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The relaxation to equilibrium of a confined gas

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Abstract. The rate and manner of a monatomic gas relaxing to equilibrium in a confined enclosure is studied. We point out the nature of the eigenvalue spectrum associated with the linearized Boltzmann equation and the effect on this of the gas–surface scattering interaction. In particular, we note the existence of a long-lived sinusoidally-damped behaviour which depends on the viscosity and thermal conductivity of the gas, the gas–surface interaction and the size of the container. General results are obtained using transport theory, and more explicit expressions in the hydrodynamic limit.

1. Introduction

The rate and manner of the relaxation to equilibrium of a spatially uniform gas have been studied by a number of authors, whose findings are summarized by Williams (1971). In general, it is found that, after an initially very rapid non-exponential decay, the distribution function approaches the Maxwellian form exponentially with a decay constant which is characterized by the force law between the constituent atoms. The nature of this decay has been studied in some detail for the Maxwell and hard-sphere models.

In addition to the isotropic disturbance, the rates of relaxation of the angular harmonics have been examined and their characteristic decay times calculated. The more difficult problem of a spatially non-uniform disturbance has only recently been cursorily examined by Kuščer (1969). Kuščer has considered the gas to be confined in a convex container of volume V and temperature T. He notes that the rate of relaxation of the disturbed gas is now governed by the scattering law describing interactions of the gas atoms with the walls of the container as well as the interatomic scattering law. One interesting consequence of this fact is that the equilibrium solution of the Boltzmann equation is the Maxwellian function corresponding to a simple zero eigenvalue. In the case of the infinite medium mentioned earlier it can be shown that momentum and energy multiplied by the Maxwellian are also eigenfunctions corresponding to zero eigenvalues.

Kuščer's basic analysis depended on the isotropic scattering approximation which, in gas theory, is well known to lead to violation of momentum and energy in interparticle interactions and therefore to incorrect results regarding the decay rate of disturbances. Such an approximation was made earlier by Williams (1968a) when studying the propagation of sound waves in pipes. It is interesting to note that a similar behaviour regarding the absence of momentum and energy eigenfunctions was found in this case also and more will be said about the phenomenon below.

The purpose of the present paper is to expand on Kuščer's initial study, with particular regard to the limitations of the isotropic scattering approximation which we shall show, contrary to Kuščer's assertions, can lead to new difficulties and introduce further interesting phenomena. Our general analysis will be based upon the Boltzmann transport equation but for ease of computation we also employ the associated hydrodynamic approximation.

2. General theory

The basic equation describing the decay of a gas to equilibrium following a disturbance is

$$\left(\frac{\partial}{\partial t}+\boldsymbol{v}\cdot\nabla\right)f(\boldsymbol{v},\boldsymbol{r},t)=J(f,f) \tag{1}$$

where $f(\ldots)$ is the particle distribution function and $J(\ldots)$ the collision operator.

If the gas is confined, it is subject to a boundary condition of the form

$$-\boldsymbol{v}\cdot\boldsymbol{n}f(\boldsymbol{v},\boldsymbol{r}_{\mathrm{s}},t)=\int_{\boldsymbol{v}'\cdot\boldsymbol{n}>0}\mathrm{d}\boldsymbol{v}'\,\boldsymbol{v}'\cdot\boldsymbol{n}P(\boldsymbol{v}'\rightarrow\boldsymbol{v}\,;\boldsymbol{r}_{\mathrm{s}})f(\boldsymbol{v}',\boldsymbol{r}_{\mathrm{s}},t) \tag{2}$$

where $\boldsymbol{v}\cdot\boldsymbol{n}<0$, $\boldsymbol{n}$ being a unit normal pointing out of the gas as the point $\boldsymbol{r}_{\mathrm{s}}$ on the surface of the container. $P(\boldsymbol{v}'\rightarrow\boldsymbol{v},\boldsymbol{r}_{\mathrm{s}})$ is the wall-particle scattering kernel as discussed by Kuščer (1971).

We are interested only in small deviations from equilibrium and therefore write

$$f(\boldsymbol{v},\boldsymbol{r},t)=f_{\mathrm{M}}(\boldsymbol{v})(1+h(\boldsymbol{v},\boldsymbol{r},t)) \tag{3}$$

where

$$f_{\mathrm{M}}(\boldsymbol{v})=n_0\left(\frac{m}{2\pi kT}\right)^{3/2}\mathrm{e}^{-mv^2/2kT} \tag{4}$$

is the equilibrium distribution and h is the perturbation whose behaviour is of interest.

