# **On Knudsen Flows within Thin Tubes**<sup>1</sup>

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The dynamics of a test particle in an infinite tube is investigated. It is proven that the evolution tends to that of a diffusion process as the radius of the tube decreases to zero. This justifies the hypotheses underlying an experiment of Clausing (1930).

KEY WORDS: Knudsen flow, infinite tube, diffusion approximation.

# 1. INTRODUCTION

In this paper we study the time evolution of a rarefied gas within a long thin tube. The main point of our investigations is the following hypothesis: Assuming that collisions between gas particles can be neglected, the dynamics of the gas is well-approximated by a diffusion process.

It was Clausing<sup>(1)</sup> who in 1930 used this hypothesis to find out by experiment some information concerning the gas-surface interaction. As far as we know, the diffusion ansatz for a flow like this—although confirmed by a paper of Armand<sup>(2)</sup>—has never been derived rigorously. Simulations carried out in order to clear up the problem<sup>(3,4)</sup> ended up with diverging results. Pack and Yamamoto<sup>(5,6)</sup> investigated asymptotic properties of the flow which again confirmed the diffusion hypothesis.

As we show in the following, the distribution of the gas converges indeed to that of a diffusion process if the radius r of the tube decreases to zero. In particular, we investigate the dynamics of a test particle within an infinite tube. Between collisions with the wall it moves straight on. When hitting the wall it is either reflected elastically or absorbed by the wall for some random time and then reemitted diffusely.

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In Section 2, we describe the motion of the test particle by means of a stochastic process. In Section 3 we pass over to the limit  $r \rightarrow 0$  and show that the result is a diffusion process, provided the adsorption time and the temperature of the wall are properly scaled. The result we prove is a version of Donsker's invariance principle. Section 4 is devoted to Clausing's experiment, the controversies following it, and the relation of the results of this paper with Clausing's hypothesis.

# 2. KNUDSEN FLOW IN AN INFINITE CYLINDER

# The model

We study the motion of a particle moving in an infinite cylinder with radius r. The axis of the cylinder is supposed to be the z axis of a fixed Cartesian coordinate system.

Between collisions with the wall of the cylinder the particle moves with constant velocity. At the wall, it is assumed to be reflected according to some Maxwellian reflection law with accommodation coefficient and delay time. This means precisely: When hitting the wall, the particle may be reflected elastically. The probability for such an event is  $\lambda$ ,  $\lambda$  being a fixed number in [0, 1). With probability  $1 - \lambda$  the particle is trapped by the wall for some time  $\tau$ .  $\tau$  is randomly distributed with probability density

$$p_{\tau}(\tau) = \sigma \cdot e^{-\sigma\tau} \tag{1}$$

with  $\sigma$  a strictly positive number. (The case  $\sigma = \infty$  is also possible and has to be interpreted as  $p_{\tau}(\tau) = \delta(\tau)$ .) Afterward it is diffusely reflected. This means that the particle is reemitted from the wall with a random velocity being distributed with a certain probability density (see Ref. 6, Sect. 3). Denote by w the velocity component parallel to the axis, by  $v_{\perp}$  the velocity component in the direction of the inner normal at the reemission point, and by  $v_{\parallel}$  the component perpendicular to  $v_{\perp}$  and w. Then the probability density for the velocity starting from the wall is

$$p_{v,w}(v_{\perp}, v_{\parallel}, w) = 2\alpha v_{\perp} \cdot e^{-\alpha v_{\perp}^2} \sqrt{\frac{\alpha}{\pi}} e^{-\alpha v_{\parallel}^2} \sqrt{\frac{\alpha}{\pi}} e^{-\alpha w^2} \quad \text{for} \quad v_{\perp} > 0 \quad (2)$$

 $\alpha$  is a quantity proportional to the inverse of the wall temperature.

