{3k^2 + 3k + 1}{k^\alpha}.$$

The force $m\overline{\boldsymbol{F}}^{d_m}$ on the molecule at $\boldsymbol{X}$ by the molecules between $d_m < r < L_\delta$ is found to be bounded in similar way as

$$|\overline{\boldsymbol{F}}^{d_m}| < \frac{4}{3}\pi\frac{C_F\mathcal{U}_0C_L}{L}\left(\frac{d_M}{d_m}\right)^{\alpha-3}.$$

In this formula, the time average $\overline{N}_m/d_m^3$ of the number of molecules N_m in a volume d_m^3 is assumed to by bounded by $C_\rho\left(\overline{N}_{\delta 0}/L_\delta^3\right)$, i.e.,

$$\overline{N}_m/d_m^3 < C_\rho\left(\overline{N}_{\delta 0}/L_\delta^3\right).$$

This is a stronger condition than that on $\overline{N}_\delta/L_\delta^3$.

These forces are small. It takes infinite time in the gas dynamic time scale for the particle is subject to appreciable velocity change.

Discussion of the average of velocity change of the molecules in $V_\delta|_{t=0}$ for a finite time ⇒the velocity change of almost all molecules is negligible under a weaker condition⇒no contribution of $\overline{\boldsymbol{F}}^{d_m}$ to the limiting equation

Nondimensional form

$$\mathrm{Sh}\frac{\partial \widehat{f}}{\partial \widehat{t}}+\zeta_i\frac{\partial \widehat{f}}{\partial x_i}+\frac{\partial \widehat{F}_i\widehat{f}}{\partial \zeta_i}=\frac{1}{\tilde{k}}\widehat{J}(\widehat{f},\widehat{f}),$$

$$\widehat{J}(\widehat{f},\widehat{f})$$

$$=\int_{\mathrm{all}\,\boldsymbol{\zeta}_*}\int_0^{2\pi}\int_0^{\infty}|\boldsymbol{\zeta}_*-\boldsymbol{\zeta}|\Big(\widehat{f}'\widehat{f}'_*-\widehat{f}\widehat{f}_*\Big)\widehat{b}\mathrm{d}\widehat{b}\mathrm{d}\varphi\mathbf{d}\boldsymbol{\zeta}_*,$$

$$\left.\begin{array}{l} x_i=X_i/L,\quad \widehat{t}=t/t_0,\qquad \zeta_i=\xi_i/(2RT_0)^{1/2},\\ \widehat{f}=f/\rho_0(2RT_0)^{-3/2},\qquad \widehat{F}_i=F_i/(2RT_0/L),\\ \widehat{b}=b/d_M,\ \ (b:\ \text{impact parameter}). \end{array}\right\}$$

$$\left.\begin{array}{l} \mathrm{Sh}=L/t_0(2RT_0)^{1/2},\\ \tilde{k}=1/(\rho_0/m)d_M^2L=1/C_L. \end{array}\right\}$$

The parameter $\tilde{k}$ is expressed with d_M. The size d_M is appropriate to express the collision effect, irrespective of a finite or infinite-range potential, if the integral is convergent. The glancing collision is negligible, and only the head-on collision with its impact parameter b of the order of d_M contributes to the collision.

The effect of multiple collision for an infinite-range potential

The collision frequency of binary collision is determined by d_M as for a finite-range potential. The difference is the time of duration of interaction, which is of the order of $d_m/(2RT_0)^{1/2}$ in contrast to $d_M/(2RT_0)^{1/2}$ for a finite-range potential.

When the density of the gas is doubled, the collision frequency of the binary collision is doubled, but the increase of the frequency of the triple collision is $C_L(d_m/L)$ times of that of binary collision. Thus it is negligible.

5. EFFECT OF GRAVITATIONAL FORCE

The gravitational force acts between all the pairs of molecules. It is neglected in the Boltzmann equation. On the other hand, the collision integral of the Boltzmann equation diverges for the potential proportional to r^{-1}. This point is discussed.

Consider an infinite expanse of a gas where the density approaches the uniform state with the speed faster $1/|\boldsymbol{X}|$. First, take a gas consisting of hard-sphere molecules of diameter d_M. A molecule at $\boldsymbol{X}$ is subject to the gravitational force $m\boldsymbol{F}_G$

$$\begin{aligned} m\boldsymbol{F}_G &= -m^2 G \sum_{\boldsymbol{X}_0 \text{ with } r>d_M} \frac{(\boldsymbol{X}-\boldsymbol{X}_0)}{r^3}, \\ G &= 6.667384 \times 10^{-11} \mathrm{m}^3/\mathrm{kg\,s}^2, \end{aligned}$$

from another molecule at $\boldsymbol{X_0}$ when $|\boldsymbol{X_0} - \boldsymbol{X}| > d_M$.

