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Model of Nonequilibrium Ensemble: Knudsen Gas*

JOEL L. LEBOWITZ,† *Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut*

AND

HARRY L. FRISCH, *Bell Telephone Laboratories, Murray Hill, New Jersey*

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An example of a nonequilibrium ensemble is constructed, a Knudsen gas in a container whose walls are maintained at different temperatures. The approach to a stationary state is investigated, and an iteration procedure for finding the stationary velocity distribution is derived. An explicit stationary solution is found for the case where a Knudsen accommodation coefficient completely characterizes the effect of gas collisions with the walls. The heat transport is found. A stochastic mathematical model which mimics in certain aspects the above system is investigated.

1. INTRODUCTION

THE distribution in phase space of a system in equilibrium with its surroundings is specified by the values of a small number of suitable physical parameters, such as the temperature, chemical potential of the components, etc. To date no set of analogous parameters generally characterizing a distribution of systems not in equilibrium is known. Recently it has been possible to construct[1,2] models of Gibbs-type ensembles for open systems not in equilibrium which in principle at least would be capable of furnishing such a description. While the internal dynamics of the system is governed by its Hamiltonian H, the interactions of the system with its surroundings (reservoirs) are assumed to be described in terms of impulsive interactions (collisions). The surroundings are to consist of an infinite number of independent, identical components, each of which is to interact with the system but once.[2] The ensemble density, $\mu(\mathbf{x},t)$, in phase space of the system ($\mathbf{x}$), now obeys an integro-differential equation:

$$\frac{\partial\mu}{\partial t}+(\mu,H)=\int[K(\mathbf{x};\mathbf{x}')\mu(\mathbf{x}')-K(\mathbf{x}';\mathbf{x})\mu(\mathbf{x})]d\mathbf{x}',$$

where $K(\mathbf{x};\mathbf{x}')d\mathbf{x}'$ is the transition probability per unit time from the state $\mathbf{x}'$ to $\mathbf{x}$ due to collisions suffered by the system with the reservoirs. So far it has not been possible to find general solutions of this equation.

This paper stems from a previous attempt[3] to investigate a special class of these systems, namely those which interact with their surroundings only at their spatial boundaries.[4] The particular problem we shall study is that of an extremely rarified gas (i.e., a Knudsen gas), so that collisions between the molecules can be neglected, in a container whose walls are kept at different temperatures.[5-7] We shall exhibit explicit stationary nonequilibrium ensembles corresponding to particular stochastic models for the collisions between the gas and the walls. Certain properties of these stationary solutions (of the general integro-differential equation) will be derived and finally the approach to the stationary distribution will be investigated.

2. KNUDSEN GAS

We wish to describe the time evolution of a gas so rarified that collisions between the molecules composing it may be neglected. The only forces acting on a molecule arise at the walls of the container holding this Knudsen gas. As stated in the introduction the interaction between a molecule and a wall which here acts as our temperature reservoir is impulsive.[1,2] The state of a molecule (system) after a collision with the wall will be determined both by its own state and that of the wall at the "beginning" of the collision. We can only specify a certain probability that the walls are in some particular state prior to collision. In turn this implies that for any initial state of the molecule there will be many final states (after the collision) corresponding to different initial states of the wall. In short, in view of the nature of the reservoirs alluded to in the introduction[1,2] there will exist a stochastic kernel $K(\mathbf{v};\mathbf{v}')$ such that if the velocity of the system prior to collision is $\mathbf{v}'$, then $K(\mathbf{v};\mathbf{v}')d\mathbf{v}$ is the probability that the system will have a velocity in the range ($\mathbf{v}$, $\mathbf{v}+d\mathbf{v}$) after the collision.[8]

Without any loss in generality we may consider our container to be a right cylinder whose axis is the x axis of unit length, i.e., $0\leq x\leq 1$. We assume that molecules

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[†] National Science Foundation post-doctoral fellow.

[1] P. G. Bergmann and J. L. Lebowitz, Phys. Rev. **99**, 578 (1955).

[2] J. L. Lebowitz and P. G. Bergmann, Ann. Phys. **1**, 1 (1957).

[3] H. L. Frisch and J. L. Lebowitz, Phys. Rev. **95**, 643 (1954).

[4] The general problem of replacing the integro-differential equation by the Liouville equation with "stochastic boundary conditions" has been investigated by Salwen, Sadowski, and Bergmann, Bull. Am. Phys. Soc. Ser. II, **1**, 221 (1956).

[5] C. S. Wang Chang and G. E. Uhlenbeck, "The heat transport between two parallel plates as functions of the knudsen number," University of Michigan report, September, 1953 (unpublished).