Since the whole limiting procedure we are going to develop in Section 3 is a matter of scaling, we introduce the rescaled probability densities

$$q_{v}(v_{\perp}, v_{\parallel}) := 2v_{\perp}e^{-v_{\perp}^{2}} \cdot \frac{1}{\sqrt{\pi}}e^{-v_{\parallel}^{2}}$$

and

$$q_w(w) := \frac{1}{\sqrt{\pi}} e^{-w^2}$$

Now suppose the particle is reemitted from the emission point  $(r \cos \theta_o, r \sin \theta_o, z_0)^T$  at time  $t_o$  with some random velocity  $(v_{\perp}, v_{\parallel}, w)$  distributed by (2). Without lack of generality we put  $t_o = 0$ ,  $z_o = 0$ , and  $\theta_o = 0$ . Then it hits the wall again at some later time t' at some new point  $(r \cos \theta', r \sin \theta', z')^T$ . Our first aim is to find out the probability density  $p_t$  for t' and the joint densities  $p_{t,w}$  for t' and w and  $p_{t,z}$  for t' and z'. Clearly, the velocity and the points at the wall are related by

$$(v_{\perp}, v_{\parallel}, w) = \left[\frac{r}{t'} \cdot (1 - \cos \theta'), \frac{r}{t'} \cdot \sin \theta', w\right]$$
  
=  $\frac{1}{t'} [r(1 - \cos \theta'), r \sin \theta', z']$  (3)

Applying the transformations (3) to formula (2), calculating the Jacobians, and integrating over  $\theta'$  (and w) yields

Lemma 1.

(a) 
$$p_t(t') = \frac{1}{\sqrt{\alpha} r} q_t \left(\frac{t'}{\sqrt{\alpha} r}\right)$$

where  $q_t$  is the rescaled probability density

$$q_{t}(t) = \frac{2}{\sqrt{\pi} t^{4}} \cdot \int_{0}^{2\pi} (1 - \cos \theta)^{2} \cdot \exp[-(2/t^{2})(1 - \cos \theta)] d\theta$$

(b) 
$$p_{t,w}(t', w) = p_t(t') \cdot \sqrt{\alpha} q_w(\sqrt{\alpha} w)$$

(in particular, t' and w are independent)

(c) 
$$p_{t,z}(t', z') = p_t(t') \cdot \frac{\sqrt{\alpha}}{t'} q_w\left(\frac{\sqrt{\alpha} z'}{t'}\right)$$

(t', z') are the coordinates of the first contact with the wall after the time  $t_o = 0$ . This contact may result in either an elastic or a diffuse reflection. Define by  $(t_1, z_1)$  the coordinates of the first diffuse reflection. Again we are looking for the corresponding densities  $p_t^{\lambda}(t_1)$ ,  $p_{t,w}^{\lambda}(t_1, w)$  and  $p_{t,z}^{\lambda}(t_1, z_1)$ . Since an elastic rescattering does not affect the motion in the z direction,

 $(t_1, z_1)$  and (t', z') are related in the following way: If the particle has been reflected elastically exactly *n* times before the first diffuse reflection then

$$(t_1, z_1) = \frac{1}{n+1} (t', z')$$

The probability of having *n* elastic and then a diffuse reflection is  $\lambda^n \cdot (1-\lambda)$ . Thus, by conditioning on the number *n* we get

Lemma 2.

(a) 
$$p_t^{\lambda}(t_1) = \frac{1}{\sqrt{\alpha} r} q_t^{\lambda} \left( \frac{t_1}{\sqrt{\alpha} r} \right)$$

with the rescaled probability density

$$q_t^{\lambda} = (1-\lambda) \cdot \sum_{n=0}^{\infty} \lambda^n \cdot \frac{1}{n+1} q_t \left(\frac{t}{n+1}\right)$$

(b) 
$$p_{t,w}^{\lambda}(t_1, w) = p_t^{\lambda}(t_1) \cdot \sqrt{\alpha} q_w(\sqrt{\alpha} w)$$