The time average $m\overline{\boldsymbol{F}}_{G1}$ of the force on $\boldsymbol{X}$ by the molecules in $d_M < r < L_\delta$ can be obtained in similar way to the case $\alpha > 3$:

$$\begin{aligned} |\overline{\boldsymbol{F}}_{G1}| &< \frac{4}{3}\pi m G C_\rho \left(\frac{\overline{N}_{\delta 0}}{L_\delta^3}\right) \\ &\quad \times \sum_{k=1}^{[L_\delta/d_M]_{\mathrm{I}}} \frac{d_M^3[(k+1)^3 - k^3]}{(d_M k)^2} \\ &= C_{G1} C_\rho \rho_0 G L \left(\frac{L_\delta}{L}\right), \end{aligned}$$

where C_{G1} is chosen so as to satisfy

$$C_{G1} > \frac{4}{3}\pi \frac{d_M}{L_\delta} \sum_{k=1}^{[L_\delta/d_M]_{\mathrm{I}}} (3 + \frac{3}{k} + \frac{1}{k^2}).$$

In this derivation, the time average $\overline{N}_M/d_M^3$ of the number of molecules N_M in a volume d_M^3 is assumed to by bounded by $C_\rho\left(\overline{N}_{\delta 0}/L_\delta^3\right)$, which is too strong to be satisfied. The discussion of the average of velocity change in the preceding discussion $\Rightarrow$ $\overline{\boldsymbol{F}}_{G1} \to 0$ under a weaker condition.

The time average of the force on $\boldsymbol{X}$ by the molecules in $r \geq L_\delta$ can be obtained with some modifications to the case $\alpha > 3$. First, consider the contribution $m\overline{\boldsymbol{F}}_{G2}$ of the molecules in $L_\delta \leq r < \{[(L/L_\delta)^\epsilon]_{\rm I} + 1\}L_\delta$. Collecting the contribution from the subdivided shells $\{L_\delta k \leq r < L_\delta(k+1),\ k = 1, 2, \cdots, [(L/L_\delta)^\epsilon],\ 0 < \epsilon < 1\}$, we have

$$\begin{aligned} |\overline{\boldsymbol{F}}_{G2}| &< \frac{4}{3}\pi m G C_\rho \left(\frac{\overline{N}_{\delta 0}}{L_\delta^3}\right) \\ &\quad \times \sum_{k=1}^{[(L/L_\delta)^\epsilon]_{\rm I}} \frac{L_\delta^3[(k+1)^3 - k^3]}{(L_\delta k)^2} \\ &= C_{G2} C_\rho \rho_0 G L \left(\frac{L_\delta}{L}\right)^{1-\epsilon}, \end{aligned}$$

where C_{G2} is chosen so as to satisfy

$$C_{G2} > \frac{4}{3}\pi \left(\frac{L_\delta}{L}\right)^\epsilon \sum_{k=1}^{[(L/L_\delta)^\epsilon]_{\rm I}} (3 + \frac{3}{k} + \frac{1}{k^2}).$$

The contribution to the force from the molecules in $r > [(L_\delta/L)^{1-\epsilon} + 1]L$

In this domain, $L_\delta \ll r$ and r is uniform over L_δ^3. Thus, the summation can be expressed with the corresponding integral in the gas dynamic limit. The force $m\overline{\boldsymbol{F}}_{G3}$ on the molecule in the gas dynamic limit is given as

$$\overline{\boldsymbol{F}}_{G3} = -G \int_{\mathrm{all}\boldsymbol{X}_0} \frac{(\boldsymbol{X} - \boldsymbol{X}_0)\rho(\boldsymbol{X}_0)}{r^3} \mathbf{d}\boldsymbol{X}_0.$$

Owing to the assumption that the density approaches the uniform state with the speed faster $1/|\boldsymbol{X}|$, the integral converges. This is the only contribution. (The contribution of $\overline{\boldsymbol{F}}_{G1}$ and $\overline{\boldsymbol{F}}_{G2}$ vanishes.) Thus,

$$\boldsymbol{F}^G = \overline{\boldsymbol{F}}_{G3}.$$

This force varies in gas dynamic scale in space and in time and does not bring about an abrupt change of velocity. Thus, this is included in the external force term.