[6] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), p. 311 ff.

[7] M. Knudsen, Ann. Physik **34**, 593 (1911).

[8] Note that the kernel function does not depend on time.

are perfectly reflected except from the normal bounding walls at $x=1$ and $x=0$. This reduces our problem to that of a one-dimensional gas.[9]

Let N be the total number of molecules in our gas, v the x component of their velocity. The probability of finding a particle in the interval $(x, x+dx)$ having its velocity in the range $(v, v+dv)$ at time t we denote by $f(x,v;t)dxdv$. The one-particle distribution function is normalized, i.e.,

$$\int_{-\infty}^{\infty} dv \int_0^1 f(x,v;t)dx=1. \tag{1}$$

At any time there will be two noninteracting streams of molecules; one going to the right with $v>0$ and one to the left with $v<0$. Because there are no collisions between the molecules, $f(x,v;t)$ may be discontinuous at $v=0$, not only near the walls but also in the interior. The mean free path is the length of the cylinder. We therefore break up $f(x,v;t)$ into two parts, one for each stream,

$$\begin{aligned} f(x,v;t) &= f_+(x,v;t) \quad \text{for } v>0 \\ &= f_-(x,v;t) \quad \text{for } v<0. \end{aligned} \tag{2}$$

Since no forces are acting in the interior of the cylinder, we can write

$$\begin{aligned} \partial f_+/\partial t + v\partial f_+/\partial x &= 0, \\ \partial f_-/\partial t - v\partial f_-/\partial x &= 0 \end{aligned} \tag{3}$$

in $0<x<1$, $v\geq 0$. The stochastic boundary conditions on f are

$$\begin{aligned} vf_+(0,v;t) &= \int_0^\infty K_0(v;v')v'f_-(0,v';t)dv', \\ vf_-(1,v;t) &= \int_0^\infty K_1(v;v')v'f_+(1,v';t)dv' \end{aligned} \tag{4}$$

with $K_0(v;v')$ and $K_1(v;v')$ the stochastic kernels for the walls $x=0$, and $x=1$. The specification of initial data for f_+ and f_- completely prescribes with (3) and (4) the temporal evolution of the distribution of the system.

From the definition of the kernels it follows that

$$P_i(v) = \int_0^\infty K_i(v';v)dv' = 1, \quad i=0,1. \tag{5}$$

This insures that the normalization of f is preserved in time.

The explicit form of the kernels, K, will depend on the nature of the forces between the system and the wall and on the temperature of the wall. When both walls are at the same temperature, $T_0=T_1=T$, we expect from the general principles of statistical mechanics that a stationary solution of (3) and (4) is the canonical distribution:

$$\begin{gathered} f_+(v) = f_-(v) = (1/Z)\exp[-\beta mv^2/2], \\ \beta=(kT)^{-1}, \quad Z=\int_{-\infty}^{\infty}\exp(-\beta mv^2/2)dv=(2\pi/\beta m)^{\frac{1}{2}}. \end{gathered} \tag{6}$$

A necessary and sufficient condition for this to be the case is that the kernels should have the following symmetry property[2]

$$K_i(v;v') = R_i(v;v')\exp(\beta_i mv'^2/2)/v', \tag{7}$$

where

$$\int_0^\infty R_i(v;v')dv' = \int_0^\infty R_i(v';v)dv', \quad i=0,1.$$

This can be verified by substituting the canonical distribution (6) into (3) and (4). Since our two walls act independently we may write in general (i.e., when $T_1\neq T_0$),

$$\begin{aligned} K_0(v;v') &= R_0(v;v')\exp[+\beta_0 mv'^2/2]/v', \\ K_1(v;v') &= R_1(v;v')\exp[+\beta_1 mv'^2/2]/v'. \end{aligned} \tag{8}$$

3. STATIONARY SOLUTIONS

One of the questions of greatest physical interest concerning the time evolution of a system obeying (3) and (4) is: Is a stationary distribution of the system independent of a given initial distribution attained in sufficiently long time and what is the form of this stationary distribution? It is clear from (3) that if we exclude the case where a finite fraction of molecules have zero velocity that any stationary solution will be independent of the position x. Let $f_+(v)$ and $f_-(v)$ be such distributions which by virtue of (4) satisfy

$$\begin{aligned} vf_+(v) &= \int_0^\infty K_0(v;v')v'f_-(v')dv', \\ vf_-(v) &= \int_0^\infty K_1(v;v')v'f_+(v')dv'. \end{aligned} \tag{9}$$

Substituting the first of these equations into the second and vice versa we find that

$$\begin{aligned} vf_-(v) &= \int_0^\infty K_2^-(v;v')v'f_-(v')dv', \\ vf_+(v) &= \int_0^\infty K_2^+(v;v')v'f_+(v')dv'. \end{aligned} \tag{10}$$

where

$$K_2^+(v;v') = \int_0^\infty K_0(v;v'')K_1(v'';v')dv'',$$

$$K_2^-(v;v') = \int_0^\infty K_1(v;v'')K_0(v'';v')dv''.$$

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[9] For real gases the neglect of the y and z dependence may not be justified.