(c) 
$$p_{t,z}^{\lambda}(t_1, z_1) = p_t^{\lambda}(t_1) \cdot \frac{\sqrt{\alpha}}{t_1} q_w \left(\frac{\sqrt{\alpha} z_1}{t_1}\right) = :\frac{1}{\sqrt{\alpha} r^2} q_{t,z}^{\lambda} \left(\frac{t_1}{\sqrt{\alpha} r}, \frac{z}{r}\right)$$

The collision time densities can be characterized as follows

**Lemma 3.**  $q_t$  and  $q_t^{\lambda}$  are bounded. Further  $q_t(t) = 1/t^4 \cdot \gamma(t)$  and

$$q_t^{\lambda}(t) = \frac{1}{t^4} \cdot \gamma^{\lambda}(t)$$

where  $\gamma$  and  $\gamma^{\lambda}$  are monotonely increasing functions with

$$\gamma(\infty) := \lim_{t \to \infty} \gamma(t) = 6\sqrt{\pi}$$

and

$$\gamma^{\lambda}(\infty) := \lim_{t \to \infty} \gamma^{\lambda}(t) = 6\sqrt{\pi} \cdot \frac{1 + 4\lambda + \lambda^2}{(1 - \lambda)^3}$$

Proof. In order to prove boundedness, we have to show that

$$\frac{1}{t^4} \int_0^{2\pi} (1 - \cos \theta)^2 \exp\left[-\frac{2}{t^2} (1 - \cos \theta)\right] d\theta$$

is bounded in a neighborhood of zero. To this aim, it is obviously enough to show boundedness of

$$g_{\theta_o}(t) := \frac{1}{t^4} \int_0^{\theta_o} (1 - \cos \theta)^2 \exp[-(2/t^2)(1 - \cos \theta)] \, d\theta$$

for some fixed  $\theta_o > 0$ .

We choose  $\theta_o$  such that for all  $\theta \in [0, \theta_o]$ 

$$\frac{1}{4}\theta^2 \leq 1 - \cos \theta \leq \frac{1}{2}\theta^2$$

Then

$$g_{\theta_o}(t) \leq \frac{1}{4t^4} \int_0^{\theta_o} \theta^4 \cdot \exp\left(-\frac{1}{2} \cdot \frac{\theta^2}{t^2}\right) d\theta$$
$$\leq \frac{1}{4} t \int_0^\infty \theta^4 \cdot \exp\left(-\frac{1}{2} \theta^2\right) d\theta < \infty$$

From the preceding lemmata we obtain

$$y(t) = \frac{2}{\sqrt{\pi}} \int_0^{2\pi} (1 - \cos \theta)^2 \cdot \exp[-(2/t^2)(1 - \cos \theta)] \, d\theta$$

and

$$\gamma^{\lambda}(t) = (1-\lambda) \sum_{n=0}^{\infty} \lambda^n \cdot (n+1)^3 \cdot \gamma\left(\frac{t}{n+1}\right)$$

Since for every  $\theta$ , exp $[-(2/t^2)(1-\cos \theta)]$  is an increasing function of t, the monotonicity property of  $\gamma$  and  $\gamma^{\lambda}$  is evident. By Lebesgue's theorem and the fact that

$$\lim_{t \to \infty} \exp(-(2/t^2)(1 - \cos \theta)) = 1$$

follow

$$\gamma(\infty) = \frac{2}{\sqrt{\pi}} \int_0^{2\pi} (1 - \cos \theta)^2 \, d\theta$$

and

$$\gamma^{\lambda}(\infty) = \gamma(\infty) \cdot (1-\lambda) \cdot \sum_{n=0}^{\infty} \lambda^n \cdot (n+1)^3$$

The calculation of these terms ends up with the stated results.

#### An Associated Markov Chain

From now on, we only study the z component of the particle moving in the cylinder. Since elastic reflections do not affect the motion parallel to the axis we may forget about them.