Insertion of (3) into (1) and neglect of second-order terms leads to the following linear transport equation for $h(\boldsymbol{v},\boldsymbol{r},t)$:

$$\left(\frac{\partial}{\partial t}+\boldsymbol{v}\cdot\nabla+V(v)\right)h(\boldsymbol{v},\boldsymbol{r},t)=\int\mathrm{d}\boldsymbol{v}'\,K(\boldsymbol{v}'\rightarrow\boldsymbol{v})\,\mathrm{e}^{-mv'^2/2kT}h(\boldsymbol{v}',\boldsymbol{r},t) \tag{5}$$

and for the boundary condition

$$-\boldsymbol{v}\cdot\boldsymbol{n}h(\boldsymbol{v},\boldsymbol{r}_{\mathrm{s}},t)=\int_{\boldsymbol{v}'\cdot\boldsymbol{n}>0}\mathrm{d}\boldsymbol{v}'\,\boldsymbol{v}'\cdot\boldsymbol{n}P(\boldsymbol{v}'\rightarrow\boldsymbol{v};\boldsymbol{r}_{\mathrm{s}})\,\mathrm{e}^{-mv'^2/2kT}h(\boldsymbol{v}',\boldsymbol{r}_{\mathrm{s}},t). \tag{6}$$

We shall be interested in the existence of solutions of equation (5) subject to the boundary condition (6), in the form

$$h(\boldsymbol{v},\boldsymbol{r},t)\sim h_\lambda(\boldsymbol{v},\boldsymbol{r})\,\mathrm{e}^{-\lambda t}. \tag{7}$$

The equation for h_λ is therefore

$$(V(v)-\lambda+\boldsymbol{v}\cdot\nabla)h_\lambda(\boldsymbol{v},\boldsymbol{r})=\int\mathrm{d}\boldsymbol{v}'\,K(\boldsymbol{v}'\rightarrow\boldsymbol{v})\,\mathrm{e}^{-mv'^2/2kT}h_\lambda(\boldsymbol{v}',\boldsymbol{r}) \tag{8}$$

with the boundary condition as for $h(\ldots)$ in equation (6).

We therefore have an eigenvalue problem for λ. Kuščer has made the point that the line $\mathrm{Re}(\lambda)=\tilde{\lambda}$, where $\tilde{\lambda}=(V(v))_{\min}$, is a natural dividing line for studying eigenvalues. $\mathrm{Re}(\lambda)>\tilde{\lambda}$ is generally associated with singular solutions representing the rapid initial transients whilst $\mathrm{Re}(\lambda)<\tilde{\lambda}$ is expected to contain isolated discrete eigenvalues $\lambda_0, \lambda_1, \ldots \lambda_N$.

The sequence of discrete eigenvalues will in general be very much more complicated than in the case of the infinite medium. This is because we must examine spatial modes as well as energy and angular ones. In the present work we confine ourselves to the case of the fundamental spatial mode and to the rate and manner at which this decays.

3. Elementary spatial solutions

Kuščer has attacked the problem by using the isotropic scattering approximation for $K(\boldsymbol{v}'\to\boldsymbol{v})$, i.e.

$$K(\boldsymbol{v}'\to\boldsymbol{v})\simeq\frac{1}{4\pi}K_0(v'\to v) \tag{9}$$

and has converted (8) into an integral equation for the angular integrated disturbance

$$h_\lambda^{(0)}(v,\boldsymbol{r})=\int \mathrm{d}\boldsymbol{\Omega}_v h_\lambda(\boldsymbol{v},\boldsymbol{r}). \tag{10}$$

At this stage, however, we wish to avoid the approximation implied by (9) and so look for further elementary solutions in the form

$$h_\lambda(\boldsymbol{v},\boldsymbol{r})\sim\tilde{h}_\lambda(\boldsymbol{v},\pm\boldsymbol{B})\,\mathrm{e}^{\pm\mathrm{i}\boldsymbol{B}\cdot\boldsymbol{r}} \tag{11}$$

where $\boldsymbol{B}$ is an arbitrary vector to be defined below.