The stochastic kernels K_2^+ and K_2^- are normalized [see (5)]:

$$\int_0^\infty K_2^+(v;v')dv=\int_0^\infty K_2^-(v;v')dv=1.$$

We shall now show that when a stationary distribution exists it will be approached in the course of time for almost all initial distributions. The proof consists in constructing a functional W, which is a minimum for the stationary distribution and showing that for any other distribution the time rate of change of W is negative. Let $f^s(v)$ be the stationary distribution satisfying (3) and (4). We define W to be

$$\begin{aligned} W&=\int_0^1\int_{-\infty}^\infty f(x,v;t)[\ln f(x,v;t)-\ln f^s(v)]dvdx \\ &=\int_0^1\int_{-\infty}^\infty [f(\ln f-\ln f^s)+f^s-f]dvdx \qquad (11) \\ &=\int_0^1\int_{+0}^\infty \{[f_+(\ln f_+-\ln f_+{}^s)+f_+{}^s-f_+] \\ &\qquad +[f_-(\ln f_--\ln f_-{}^s)+f_-{}^s-f_-]\}dvdx. \end{aligned}$$

The integrand in the square bracket is always positive[10] and is zero only when $f=f^s$. Hence W can serve as measure of the deviation of the distribution function at time t from the stationary distribution. The time rate of change of W when f obeys (3) and (4) is given, after some manipulations, by

$$\begin{aligned} \frac{dW}{dt}=&-\int_0^\infty dv\int_0^\infty dv'K_0(v;v')v'f_-{}^s(v') \\ &\times\{\varphi_-(0,v';t)\ln\varphi_-(0,v';t)-\varphi_-(0,v';t)\ln\varphi_+(0,v;t) \\ &\varphi_+(0,v;t)-\varphi_-(0,v';t)\}-\int_0^\infty dv\int_0^\infty dv' \qquad (12) \\ &\times K_1(v;v')v'f_+{}^s(v')\{\varphi_+(1,v';t)\ln\varphi_+(1,v';t) \\ &-\varphi_+(1,v';t)\ln\varphi_-(1,v;t)+\varphi_-(1,v;t) \\ &\qquad -\varphi_+(1,v';t)\}, \end{aligned}$$

where

$$\varphi_-(x,v;t)=f_-(x,v;t)/f_-{}^s(v)$$

and

$$\varphi_+(x,v;t)=f_+(x,v;t)/f_+{}^s(v).$$

The terms in the curly brackets are always nonnegative[10] and vanish if

$$\begin{aligned} \varphi_-(0,v';t)&=\varphi_+(0,v;t), \\ \varphi_-(1,v';t)&=\varphi_+(1,v;t). \end{aligned} \qquad (13)$$

Assuming that the velocity space cannot be decomposed into noncommunicating regions, other than the point $v=0$ which we shall ignore, such that a molecule starting out in one such region can never get to another one, then W will keep decreasing until (13) is satisfied. But (13) can remain an equality only if

$$\varphi_-=\varphi_+=1,\quad\text{or}\quad f_+=f_+{}^s\quad\text{and}\quad f_-=f_-{}^s.$$

Hence f will approach f^s as $t\to\infty$. We should note that when $T_1=T_2=T$, W reduces to the Helmholtz free energy divided by kT and dW/dt is the entropy production divided by k.

In the more general case when the two wall temperatures are not equal the entropy production σ is given by

$$\sigma=\dot{S}-J_0/T_0-J_1/T_1,$$

where the J's are the energy fluxes from the walls at $x=0$ and $x=1$ and S is the entropy of the system.[2] This σ is given by

$$\begin{aligned} \sigma=&\int\int_0^\infty R_0(v';v)\nu_-(0,v;t) \\ &\times[\ln\nu_-(0,v;t)-\ln\nu_+(0,v';t)]dvdv' \\ &+\int\int_0^\infty R_1(v',v)\nu_+(1,v;t)[\ln\nu_+(1,v;t) \\ &\qquad -\ln\nu_-(1,v';t)]dvdv'\geq 0, \end{aligned}$$

where

$$\nu_\mp(i,v;t)=\exp(\beta_i mv^2/2)f_\mp(i,v;t)\qquad i=0,1.$$

Minimizing the entropy production does not lead to the stationary distribution of velocities even for small wall-temperature differences.

