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# Transition of Diffusion Mechanism from Molecular Thermal Motion to Macroscopic Temporary Fluctuation

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**Abstract.** Two different mechanisms of the diffusion of gas are studied numerically and analytically. In the numerical study, the diffusion coefficient of argon gas between two infinite parallel plates is calculated based on the Einstein relation. The molecular displacements in the directions parallel to the plates are obtained using the DSMC method. The diffusion coefficients so obtained are compared with those predicted by the Chapman-Enskog theory. They are in excellent agreement when the distance between the plates  $h=50\lambda$ , but become much different when  $h=500\lambda$ . An analysis reveals that molecular collisions have two-fold effects: viscous damping and nonlinear excitation. When macroscopic temporary fluctuation appears, no matter resulting from an external disturbance or from a local non-uniformity, due to the viscous damping effect reduces as the Knudsen number decreases, the diffusion coefficients in the  $x$  and  $z$  directions without the solid walls restraint change greatly with time, and deviate from the Chapman-Enskog theory that does not take into account the macroscopic temporary fluctuation. This indicates that under an external disturbance or a local non-uniformity, a transition of diffusion mechanism from molecular thermal motion to macroscopic temporary fluctuation occurs as the Knudsen number decreases.

**Keywords:** diffusion coefficient, Einstein relation, Chapman-Enskog theory, molecular thermal motion, macroscopic temporary fluctuation.

**PACS:** 47.57.eb, 51.20+d, 51.10+y

## DIFFUSION COEFFICIENT

Transport phenomenon is an essential feature of fluids. In classical fluid dynamics, transport coefficients are phenomenological that are usually determined by experiment. Further studies revealed that the transport coefficients is related to molecular motion [1, 2]. For example, according to the Einstein relation [1], the diffusion coefficient in  $x$  direction

$$D_x = \overline{\Delta x^2}/(2t) \quad \text{when } t \gg \tau_c, \quad (1)$$

where  $\overline{\quad}$  denotes statistical average,  $\Delta x$  is the displacement during a time interval  $t$ , and  $\tau_c$  is the mean collision time of molecules.

For dilute gases, when the transport processes are dominated by molecular thermal motion, according to the Chapman-Enskog theory [2], the diffusion coefficient for hard-sphere molecules can be approximately written as

$$D_m \approx 0.6\lambda\bar{c}, \quad (2)$$

where  $\lambda$  is the mean free path, the mean speed of thermal motion  $\bar{c} = \sqrt{8kT/\pi m}$ ,  $k$  the Boltzmann constant,  $T$  the temperature, and  $m$  the molecular mass.

## KNUDSEN NUMBER EFFECT

Consider two cases of argon gas between two infinite parallel plates in the distance of  $h$ . Similar to the Rayleigh-Benard problem, the lower plate has a higher temperature than the upper plate, and there exists a gravity acceleration in the  $y$  direction normal to the plates.

Except for the distance between the two plates, the two cases have the same conditions. The boundary conditions at the lower and upper plates are fully diffusely reflecting, with the temperatures of 330K & 270K, respectively. The gravity acceleration  $g=6.8 \times 10^8 \text{m/s}^2$ . The diffusion coefficients  $D_x$  &  $D_z$  are calculated based on the

Einstein relation (1), while the displacements in the x and z directions are obtained using the DSMC method [3]. The DSMC calculations are unsteady that start from a linear temperature distribution at rest with the number density of  $2.45 \times 10^{25} \text{m}^{-3}$ . The total number of simulated molecules are same to be 20,000 for the two cases to ensure the statistical scatter due to the sample size at the same level. The cell sizes and time steps are also same, which are  $0.5\lambda$  and  $0.5\tau_c$ , respectively.

Figure 1 presents the normalized diffusion coefficients in the x and z directions ( $D_x$  &  $D_z$ ) for the two cases. The normalization factor  $D_m$  is given by Eq. (2). We can see that the values of  $D_x$  &  $D_z$  are almost invariable and close to 1 when  $h = 50$ , but vary greatly with time and far deviate from 1 when  $h = 500$ .