Note that $\boldsymbol{X}$ here is after the gas dynamic limit. There is no distinction L_δ, d_m, etc. in the present $\boldsymbol{X}$.

$$\frac{\partial f}{\partial t}+\xi_i\frac{\partial f}{\partial X_i}+F_i^G\frac{\partial f}{\partial \xi_i}+\frac{\partial F_i f}{\partial \xi_i}=J(f,f),$$

where

$$J(f,f)=\frac{1}{m}\int_{\mathrm{all}\,\boldsymbol{\alpha},\,\mathrm{all}\,\boldsymbol{\xi}_*}(f'f'_*-ff_*)B\mathrm{d}\Omega(\boldsymbol{\alpha})\mathbf{d}\boldsymbol{\xi}_*,$$

$$B=d_M^2|(\xi_{i*}-\xi_i)\alpha_i|/2,$$

$$\boldsymbol{F}^G=-G\int_{\mathrm{all}\boldsymbol{X}_0}\frac{(\boldsymbol{X}-\boldsymbol{X}_0)\rho(\boldsymbol{X}_0)}{r^3}\mathbf{d}\boldsymbol{X}_0.$$

DISCUSSIONS

When the problem is given,

The data d_M, L, RT_0, p_0 are specified.

- Confirm that nd_M^3 is small.
- Specify L_δ. This depends on the accuracy required or the precision of the apparatus.
- Determine d_m.
- Confirm that d_M/L, d_m/d_M, L_δ/L, C_L satisfy the requirement.

It is not always easily satisfied for a gas.

$d_M = 3 \times 10^{-10}\mathrm{m}$,

At standard pressure

$$\begin{aligned}&\overline{N}_{\delta 0}/L_\delta^3 = 2.7 \times 10^{25}\mathrm{m}^{-3}\\&\left(\overline{N}_{\delta 0}/L_\delta^3\right) d_M^3 = 7 \times 10^{-4},\\&\left(\overline{N}_{\delta 0}/L_\delta^3\right)^{1/3} = 3 \times 10^{8}\mathrm{m}^{-1}\\&D_{\mathrm{sp}} = 3 \times 10^{-9}\mathrm{m},\\&d_M/D_{\mathrm{sp}} = 10^{-1}.\end{aligned}$$

No space between d_M and D_{sp} for d_m satisfying the requirement.

For the pressure $1/10^3$ atm of the standard pressure,

$$d_M/D_{\mathrm{sp}} = 10^{-2}.$$

In this case, if the potential decays fast, the contributions of the tail of the potential and triple collisions are fairly small for $d_m/d_M = 10$ and $D_{\mathrm{sp}}/d_m = 10$, .

The perfect gas condition is hard condition for moderate pressure.

Examples from micro flow

1)

$$d_M = 3 \times 10^{-10}\text{m}, \quad L = 10^{-6}\text{m}.$$

For the choice

$$L_\delta / L = 0.1,$$

we have

$$L_\delta = 10^{-7}\text{m}, \quad d_M / L_\delta = 3 \times 10^{-3}.$$

At the standard pressure:

$$\overline{N}_0 = 2.7 \times 10^7,$$

$$\overline{N}_{\delta 0} = 2.7 \times 10^4, \quad \overline{\mathcal{F}}_{\delta 0} = 2.7 \times 10,$$

$$C_L = 2.4.$$

When the pressure is at 1/10 atm, $\overline{N}_{\delta 0}$:

$$\overline{N}_{\delta 0} = 2.7 \times 10^3,$$

$$\overline{\mathcal{F}}_{\delta 0} = 2.7,$$

$$C_L = 2.4 \times 10^{-1}.$$

2)

$$d_M = 3 \times 10^{-10}\mathrm{m}, \quad L = 10^{-6}\mathrm{m}.$$

For the choice

$$L_\delta / L = 5 \times 10^{-2},$$

we have

$$L_\delta = 5 \times 10^{-8}\mathrm{m}, \quad d_M / L_\delta = 6 \times 10^{-3}.$$

At the standard pressure:

$$\overline{N}_0 = 2.7 \times 10^{7},$$

$$\overline{N}_{\delta 0} = 3.4 \times 10^{3},$$

$$\overline{\mathcal{F}}_{\delta 0} = 4.2 \times 10^{-1},$$

$$C_L = 2.4.$$

When the pressure is at 1/10 atm,

$$\overline{N}_{\delta 0} = 3.4 \times 10^{2},$$

$$\overline{\mathcal{F}}_{\delta 0} = 4.2 \times 10^{-2},$$

$$C_L = 2.4 \times 10^{-1}.$$

When $\overline{\mathcal{F}}_{\delta 0}$ is not large, the problem is not appropriate to be studied by molecular gas dynamics. It is to be studied by molecular dynamics.

In applications, we have to pay attention to the assumption put in the derivation of the Boltzmann equation.