In general the problem of solving for the stationary distribution $f^s(v)$ in (10) may be quite difficult. Still, by making use of the stochastic nature of the kernels K_2^+ and K_2^-, we can give an iteration procedure for improved approximations to the stationary distribution. Starting with some trial functions $f_+{}^0(v)$ and $f_-{}^0(v)$, we define

$$\begin{aligned} vf_+{}^{2n+2}(v)&=\int_0^\infty K_2^+(v;v')v'f_+{}^{2n}(v')dv', \\ vf_-{}^{2n+2}(v)&=\int_0^\infty K_2^-(v;v')v'f_-{}^{2n}(v')dv', \\ n&=0,1,\cdots. \end{aligned} \qquad (14)$$

We claim that

$$\begin{aligned} \lim_{n\to\infty} f_+{}^{2n}(v)&=f_+{}^s(v), \\ \lim_{n\to\infty} f_-{}^{2n}(v)&=f_-{}^s(v). \end{aligned} \qquad (15)$$

The outline of the proof of (15) follows that used above in showing the approach of the nonstationary distribution to the stationary one. The functional which is

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[10] Since $G(x;y)=x\int_1{}^{y/x}\ln t dt=y[\ln y-\ln x]-y+x\geq 0$.

now used is W_n where, e.g.,

$$W_{2n}=\int_0^\infty \{v\bar{f}_+^{2n}(v)[\ln f_+^{2n}(v)-\ln \bar{f}_+^{s}(v)] -vf_+^{2n}(v)+v\bar{f}^s(v)\}dv + \int_0^\infty \{vf_-^{2n}(v)[\ln f_-^{2n}(v)-\ln \bar{f}_-^{s}(v)] -vf_-^{2n}(v)+v\bar{f}^s(v)\}dv, \quad (16)$$

with

$$f_\mp^n=f_\mp^n(v)\bigg/\int_0^\infty vf_\mp^n(v)dv,$$

$$\bar{f}_\mp^s=f_\mp^s(v)\bigg/\int_0^\infty vf_\mp^s(v)dv.$$

We show then that $W_{2n+2}\leq W_{2n}$ unless $\bar{f}^n=\bar{f}^s$.

4. KNUDSEN GAS WITH ACCOMMODATION COEFFICIENTS AT THE WALLS

We consider now an explicit example of the foregoing theory. We will assume that at each wall a certain fraction of the incident molecules is specularly reflected while the remainder is diffusely reflected. The diffuse reflection is to be such as to lead to a redistribution of the velocities independent of the initial velocities of the molecules. This redistribution may be thought of as due to surface adsorption and subsequent release of the molecule at the wall. The kernels will have the form

$$K_0(v;v')=(1-\alpha_0)\delta(v-v')+\alpha_0 H_0(v),$$
$$K_1(v;v')=(1-\alpha_1)\delta(v-v')+\alpha_1 H_1(v); \quad (17)$$
$$\int_0^\infty H_i(v)dv=1,\quad i=0,1,$$

where $(1-\alpha_0)$ and $(1-\alpha_1)$ are the fraction of molecules specularly reflected at the walls at $x=0$ and $x=1$, respectively. In order to satisfy Eq. (7) we must choose $H_i(v)$, $i=0, 1$, to be

$$H_i(v)=v\exp(-\beta_i mv^2/2)\ (\beta_i m). \quad (18)$$

The thermal accommodation coefficient a_0 at the wall $x=0$ is defined to be:

$$a_0=(J_- - J_+)/(J_- - J_0'),$$

where J_- is the energy carried across per unit time by molecules moving towards the wall at $x=0$, J_+ is the corresponding energy carried by the molecules away from the wall, and J_0' is the energy which would be carried by the same current of molecules moving away from the wall if their velocity distribution were Maxwellian corresponding to the temperature T_0 of the wall at $x=0$. Since these energies are purely kinetic, we have

$$a_0=\frac{\displaystyle\int_0^\infty v^3f_-(v)dv-\int_0^\infty v^3f_+(v)dv}{\displaystyle\int_0^\infty v^3f_-(v)dv-\int_0^\infty v^3\exp(-\beta_0mv^2/2)dv\left[\int_0^\infty vf_-(v)dv\bigg/\int_0^\infty v\exp(-\beta_0mv^2/2)dv\right]}. \quad (19)$$

If we substitute $K_0(v;v')$ given by (17) and (18) into $vf_+(v)$ of (9) and insert this into (19), we find that $\alpha_0=a_0$ and by symmetry $\alpha_1=a_1$.