With (11), equation (8) can be written

$$(V(v)-\lambda\pm\mathrm{i}\boldsymbol{v}\cdot\boldsymbol{B})\tilde{h}_\lambda(\boldsymbol{v},\pm\boldsymbol{B})=\int \mathrm{d}\boldsymbol{v}'\,K(\boldsymbol{v}'\to\boldsymbol{v})\,\mathrm{e}^{-mv'^2/2kT}\tilde{h}_\lambda(\boldsymbol{v}',\pm\boldsymbol{B}). \tag{12}$$

Now, choosing the direction of $\boldsymbol{B}$ such that $\boldsymbol{v}\cdot\boldsymbol{B}=vB\cos\theta\equiv vB\mu$, we can rewrite (12) in the form

$$\begin{aligned}(V(v)-\lambda\pm\mathrm{i}vB\mu)&\tilde{h}_\lambda(v,\mu,\pm B)\\&=\sum_{l=0}^{\infty}\frac{2l+1}{2}\mathrm{P}_l(\mu)\int_0^\infty \mathrm{d}v'\,v'^2K_l(v'\to v)\,\mathrm{e}^{-mv'^2/2kT}h_l(v',\lambda,\pm B)\end{aligned} \tag{13}$$

where

$$K(\boldsymbol{v}'\to\boldsymbol{v})=\sum_{l=0}^{\infty}\frac{2l+1}{4\pi}K_l(v'\to v)\mathrm{P}_l(\hat{\boldsymbol{v}}'\cdot\hat{\boldsymbol{v}}) \tag{14}$$

$$\tilde{h}_\lambda(v,\mu,B)=\int_0^{2\pi}\mathrm{d}\phi\,\tilde{h}_\lambda(\boldsymbol{v},B) \tag{15}$$

and

$$h_l(v,\lambda,B)=\int_{-1}^{1}\mathrm{d}\mu\;\mathrm{P}_l(\mu)\int_0^{2\pi}\mathrm{d}\phi\,\tilde{h}_\lambda(\boldsymbol{v},B) \tag{16}$$

with $\mathrm{d}\boldsymbol{\Omega}_v=\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$.

Dividing (13) by $(V(v)-\lambda\pm \mathrm{i}vB\mu)$, multiplying by $\mathrm{P}_m(\mu)$ and integrating over $\mu(-1,1)$, leads to the following set of coupled integral equations for the angular moments $h_l(\ldots)$:

$$h_m(v,\lambda,\pm B)=\sum_{l=0}^{\infty}\frac{2l+1}{2}\int_{-1}^{1}\frac{\mathrm{d}\mu\ \mathrm{P}_l(\mu)\mathrm{P}_m(\mu)}{V(v)-\lambda\pm \mathrm{i}Bv\mu}\int_0^{\infty}\mathrm{d}v'\,v'^2K_l(v'\to v)\,\mathrm{e}^{-mv'^2/2kT}$$
$$\times h_l(v',\lambda,\pm B). \tag{17}$$

We thus have an eigenvalue problem for λ as a function of the parameter B. Whilst a solution of these equations is feasible, either by numerical methods or pertubation theory, we can avoid a great deal of labour by simply noting that equation (12) is nothing more than the sound wave dispersion law equation with $-\mathrm{i}\lambda=\omega$, the frequency, and $B=K$, the wavenumber. For small values of ω it is known (Wang Chang and Uhlenbeck 1952) that ω and K are related by the formula

$$K=\pm\frac{\omega}{V_0}(1-a\omega^2)\pm\frac{\mathrm{i}\omega^2}{\rho V_0^3}\left(\frac{2}{3}\mu_\mathrm{v}=\frac{2m}{15k}\lambda_\mathrm{T}-b\omega^2\right)+\ldots \tag{18}$$

where V_0 is the normal velocity of sound $(5kT/3m)^{1/2}$, ρ is the gas density, μ_v is the viscosity and λ_T the thermal conductivity. a and b are constants which are functions of μ_v and λ_T.

In addition there is another root

$$K=\left(\frac{2\rho \mathrm{i}\omega}{3\mu_\mathrm{v}}\right)^{1/2}+\ldots$$

which corresponds to a diffusive rather than a propagating mode. We shall, however, not consider this further complication.

Associating λ with $\mathrm{i}\omega$ and B with K and inverting the series we find that

$$\lambda=\pm \mathrm{i}BV_0+\frac{1}{\rho}\left(\frac{2m}{15k}\lambda_\mathrm{T}+\frac{2}{3}\mu_\mathrm{v}\right)B^2+\ldots\equiv\pm \mathrm{i}BV_0+\eta B^2+\ldots. \tag{19}$$