Now suppose the particle is trapped by the wall at  $z_o$  at time  $t_o$ . It remains at the wall for some random time  $\tau_o$  being distributed by (1) and then leaves again with some velocity  $w_o$ . The next trapping and change of velocity take place at some coordinates  $(t_1, z_1)$  related to  $w_o, z_o, t_o$  and  $\tau_o$  by

$$z_1 = z_o + (t_1 - t_o - \tau_o) \cdot w_o$$

 $(t_1 - t_o - \tau_o, z_1 - z_o)$  is distributed by the density  $p_{t,z}^{\lambda}$ . From  $z_1$  the particle leaves again after some time  $\tau_1$  with a new velocity  $w_1$ , and so on.

One can formulate these dynamics well in terms of a discrete Markov process  $(D_n, T_n, Z_n)$ . Again, we put  $t_o = 0$  and  $z_o = 0$ . Then the process is defined by

$$(T_o, Z_o) = (0, 0) \tag{4a}$$

the delay times  $D_n$  are independent of  $(T_n, Z_n)$  and distributed with density  $p_t(\tau)$  (see eq. 1); (4b)

the increments  $[Z_{n+1}-Z_n, T_{n+1}-(T_n+D_n)]$  are independent of  $(D_n, T_n, Z_n)$  and distributed with density  $p_{t,z}^{\lambda}$  given by Lemma 2. (4c)

We further define the random variables  $W_n$  by

$$Z_{n+1} = Z_n + [T_{n+1} - (T_n + D_n)] \cdot W_n$$
(5)

 $W_n$  describes the velocity after the *n*th collision. It is independent of  $(D_n, T_n, Z_n)$  and distributed with density  $\sqrt{\alpha} q(\sqrt{\alpha} w)$ . Further on, we need the following result:

Lemma 4.

$$\lim_{n \to \infty} T_n = \infty \qquad \text{a.s.} \tag{6}$$

*Proof.* (6) is an immediate consequence of the law of large numbers:

$$\lim_{n \to \infty} \frac{1}{n} T_n = \int_0^\infty t \cdot p_t^\lambda * p_z(t) \, dt > 0 \qquad \text{a.s.}$$

The actual position of the particle at time t is described by a continuous family  $[Z(t)]_{t\geq 0}$  of random variables which are defined by

$$Z(t) = Z_n \qquad \text{if} \quad T_n \leq t < T_n + D_n$$
  
=  $Z_n + [t - (T_n + D_N)] \cdot W_n \qquad \text{if} \quad T_n + D_n \leq t < T_{n+1}$  (7)

where  $W_n$  is defined by (5). Since property (6) holds, Z(t) is well-defined for all  $t \ge 0$ . Let's point out, however, that the set  $[Z(t)]_{t\ge 0}$  does not define a Markov process.

# 3. THE DIFFUSION LIMIT

#### The Rescaling Procedure

The random variables  $T_{n+1} - T_n$  and the deviations  $Z_{n+1} - Z_n$  of the process defined by (4) depend on the parameters  $r, \alpha$ , and  $\sigma$ . To obtain convergence to a diffusion process in the limit  $r \to 0$ ,  $\alpha$  and  $\sigma$  have to be rescaled in such a way that the ratio

$$\rho := \frac{E(Z_{n+1} - Z_n)^2}{E(T_{n+1} - T_n)}$$
(8)

converges to a positive constant. To this aim we assume  $\alpha$  and  $\sigma$  to be of the form

$$\alpha = \alpha_o \cdot r^2 \tag{9}$$

$$\sigma = \frac{\sigma_o}{\sqrt{\alpha_o} \cdot r^2} \tag{10}$$

 $\alpha_o$  and  $\sigma_o$  being fixed constants. ( $\sigma_o$  may be infinite.)