The stationary distribution corresponding to the kernels given by (17) and (18) can be found from (9) and (10) to be (see Appendix I)

$$f_+(v)=\frac{\alpha_0m\beta_0\exp(-\beta_0mv^2/2)+\alpha_1(1-\alpha_0)m\beta_1\exp(-\beta_1mv^2/2)}{\frac{1}{2}[\alpha_0(2-\alpha_1)(\pi m\beta_0/2)^{\frac{1}{2}}+\alpha_1(2-\alpha_0)(\pi m\beta_1/2)^{\frac{1}{2}}]},$$
$$f_-(v)=\frac{\alpha_1m\beta_1\exp(-\beta_1mv^2/2)+\alpha_0(1-\alpha_1)m\beta_0\exp(-\beta_0mv^2/2)}{\frac{1}{2}[\alpha_0(2-\alpha_1)(\pi m\beta_0/2)^{\frac{1}{2}}+\alpha_1(2-\alpha_0)(\pi m\beta_1/2)^{\frac{1}{2}}]}, \quad (20)$$

the kernel $K_2^+(v;v')$ being

$$K_2^+(v;v')=(1-\alpha_0)(1-\alpha_1)\delta(v-v')+\alpha_0m\beta_0v\exp(-\beta_0mv^2/2)+\alpha_1(1-\alpha_0)m\beta_1v\exp(-\beta_1mv^2/2). \quad (21)$$

From (20) we can calculate the rate of heat transfer from the wall at $x=0$ to that at $x=1$, J_0. J_0 is the difference between the heat transfer by molecules with $v>0$, J_+ and that by molecules with $v<0$, J_-, i.e.,

$$J_0=J_+-J_-. \quad (22)$$

We find that

$$J_0=\frac{\left(\dfrac{\alpha_0\alpha_1}{\alpha_0+\alpha_1-\alpha_0\alpha_1}\right)Nk(T_0-T_1)}{\left[\left(1+\dfrac{\alpha_0-\alpha_1}{\alpha_0+\alpha_1-\alpha_1\alpha_0}\right)\left(\dfrac{\pi m}{2kT_0}\right)^{\frac{1}{2}}+\left(1+\dfrac{\alpha_1-\alpha_0}{\alpha_0-\alpha_1-\alpha_0\alpha_1}\right)\left(\dfrac{\pi m}{2kT_1}\right)^{\frac{1}{2}}\right]}, \quad (23)$$

which to terms $O(T_0-T_1)^2$ reduces to

$$J_0=\left(\frac{\alpha_0\alpha_1}{\alpha_0+\alpha_1-\alpha_0\alpha_1}\right)\frac{Nk}{(2\pi m/kT_0)^{\frac{1}{2}}}(T_0-T_1).$$

This result differs from that given by Kennard[11] since we neglect the redistribution of kinetic energy in the y and z directions. For a truly one-dimensional gas the flux J given by Kennard reduces precisely to the above expression.

Thus, for this simple kernel we can find the stationary distribution explicitly. However, in order to study the "temporal" evolution of the distribution we must resort to a picture involving the discrete collisions. We mean by this that instead of looking directly at $f(x,v;t)$ we concentrate on a representative molecule of the gas and find the probability of its having a velocity in the range $(v, v+dv)$ after undergoing n collisions with the walls. We call this probability $p_n(v)dv$. Since we neglect interactions between the molecules there will be no change in the velocity of a particle between collisions with the wall. Assuming for simplicity that $f(x,v;0)=f_+(x,v;0)$, we set

$$p_0(v)=\int_0^1 dx f_+(x,v;0),$$

and hence

$$p_{2n+1}(v)=\int_0^\infty K_1(v;v')p_{2n}(v')dv',$$

$$p_{2n+2}(v)=\int_0^\infty K_0(v;v')p_{2n+1}(v')dv',$$

$$n=0,1,\cdots.$$

These equations are equivalent to (14) and make transparent the physical meaning of the iteration procedure given there. As was shown there, when a stationary distribution exists, then

$$\lim_{n\to\infty}p_{2n+1}(v)=\lim_{t\to\infty}\frac{vf_-(x,v;t)}{\int_0^\infty vf_-(x,v;t)dv}=\frac{vf_-^s(v)}{\int_0^\infty vf_-^s(v)dv},$$

$$\lim_{n\to\infty}p_{2n+2}(v)=\lim_{t\to\infty}\frac{vf_+(x,v;t)}{\int_0^\infty vf_+(x,v;t)dv}=\frac{vf_+^s(v)}{\int_0^\infty vf_+^s(v)dv}.$$