In terms of the elementary solutions, therefore, we can write the form of decay of $h(\boldsymbol{v},\boldsymbol{r},t)$ in a system for which h varies only in the x direction as

$$h(\boldsymbol{v},x,t)\sim\tfrac{1}{2}\mathrm{e}^{-\lambda t}(\tilde{h}_\lambda(\boldsymbol{v},B)\,\mathrm{e}^{\mathrm{i}Bx}+\tilde{h}_\lambda(\boldsymbol{v},-B)\,\mathrm{e}^{-\mathrm{i}Bx})$$
$$+\tfrac{1}{2}\mathrm{e}^{\lambda^* t}(\tilde{h}_\lambda^*(\boldsymbol{v},B)\,\mathrm{e}^{-\mathrm{i}Bx}+\tilde{h}_\lambda^*(\boldsymbol{v},-B)\,\mathrm{e}^{\mathrm{i}Bx}) \tag{20a}$$

or with $\tilde{h}_\lambda(\boldsymbol{v},B)=\Lambda_0(\boldsymbol{v},B)+\mathrm{i}\Lambda_1(\boldsymbol{v},B)$ and $\lambda=\alpha+\mathrm{i}\beta$, in the more suggestive form

$$h(\boldsymbol{v},x,t)\sim\mathrm{e}^{-\alpha t}[\Lambda_0(\boldsymbol{v},B)\cos(Bx-\beta t)+\Lambda_0(\boldsymbol{v},-B)\cos(Bx+\beta t)$$
$$-\Lambda_1(\boldsymbol{v},B)\sin(Bx-\beta t)+\Lambda_1(\boldsymbol{v},-B)\sin(Bx+\beta t)]. \tag{20b}$$

We note therefore that the gas relaxes to equilibrium in the form of damped travelling waves. The decay constant ηB^2 depends upon the values of the viscosity, thermal conductivity and gas density and also on B. Similarly the frequency β of the damped oscillation is equal to V_0B. It remains, therefore, to discuss the nature of B. Before doing so, however, let us consider Kuščer's approximation of isotropic scattering. In that case the value of λ is given by

$$\lambda=D_0B^2+\ldots \tag{21}$$

where D_0 is the Maxwellian average of the solution of a certain integral equation. For Maxwell molecules D_0 is equal to $3\mu_v/2\rho$ which corresponds to the diffusive mode mentioned earlier.

It may be seen from this approximation that the complete character of the decay has been changed since, owing to the absence of the complex terms in λ, the decay is simply exponential. Clearly, therefore, a realistic description of the scattering kernel $K(\boldsymbol{v}'\rightarrow\boldsymbol{v})$ is required.

4. The parameter B

We have not yet specified B, and in order to do this it is necessary to introduce the boundary conditions of the problem. To anticipate the result, we shall note that, for a gas confined by parallel plates at $x=-d/2$ and $x=d/2$ with a combination of diffuse and specular boundary conditions, the smallest value of B is given by $B=\pi/(d+2x_0(B))$. For small values of B, the quantity $x_0(B)$ is independent of B, thus B can be viewed as a measure of the system size. The analogy with neutron transport theory is self-evident, where B^2 is referred to as the *buckling* of the system.

We see, then, from equation (20) that for large systems the rate of decay to equilibrium is small and the frequency of oscillations also small. For example in hydrogen gas at 300K and a pressure of 76 cm Hg confined between plates 10 cm apart, we find that $V_0=10^5\ \mathrm{cm\,s^{-1}}$ and hence $BV_0\simeq 0{\cdot}3\times10^5\ \mathrm{s^{-1}}$. Using the fact that $\lambda_{\mathrm{T}}=15k\mu_v/4m$ we get for hard spheres

$$\eta = l_f\times10^5\ \mathrm{cm^2\,s^{-1}}$$

where l_f is the mean free path of hydrogen atoms. According to Newman and Searle (1950) l_f at NTP is about 10^{-5} cm, thus η is of order unity. The decay constant ηB^2 is then roughly $0{\cdot}1\ \mathrm{s^{-1}}$ which corresponds to a relaxation time $\tau(=1/\eta B^2)$ of 10 s. This is a remarkably long time and indicates that in relaxing to equilibrium the disturbance travels back and forth between the boundaries many thousands of times before finally settling down. This is in contrast to neutron decay in a moderator which relaxes to equilibrium in milliseconds.

We have only mentioned superficially the significance of B and have not indicated how it should be obtained from the transport equation. The complete calculation is beyond the scope of the present paper; however, a few words are in order. Basically, the method is similar to that used in neutron transport calculations and can be tackled in one of two distinct ways. In the first, the transport equation is treated in its full generality with no approximations being made to the kernel or the boundary conditions. The solution is written in the form

$$h_\lambda(\boldsymbol{v},x)=\tilde{h}_\lambda(\boldsymbol{v},B)\,\mathrm{e}^{\mathrm{i}Bx}+\tilde{h}_\lambda(\boldsymbol{v},-B)\,\mathrm{e}^{-\mathrm{i}Bx}+\rho_{\mathrm{T}}(\boldsymbol{v},x) \tag{22}$$