Instead of looking at the particular process defined in the preceding section we study the following more general setting: Suppose  $\mu_o$  to be an arbitrary probability measure on  $\mathbb{R}_+ \times \mathbb{R}$  satisfying

$$\int x \, d\mu_o(x, t) = 0$$

$$\tilde{t} := \int t \, d\mu_o(x, t) < \infty \tag{11}$$

$$\rho := \frac{1}{t} \cdot \int x^2 \, d\mu_o(x, t) < \infty \tag{12}$$

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Define the Markov chains  $(Z, T)_n^{(r)}$  by

$$(Z, T)_o^{(r)} := (0, 0)$$

and

$$(Z, T)_n^{(r)} := \sum_{k=1}^n (X, \tau)_k^{(r)}$$
(13)

 $(X, \tau)_k^{(r)}, k = 1, 2, ...,$  being i.i.d. random variables distributed with

$$d\mu^{(r)}(x, t) = \frac{1}{r^3} d\mu_o\left(\frac{x}{r}, \frac{t}{r^2}\right)$$
(14)

Further, define the continuous time process  $Z^{(r)}(t)$  by

$$Z^{(r)}(t) = Z_n^{(r)} + \Delta Z^{(r)}(t) \qquad \text{if} \quad T_n^{(r)} \le t < T_{n+1}^{(r)}$$
(15)

where  $\Delta Z^{(r)}(t)$  is a family of random variables with trajectories which are continuous and monotone in each interval  $[T_n^{(r)}, T_{n+1}^{(r)}]$  with limits

$$\Delta Z^{(r)}(T_n^{(r)}) = 0$$

$$\lim_{t \uparrow T_{n+1}^{(r)}} \Delta Z^{(r)}(t) = X_{n+1}^{(r)}$$
(16)

As in the proof of Lemma 4 follows

$$\lim_{n \to \infty} T_n^{(r)} = \infty \qquad \text{a.s.}$$

thus,  $Z^{(r)}(t)$  is well-defined for all  $t \ge 0$ .

In the next section we prove weak convergence of  $Z^{(r)}$  to a Brownian motion. The heuristic argument goes as follows (compare eq. 14): The number of collisions up to time t is approximately

$$N^{(r)}(t) := \frac{t}{r^2 \cdot t}$$

(strong law of large numbers). Thus

$$Z^{(r)}(t) \approx \sum_{k=0}^{N^{(r)}(t)} X_k^{(r)} = r \cdot \sum_{k=0}^{N^{(r)}(t)} X_k^{(1)}$$
$$= \sqrt{\frac{t}{t}} \cdot \frac{1}{\sqrt{N^{(r)}(t)}} \cdot \sum_{k=0}^{N^{(r)}(t)} X_k^{(1)}$$

As a consequence of the central limit theorem, the latter sum converges to the normal distribution  $\mathcal{N}(0, \rho \cdot t)$  with  $\rho$  as defined in (12). Since for  $r \to 0$ 

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the increments of  $Z^{(r)}$  are asymptotically independent,  $Z^{(r)}$  converges to a Brownian motion  $Z_{a}$  with zero drift and variance

$$E[Z_{\rho}(t) - Z_{\rho}(s)]^{2} = \rho \cdot |t - s|$$

In the subsequent section we are going to make these arguments precise.

# **Convergence to Brownian Motion**

The proof of weak convergence of  $Z^{(r)}$  to  $Z_{\rho}$  is split up into two parts which are shown in Lemma 5 and Lemma 6.