## TWOFOLD EFFECTS OF MOLECULAR COLLISIONS

The motion of an observed molecule motion is determined by colliding impacts  $F_{c,i}$  and external forces  $F_{e,i}$ ,

$$m \times dv_{o,i}/dt = F_{c,i} + F_{e,i}, \quad F_{c,i}(v_{o,i}) = m(v_{o,i}^* - v_{o,i})/\tau_c(v_o). \quad (3)$$

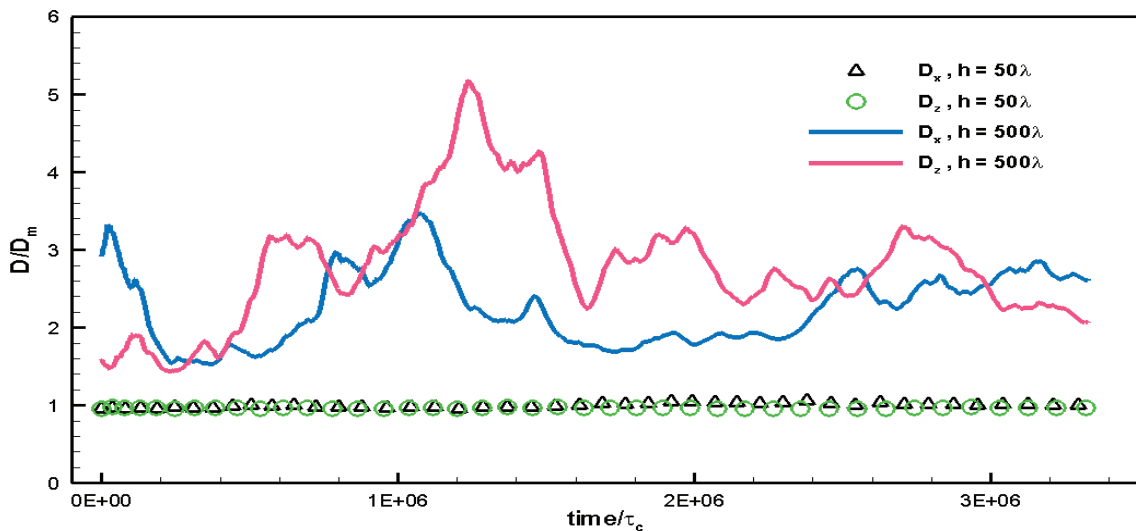
In the situation of interest here, we have

$$\frac{dv_{o,x}}{dt} = -\frac{v_{o,x}}{2\tau_c(v_o)} \left( 1 - \frac{v_{s,x} - v_r R}{v_{o,x}} \right), \quad (4)$$

$$\frac{dv_{o,y}}{dt} = -\frac{v_{o,y}}{2\tau_c(v_o)} \left( 1 - \frac{v_{s,y} - v_r \sqrt{1-R^2} \sin \theta}{v_{o,y}} \right) - g, \quad (5)$$

$$\frac{dv_{o,z}}{dt} = -\frac{v_{o,z}}{2\tau_c(v_o)} \left( 1 - \frac{v_{s,z} - v_r \sqrt{1-R^2} \cos \theta}{v_{o,z}} \right), \quad (6)$$

where superscript \* denotes post-collision, subscript s denotes a surrounding molecule that collides with the observed molecule,  $v_r$  the relative speed between the colliding pair, R and  $\theta$  two random numbers,  $R \in [0,1]$ ,  $\theta \in [0, 2\pi]$ .



**FIGURE 1.** Knudsen number effect on the diffusion coefficients of argon gas between two infinite parallel plates in the parallel directions.

Employ  $h$  and the mean speed of thermal motion as the characteristic scales of length and velocity. After normalization, Eqs. (4-6) can be written as

$$\frac{d\tilde{v}_{o,x}}{d\tilde{t}} = -\frac{1}{Kn} \times \frac{\tilde{v}_{o,x}}{2\tilde{\tau}_c(v_o)} \left( 1 - \frac{\tilde{v}_{s,x} - \tilde{v}_r R}{\tilde{v}_{o,x}} \right), \quad (7)$$

$$\frac{d\tilde{v}_{o,y}}{d\tilde{t}} = -\frac{1}{Kn} \times \frac{\tilde{v}_{o,y}}{2\tilde{\tau}_c(v_o)} \left( 1 - \frac{\tilde{v}_{s,y} - \tilde{v}_r \sqrt{1-R^2} \sin \theta}{\tilde{v}_{o,y}} \right) - \frac{\alpha}{\beta} \times \frac{Ra}{Kn^2}, \quad (8)$$

$$\frac{d\tilde{v}_{o,z}}{d\tilde{t}} = -\frac{1}{Kn} \times \frac{\tilde{v}_{o,z}}{2\tilde{\tau}_c(v_o)} \left( 1 - \frac{\tilde{v}_{s,z} - \tilde{v}_r \sqrt{1-R^2} \cos \theta}{\tilde{v}_{o,z}} \right), \quad (9)$$

where  $\sim$  denotes a normalized quantity,  $\alpha$  is a constant that is near unity,  $\beta = 2(T_1 - T_2)/(T_1 + T_2)$ , the Knudsen number  $Kn = \lambda/h$ , the Rayleigh number

$$Ra = \frac{\beta g h^3}{\nu \kappa} \sim \frac{\beta g h^3}{\lambda^2 c^2}, \quad (10)$$

and  $\nu$  and  $\kappa$  are the coefficients of viscosity and thermal conductivity, respectively.