At any given time,

$$f_+(x,v;t)=\sum_{n=0}^\infty \Phi_{2n}(x,v;t)$$

and

$$f_-(x,v;t)=\sum_{n=0}^\infty \Phi_{2n+1}(x,v;t),$$

where $\Phi_n(x,v;t)$ is the number density of particles in $(x, x+dx; v, v+dv)$ at time t which have undergone n collisions in the interval from 0 to t. The Φ's obey

$$\begin{aligned}v\Phi_{2n}(x,v;t)&=v\Phi_{2n}(0,v;t-x/v)\\&=\int_0^\infty K_0(v;v')v'\Phi_{2n-1}(0,v';t-x/v)dv'\\&\qquad\qquad\text{for } t-x/v>0\\&=0\quad\text{for } t-x/v\leq 0;\quad n>0,\end{aligned}$$

with a similar equation for Φ_{2n-1}. We thus can exhibit the relation between the temporal distribution and the discrete collisional distribution in the form

$$p_{2n}(v)=\lim_{T\to\infty}p_{2n}(x,v;T),$$

where

$$p_{2n}(x,v;T)=\int_0^T \Phi_{2n}(x,v;t)dt.$$

In the limit as $T\to\infty$, $p_{2n}(x,v;T)$ becomes independent of x, *viz.*,

$$p_{2n}(v)=\lim_{T\to\infty}\int_0^{T-x/v}d\xi\, v\,\Phi_{2n}(0,v;\xi).$$

In the next section we introduce a mathematical model in which the system is described wholly by the discrete collisional distribution.

5. MATHEMATICAL MODEL

Consider again a Knudsen gas in a right cylinder. Rather than following the behavior of this gas in time we fix our attention on the collisions suffered by a representative molecule with the walls. Without loss in generality we assume that the representative molecule starts with a positive velocity and thus collides first with the wall at $x=1$. Subsequently every even collision occurs at the wall $x=0$ and every odd collision at the wall $x=1$. Let the energy of the molecule after the $2n$th collision be $e(2n)$. This energy remains unchanged during the flight of the molecule from $x=0$ to $x=1$ [see (3)]. We assume that the collision with the walls is such that a fractional $1-a_i$ of the incident energy of the molecule is conserved and an extra positive increment $a_i\eta_i(n)$ is added to the nth collision, i.e.,

$$\begin{gathered}e(2n)=(1-a_0)\,e(2n-1)+a_0\eta_0(2n),\\ e(2n-1)=(1-a_1)e(2n-2)+a_1\eta_1(2n-1);\quad(24)\\ 0<a_i\leq 1.\end{gathered}$$

The random energies $\eta_i(n)$ are independent of one another, $\eta_0(2n)$ is independent of $e(2n-1)$, and $\eta_1(2n-1)$ is independent of $e(2n-2)$ for all n. We also assume that the probability density distribution of the $\eta_0(2n)$, $g_0(\eta)$, and the probability density distribution of $\eta_1(2n-1)$, $g_1(\eta)$ are the same for all values of n. Then $g_i(\eta)d\eta$ is the probability of finding $\eta_i(n)$ in the range

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[11] Reference 6, p. 317.

$(\eta, \eta+d\eta)$. One can show (see Appendix II) that if $f_+^{2n}(e)de$ denotes the probability that the molecule possesses an energy lying in the range $(e, e+de)$ after the $2n$th collision then

$$f_+^{2n}(e-\gamma^{2n}e(0))=\int_0^\infty h(e-\gamma e')f_+^{2n-2}(e'-\gamma^{2n}e(0))de' \tag{25}$$

where

$$\gamma=(1-a_1)(1-a_0)<1,$$

$$h(e)=\int_0^\infty g_0(e')g_1[e(a_1-a_1a_0)^{-1}-e'a_0(a_1-a_1a_0)^{-1}]de',$$

with $e(0)$ the initial energy of the molecule. If

$$\bar{e}=\int_0^\infty eh(e)de<\infty,\quad \int_0^\infty [e-\bar{e}]^2h(e)de<\infty, \tag{26}$$

then

$$\lim_{n\to\infty} f_+^{2n}(e-\gamma^{2n}e(0))=f_+^s(e),$$

exists almost everywhere and satisfies

$$f_+^s(e)=\int_0^\infty h(e-\gamma e')f_+^s(e')de'. \tag{27}$$

A similar equation is satisfied by $f_-^s(e)$ for a molecule possessing initially a negative velocity. Equation (26) is the analog of (10) since $e=\frac{1}{2}mv^2$; hence

$$vf_+^s(\tfrac{1}{2}mv^2)=\int_0^\infty vh[\tfrac{1}{2}m(v^2-\gamma v'^2)]mv'f_+^s(\tfrac{1}{2}mv'^2)dv',$$