**Lemma 5.** The finite dimensional distributions of  $Z^{(r)}$  converge to those of  $Z_{\rho}$ .

**Proof.** Let us consider at first the one-dimensional distributions. Given  $t_1 > 0$ 

$$Z^{(r)}(t_1) = r \cdot \sum_{k=1}^{N^*} X_k^{(1)} + \Delta Z^{(r)}(t_1)$$

where  $N^*$  is the random variable defined by  $T_{N^*} \leq t < T_{N^*+1}$ . Since

$$\Delta Z^{(r)}(t_1) \xrightarrow{P} 0$$

it is sufficient to prove convergence of

$$r \cdot \sum_{k=1}^{N^*} X_k^{(1)}$$

to  $\mathcal{N}(0, \rho \cdot t_1)$ . With

$$N := \left[\frac{t_1}{\overline{t} \cdot r^2}\right]$$
$$r \cdot \sum_{k=1}^{N^*} X_k^{(1)} = r \cdot \sum_{k=1}^{N} X_k^{(1)} \pm r \cdot \sum_{\min(N,N^*)}^{\max(N,N^*)} X_k^{(1)}$$

The central limit theorem states that the first r.h.s. term converges in distribution to  $\mathcal{N}(0, \rho \cdot t_1)$ . Because of the law of large numbers

$$N^* \cdot N^{-1} \to 1$$
 a.s.

and thus

$$r \cdot \sum_{\min(N,N^*)}^{\max(N,N^*)} X_k^{(1)} \to 0$$

Now suppose that for given k, all k-dimensional distributions converge to those of  $Z_{\rho}$ , and let  $t_1 < \cdots < t_{k+1}$  be fixed times. Define by  $t_{k*}$  the last collision time before and by  $t_k^*$  the first one after  $t_k$ 

$$t_{k^*} = T_n$$
  $t_k^* = T_{n+1}$  for  $T_n \le t_k < T_{n+1}$ 

Then given  $t_{k*}$  and  $t_{k}^{*}$ ,  $Z^{(r)}(t_{k+1}) - Z^{(r)}(t_{k}^{*})$  is independent of  $Z^{(r)}(t_{1}), ..., Z^{(r)}(t_{k-1}), Z^{(r)}(t_{k*})$  and distributed as  $Z^{(r)}(t_{k+1} - t_{k}^{*})$ . The convergence of the (k+1)-dimensional distribution now follows from

$$t_k^* - t_{k^*} \xrightarrow{P} 0$$

**Lemma 6.** Given  $\tau_o > 0$  arbitrary, the set of measures  $\{P^{(r)}\}$  corresponding to  $Z^{(r)}$  is tight in the space of continuous functions  $C[0, \tau_o]$ .

**Proof.** We have to show that given  $\varepsilon$ ,  $\eta > 0$  there exist  $\delta \in (0, 1)$  and  $r_o > 0$  such that in  $[0, \tau_o]$ 

$$P\{\sup_{|t-s|<\delta} |Z^{(r)}(t) - Z^{(r)}(s)| > \varepsilon\} < \eta \quad \text{for all } r \leq r_o$$

Given  $n \in N$ , define  $\delta = \delta(n) := \tau_o/n$  and let  $0 = t_o < \cdots < t_n = \tau_o$  be the equidistant partition of  $[0, \tau_o]$ .

One can see easily that

$$P\left\{\sup_{|t-s|<\delta}|Z^{(r)}(t)-Z^{(r)}(s)|>\varepsilon\right\} \leqslant P\left\{\sup_{j}\sup_{t\in [t_{j},t_{j+1}]}|Z^{(r)}(t)-Z^{(r)}(t_{j})|>\frac{\varepsilon}{3}\right\}$$
$$\leqslant \sum_{j=0}^{n-1}P\left\{\sup_{t\in [t_{j},t_{j+1}]}|Z^{(r)}(t)-Z^{(r)}(t_{j})|>\frac{\varepsilon}{3}\right\}$$

Define the random variables  $N_*(j)$  and  $N^*(j)$  such that

$$T_{N_*(j)} \leq t_j < T_{N_*(j)+1}$$

and

$$T_{N^*(j)-1} \leq t_{j+1} < T_{N^*(j)}$$

Then

$$\sup_{t \in [t_j, t_{j+1}]} |Z^{(r)}(t) - Z^{(r)}(t_j)| > \frac{\varepsilon}{3}$$

implies

$$\sup_{N_{\star}(j) \leq k \leq N^{\star}(j)} |Z_k^{(r)} - Z_{N(j)}^{(r)}| > \frac{\varepsilon}{6}$$