Equations (7-9) show the two-fold effects of molecular collisions, i.e., viscous damping and nonlinear excitation.

A) Molecular collisions will be equivalent to viscous damping, when

$$1 - \frac{\tilde{v}_{s,x} - \tilde{v}_r R}{\tilde{v}_{o,x}} > 0 \quad \text{or} \quad \tilde{v}_{o,x} > \tilde{v}_{s,x} - \tilde{v}_r R, \quad (11)$$

$$1 - \frac{\tilde{v}_{s,y} - \tilde{v}_r \sqrt{1-R^2} \sin \theta}{\tilde{v}_{o,y}} > 0 \quad \text{or} \quad \tilde{v}_{o,y} > \tilde{v}_{s,y} - \tilde{v}_r \sqrt{1-R^2} \sin \theta, \quad (12)$$

$$1 - \frac{\tilde{v}_{s,z} - \tilde{v}_r \sqrt{1-R^2} \cos \theta}{\tilde{v}_{o,z}} > 0 \quad \text{or} \quad \tilde{v}_{o,z} > \tilde{v}_{s,z} - \tilde{v}_r \sqrt{1-R^2} \cos \theta. \quad (13)$$

B) Otherwise, molecular collisions will be equivalent to nonlinear excitation whose strength increases as  $Kn$  decreases.

The two processes above occur simultaneously in real molecular motion whose comprehensive consequence depends on which process is dominant.

If the viscous damping effect including solid walls is strong enough to dissipate rapidly macroscopic temporary fluctuation resulting from an external disturbance or from a local non-uniformity, the transport process will be dominated by molecular thermal motion. Consequently, the diffusion coefficient may be well described by the Chapman-Enskog theory, e.g., the case with  $h=50\lambda$  in Fig.1, where  $D/D_m$  is close to 1 in both  $x$  and  $z$  directions.

If the viscous damping effect is not enough to dissipate rapidly macroscopic temporary fluctuation, the latter will manifest itself. As a result, the diffusion coefficient will significantly deviate from the Chapman-Enskog theory, e.g., the case with  $h=500\lambda$  in Fig. 1, where  $D/D_m$  vary greatly with time and several times larger than unity in both  $x$  and  $z$  directions without restraints.

## REYNOLDS NUMBER, TURBULENCE AND DNS

It is well known that turbulence arises when the Reynolds number (Re) exceeds a critical value. The essential feature of turbulence is a remarkable increase of the equivalent transport coefficients. The analysis above is helpful to understand the phenomenon.

As derived by Tsien [4], Re is related to Kn and the Mach number (Ma)

$$\text{Re} = 1.26\sqrt{\gamma} \times \text{Ma} / \text{Kn}, \quad (14)$$

where  $\gamma$  is the specific heat ratio of gas.

The relation (14) tells us Re increases as Kn decreases. Moreover, Ma can be regarded as a measure of external action or local non-uniformity that may lead to macroscopic temporary fluctuation. Therefore, an increase of Re amounts to a move towards macroscopic temporary fluctuation mechanism.

It is known that the cell size  $\Delta_c$  used in direct numerical simulation (DNS) of turbulence is rigorously restricted. It is not difficult to understand the requirement because the governing equation of DNS is the Navier-Stokes equations that can be derived from the Chapman-Enskog theory. This means that the DNS approach works only when the transport processes are dominated by molecular thermal motion rather than macroscopic temporary fluctuation. As shown in the present work, Kn is the critical parameter that decides if the molecular thermal motion can play a dominant role. To make the Knudsen number based on  $\Delta_c$  no less than a critical value  $\text{Kn}_c$ , the cell size has to be smaller than  $\text{Kn}_c \times \lambda$ . Since the mean free path is very small, e.g. about  $6 \times 10^{-8}$  m for air in the standard conditions (1atm & 273K), the restriction for the cell size of DNS is usually rigorous.

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## REFERENCES

1. R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport Phenomena*, 2nd ed., New York: Chemical Industry Press, 2002.
2. S. Chapman and T.G. Cowling, *The Mathematical Theory of Nonuniform Gases*, 3rd ed., Cambridge: Cambridge University Press, 1970.
3. G.A. Bird, *Molecular Gas Dynamics and the Direct Simulation Monte Carlo Method*, Oxford: Clarendon Press, 1994.
4. H. S. Tsien, *J. Aero. Sci.* **13**, 653-664 (1946).