or

$$K_2^+(v;v')=mvh[\tfrac{1}{2}m(v^2-\gamma v'^2)].$$

We assume that the average random energy imparted by the wall to the molecule is directly proportional to the temperature of the wall, thus

$$(m/k)\langle\eta(2n)\rangle=T_0,\quad (m/k)\langle\eta(2n-1)\rangle=T_1.$$

Similarly, if we denote by $\vartheta_+(2n)$ the temperature of the molecule leaving the wall at $x=0$ after the $2n$th collision, we can set

$$\vartheta_+(2n)=\frac{m}{k}\int_0^\infty ef_+^{2n}(e)de=(m/k)\langle e(2n)\rangle,$$

and

$$\vartheta_-(2n-1)=(m/k)\langle e(2n-1)\rangle.$$

From (24) it follows that, for all n,

$$\begin{aligned} a_0&=\frac{\vartheta_+(2n)-\vartheta_-(2n-1)}{T_0-\vartheta_-(2n-1)},\\ a_1&=\frac{\vartheta_-(2n-1)-\vartheta_+(2n-2)}{T_1-\vartheta_+(2n-2)}. \end{aligned} \tag{28}$$

These relations although they may be thought of as defining a thermal accommodation coefficient are not identical with that introduced by Knudsen and used by us in the previous section, since the ϑ's are the temperatures of a representative molecule and not the energy carried per unit time by the stream of molecules moving in either direction. Finally if the conditions (26) are fulfilled then as the number of collisions becomes sufficiently large, i.e., $n\to\infty$,

$$\vartheta_+(2n)\to\vartheta_+=\frac{(1-a_0)a_1T_1+a_0T_0}{a_1+a_2-a_1a_0} \tag{29}$$

exponentially with n. The relaxation number of collisions for this approach, n_r, is (see Appendix II).

$$n_r=[\ln(1/\gamma)]^{-1}. \tag{30}$$

Similar results apply to the higher energy moments. The same temperature discontinuity found for ϑ_+ or ϑ_- [see (29)] also holds for the temperatures of the gas streams in our previous model, as can be verified directly from (20).

APPENDIX I

To find $f_+(v)$, we first calculate K_2^+. Substituting (17) and (18) into (10), we find

$$\begin{aligned} K_2^+(v;v')=\int_0^\infty dv''\{[(1-\alpha_0)\delta(v-v'')\\ +\alpha_0\beta_0mv\exp(-\beta_0mv^2/2)][(1-\alpha_1)\delta(v''-v')\\ +\alpha_1\beta_1mv''\exp(-\beta_1mv''^2/2)]\}\\ =(1-\alpha_0)(1-\alpha_1)\delta(v-v')+\alpha_0m\beta_0v\\ \times\exp(-\beta_0mv^2/2)+\alpha_1(1-\alpha_0)m\beta_1v\exp(-\beta_1mv^2/2). \end{aligned}$$

Substituting this into (10) and letting

$$\psi=\int^\infty v'f_+(v')dv',$$

we find that

$$\begin{aligned} f_+(v)=\frac{\psi}{\alpha_0+\alpha_1-\alpha_0\alpha_1}\{\alpha_0m\beta_0\exp(-\beta_0mv^2/2)\\ +\alpha_1(1-\alpha_0)m\beta_1\exp(-\beta_1mv^2/2)\}; \end{aligned}$$

$f_-(v)$ is found from the above by changing $\alpha_0\to\alpha_1$ and $\beta_0\to\beta_1$. The function ψ is found by virtue of (1) to be

$$\begin{aligned} 1=\frac{\psi}{2(\alpha_0+\alpha_1-\alpha_0\alpha_1)}\{a_0(2-\alpha_1)(\pi m\beta_0/2)^{\frac{1}{2}}\\ +\alpha_1(2-\alpha_0)(\pi m\beta_1/2)^{\frac{1}{2}}\}. \end{aligned}$$

APPENDIX II

The recurrence relation (24) allows us to find by iteration $e(2n)$ in terms of the various η's and $e(0)$, *viz.*,

$$e(2n)-\gamma^{2n}e(0)=\sum_{i=0}^{n-1}\gamma^i\{(1-a_0)a_1\eta_1(2n-2i-1)+a_0\eta_0(2n-2i)\}. \qquad (31)$$

To proceed further, we extend the definitions of $g_i(\eta)$ and $f_+^{2n}(e)$ to negative values of the arguments by requiring that

$$g_i(\eta)=0 \quad \text{for } -\infty<\eta<0,$$
$$f_+^{2n}(e)=0 \quad \text{for } -\infty<e<0.$$