With  $E_i^{(r)}(\delta)$  we denote the event

$$N^*(j) - N_*(j) \leq \left[\frac{2\delta}{r^2 \cdot t}\right] = : N(\delta)$$

Then

$$P\left\{\sup_{t \in [t_j, t_{j+1}]} |Z^{(r)}(t) - Z^{(r)}(t_j)| > \frac{\varepsilon}{3}\right\}$$
$$\leqslant P\left\{\sup_{N_*(j) \leqslant k \leqslant N_*(j) + N(\delta)} |Z^{(r)}_k - Z^{(r)}_{N_*(j)}| > \frac{\varepsilon}{6}\right\} + P[\overline{E^{(r)}_j(\delta)}]$$

According to formula (10.7) in Ref. 8,

$$\begin{split} P\left\{\sup_{N_{\star}(j)\leqslant k\leqslant N_{\star}(j)+N(\delta)}|Z_{k}^{(r)}-Z_{N_{\star}(j)}^{(r)}|>\frac{\varepsilon}{6}\right\}\leqslant 2P\left\{|Z_{N(\delta)}^{(r)}|>\frac{\varepsilon}{6}-\sqrt{2}N(\delta)\ r^{2}\rho\bar{t}\right\}\\ \leqslant 2P\left\{|Z_{N(\delta)}^{(r)}|>\frac{\varepsilon}{6}-3\delta\rho\right\} \end{split}$$

Collecting all estimates yields

$$P\left\{\sup_{|t-s|<\delta} |Z^{(r)}(t) - Z^{(r)}(s)| > \varepsilon\right\}$$
  
$$\leq \frac{\tau_o}{\delta} \cdot \left(2P\left\{|Z^{(r)}_{N(\delta)}| > \frac{\varepsilon}{6} - 3\delta\rho\right\} + P[\overline{E_j^{(r)}(\delta)}]\right)$$

For fixed  $\delta$ 

$$Z_{N(\delta)}^{(r)} \xrightarrow{\mathscr{D}} \mathscr{N}(0, 2\delta\rho)$$

Thus the first term on the right-hand-side of (17) becomes arbitrarily small if  $\delta$  is small enough. Furthermore

$$P[\overline{E_j^{(r)}(\delta)}] = P\{T_{N(\delta)}^{(r)} < \delta\} \to 0 \quad \text{if} \quad r \to 0$$

since

$$T_{N(\delta)}^{(r)} = r^2 \cdot \sum_{k=0}^{N(\delta)-1} \tau_k^{(1)} \to 2\delta \qquad \text{a.s.}$$

This completes the proof.

Convergence of the finite-dimensional distributions and tightness imply weak convergence on  $C[0, \tau_o]$  (see, e.g., Ref. 8, Theorem 8.1]). This proves the following theorem:

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**Theorem.** Let  $\tau_o$  be an arbitrary positive time. Then  $Z^{(r)}$  converges weakly in  $C[0, \tau_o]$  (equipped with the uniform topology) to the Brownian motion  $Z_\rho$  with the diffusion  $\rho$  defined by (12).

# Back to the Knudsen Flow

The situation described in Section 2 is a special case of the setting studied above. In particular, the measure  $d\mu_{\rho}$  is defined by

$$d\mu_o(x, t) = \frac{1}{\sqrt{\alpha_o}} \left( q_t^{\lambda} * q_\tau \right) \left( \frac{t}{\sqrt{\alpha_o}}, x \right) dx \, dt$$

with

$$q_t^{\lambda} * q_{\tau}(t, x) = \int_{\tau=0}^t q_{\tau}(\tau) q_{t,z}^{\lambda}(t-\tau, x) d\tau$$

(compare Lemma 2) and has moments

$$\bar{t} = \sqrt{\alpha_o} \cdot \left(\frac{1}{\sigma_o} + \int_0^\infty t q_t^\lambda \, dt\right) = \sqrt{\alpha_o} \cdot \left(\frac{1}{\sigma_o} + \frac{q_t^{(1)}}{1 - \lambda}\right)$$

and

$$\rho = \frac{1}{t} \int_0^\infty t^2 q_t^{\lambda}(t) dt \cdot \frac{1}{\sqrt{\pi}} \int_{-\infty}^\infty w^2 e^{-w^2} dw$$

$$= \frac{1}{4\sqrt{\alpha_o}} \cdot \frac{1+\lambda}{1-\lambda} \cdot \frac{\sigma_o \cdot q_t^{(2)}}{(1-\lambda) + \sigma_o \cdot q_t^{(1)}}$$
(18)

 $q_t^{(i)}$  being the *i*th moment of  $q_t$ .

The next corollary follows from the theorem.

**Corollary.** Let  $\sigma$  and  $\alpha$  be scaled according to (8) and (9). Then the evolution of a test particle in the infinite tube tends to a diffusion process with diffusion constant given by (18) as r tends to zero.

## 4. CLAUSING'S EXPERIMENT

In 1930, Clausing<sup>(1)</sup> proposed the following experiment for measuring the constant  $\tau_o = 1/\alpha$ , which is the mean time the particles are adsorbed at the wall during a diffuse reflection: Two vessels A and B are connected by a long capillary tube. Vessel A contains a gas while in B there is vacuum. At time t = 0, a valve is opened and gas molecules start streaming through the

tube from A to B. Assuming that the gas flow can be approximated by a diffusion, one can find out the diffusion constant  $\rho$  from the flow J(t) entering B. J(t) grows from zero at t=0 to a constant value. The time until J(t) becomes stationary depends in a characteristic way on  $\rho$ .

Clausing derived the following formula for the diffusion constant (Ref. 1, formula 45)

$$\rho = \frac{4}{3} \cdot \frac{r^2}{\tau_o + (2r/u)} \tag{19}$$

where r is the radius of the tube and u the mean velocity of the particles being reemitted from the wall. (u is proportional to the square root of the temperature of the wall.) From (19),  $\tau_o$  can be evaluated if  $\rho$  is known through an experiment.

In the time following Clausing's proposal, the diffusion ansatz for a transport problem like this was contested. While Armand<sup>(2)</sup> justified it, Gorenflo, Pacco, and Scherzer<sup>(3)</sup>—calling into doubt several arguments of Armand—thought to refuse this way of description by results of a Monte Carlo simulation. However, the most recent simulation result we know, which has been obtained by Willrich<sup>(4)</sup> (who seems to have been much more careful in producing statistical results) again confirms Clausing's ansatz. A similar conclusion has to be drawn from the results of Pack and Yamamoto.<sup>(5,6)</sup>

As we have shown in this paper, the diffusion ansatz is indeed a correct way of describing a Knudsen flow in thin cylinders. Moreover by (18), we have obtained an exact formula for the diffusion constant. Inserting  $\lambda = 0$ , the mean velocity corresponding to density (2)

$$u = \frac{3}{4} \cdot \sqrt{\pi}/\alpha$$

and the numerically evaluated quantities

$$\int_0^\infty t^2 q_t \, dt = 5, \, 3$$

and

$$\int_0^\infty tq_t\,dt=1,\,8$$

yields

$$\rho = 1, \ 3 \cdot \frac{r^2}{\tau_o + (2, 4r)/u} \tag{20}$$

which deviates only slightly from Clausing's result (19).

We do not go into details concerning the limiting behavior of a Knudsen flow in finite cylinders ( $a \le z \le b$ ). A convenient means is to consider the process  $Z_*^{(r)}$  stopped at  $T^*$ ,  $T^*$  being the time of the first passage out of the interval [a, b].

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