We can then introduce the absolutely continuous distribution functions $G_i(\eta)$ and $F_+^{2n}(e)$:

$$G_i(\eta)=\int_{-\infty}^{\eta}g_i(\eta')d\eta',$$

$$F_+^{2n}(e)=\int_{-\infty}^{e}f_+^{2n}(e')de'.$$

Since the η_0 and η_1 are independent, the distribution function of the $(1-a_0)a_1\eta_1(2n-2i-1)+a_0\eta_0(2n-2i)$ for all values of i and n, $H(e)$, is

$$H(e)=\int_0^{\infty}G_0(e')G_1\left[\frac{e}{(1-a_0)a_1}-\frac{a_0e'}{(1-a_0)a_1}\right]de'. \qquad (32)$$

Equation (25) now follows by virtue of (31) and (32) since

$$(1-a_0)a_1\eta_1(2n-2i-1)+a_0\eta_0(2n-2i)$$

are independent random variables.

To show the approach to a stationary distribution, we introduce the reduced variables

$$y_n=e(2n)-\bar{e}(2n)-\gamma^{2n}\{e(0)-\bar{e}(0)\},$$

where

$$\bar{e}(2n)=\int_{-\infty}^{\infty}e(2n)dH[e(2n)]<\infty$$

and

$$x_{n-i}=(1-a_0)a_1\{\eta_1(2n-2i-1)-\bar{\eta}_1(2n-2i-1)\}+a_0\{\eta_0(2n-2i)-\bar{\eta}_0(2n-2i)\}.$$

The relation between the y_n and the x_{n-i} follows from (31), *viz.*,

$$y_n=\sum_{i=0}^{n-1}\gamma^i x_{n-i};\quad 0<\gamma<1, \qquad (33)$$

where the mutually independent, commonly distributed x_{n-i} possess the distribution function $H(e-\bar{e})$. We now will show that the distribution function $F_+^{2n}(e)$ of y_n converges to a stationary distribution function $F_+(e)$ as $n\rightarrow\infty$ under condition (26) that $\bar{x}_{n-1}{}^2<\infty$. To do this we consider the sequence $\tilde{y}_1, \tilde{y}_2, \cdots$ where

$$\tilde{y}_n=\sum_{i=0}^{n-1}\gamma^i x_i,$$

with x_i one of the x_{n-i}'s. It is known[12] that if $x_{n-i}<\infty$ the $\tilde{y}_n$ converge in mean of order two and hence converge in distribution, i.e., if $\tilde{F}_+^{2n}(e)$ is the distribution function of $\tilde{y}_n$ then there exists a distribution function $F_+(e)$ such that

$$\tilde{F}_+^{2n}(e)\rightarrow F_+(e) \text{ essentially as } n\rightarrow\infty.$$

But since the x_i are independent and possess a common distribution function $H(e-\bar{e})$, we note that $F_+^{2n}(e)=\tilde{F}_+^{2n}(e)$: Hence

$$F_+^{2n}(e)\rightarrow F_+(e) \text{ essentially as } n\rightarrow\infty. \qquad (34)$$

Since for $e(0)<\infty$, $y_n\rightarrow e(2n)-\bar{e}(2n)$ as $n\rightarrow\infty$, and y_n possesses a stationary distribution, then so does $e(2n)$. Equation (34) insures the desired approach to a stationary state. Equations (34) and (35) imply (27).[13]

Finally we study the approach to the stationary state of the average energy. From (31) we find, on averaging,

$$\langle e(2n)\rangle-\gamma^{2n}\langle e(0)\rangle=\left(\frac{k}{m}\right)\sum_{i=0}^{n-1}\gamma^i\{(1-a_0)a_1T_1+a_0T_0\}.$$

Evaluating this sum and multiplying both sides of this equation by k/m, we obtain [see (29)]

$$\vartheta_+(2n)-\gamma^{2n}\vartheta_+(0)=\vartheta_+(1-\gamma^{2n}),$$

or

$$\vartheta_+(2n)-e^{-2n/n_r}\vartheta_+(0)=\vartheta_+(1-e^{-2n/n_r}), \qquad (35)$$

with n_r given by (30).

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[12] See, e.g., J. L. Doob, *Stochastic Processes* (John Wiley and Sons, Inc., New York, 1953), p. 154 ff.

[13] Since $y_{n+1}-y_n=(\gamma-1)y_n+x_{n+1}$, we can immediately conclude that y_n does *not* converge in probability, i.e., for any $\epsilon>0$, $\lim_{n\rightarrow\infty}\Pr(|y_{n+1}-y_n|>\epsilon)\neq0$.