where $\rho_{\mathrm{T}}(\boldsymbol{v},x)$ is a so called spatially transient term which is expected to be small at a distance of several mean free paths from the boundaries. The other two terms on the right-hand side are referred to as asymptotics and are expected to dominate the solution over the main volume of the enclosure. A variational principle is formed by converting the integro-differential transport equation to integral form including the boundary conditions, and the extremum of the associated functional can be shown to be related to B. This result then links B to the size of the system and its physical properties. Examples of this technique can be found in Williams (1968a) and Kladnik (1965). The result is, as predicted, of the form $B=\pi/(d+2x_0(B))$ for a parallel-plate system. However, in contrast to the neutron case, $x_0(B)$ can depend quite strongly on the wall–particle boundary condition and for purely specular reflection will become infinite. $x_0(B)$ is also in general a complex quantity.

The other method for obtaining B is to attempt an analytic solution of the transport equation. This, however, is only successful if very simple models of scattering are employed when such methods as the Wiener–Hopf technique (Placzek and Seidel 1947) can be employed. We shall discuss these matters at length in another publication.

The questions that are generally asked regarding relaxation problems concern the existence of discrete decay constants λ_n. We note from our perturbation analysis for small B that increasing B moves the real part of the eigenvalues λ and λ^* nearer to the line $\mathrm{Re}(\lambda)=\tilde{\lambda}$. What is not clear is the behaviour of λ for very large B or, what is the same thing, systems of the order of a mean free path in size. Figure 1 shows schematically the behaviour of λ as a function of B as available from perturbation theory. The broken curve shows a possible behaviour for larger B but it remains to be shown that for sufficiently small systems a discrete decay constant disappears altogether. Kuščer surmises that this will be the case but only on the basis of the isotropic model; however, the fact that the eigenvalues are complex render many of the techniques developed in neutron transport theory inapplicable and this question still remains to be answered.

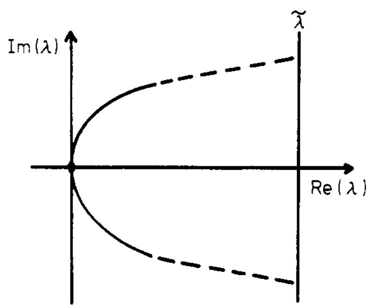

Figure 1. The full curve denotes the path traced out by λ as $|B|$ increases. The broken curve is a supposition based upon the general properties of the transport equation.

5. Solution from hydrodynamics

Whilst we have been able to draw a number of interesting conclusions from our examination of the transport equation, it was not found possible to obtain an explicit expression for the space- and time-dependent decay of the density, velocity and temperature perturbation following a disturbance. In this section, therefore, we assume that conditions are such that we may use the linearized hydrodynamic approximation to the transport equation. An attempt to include specifically transport effects is made by using slip boundary conditions for the velocity and temperature at the container walls.

To simplify the calculations we consider parallel-plate geometry with a diffuse-specular boundary condition at the wall. For such a boundary condition the slip coefficients have been calculated by Loyalka (1971). For small perturbations the hydrodynamic equations can be written

$$\frac{\partial \delta\rho}{\partial t}+\rho_0\frac{\partial \delta u}{\partial x}=0 \tag{23}$$

$$\rho_0\frac{\partial \delta u}{\partial t}=\frac{4}{3}\mu_v\frac{\partial^2 \delta u}{\partial x^2}-R\left(T_0\frac{\partial \delta\rho}{\partial x}+\rho_0\frac{\partial \delta T}{\partial x}\right) \tag{24}$$

$$\frac{3k}{2m}\rho_0\frac{\partial \delta T}{\partial t}-\lambda_T\frac{\partial^2 \delta T}{\partial x^2}=-p_0\frac{\partial \delta u}{\partial x} \tag{25}$$

where $\delta\rho$, δu and δT are perturbations from the equilibrium values of density ρ_0, velocity u_0 and temperature T_0. The boundary conditions are

$$\delta T(\mp\tfrac{1}{2}d, t)=\pm\mathscr{G}\delta T'(\mp\tfrac{1}{2}d, t) \tag{26}$$

$$\delta u(\mp\tfrac{1}{2}d, t)=\pm\zeta\delta u'(\mp\tfrac{1}{2}d, t) \tag{27}$$

$\mathscr{G}$ and ζ being the temperature and velocity slip coefficients respectively.

Equations (23)–(27) are Laplace transformed in time subject to the initial conditions

$$\delta u(x, 0)=0 \tag{28}$$

$$\delta\rho(x, 0)=S_0 \tag{29}$$

$$\delta T(x, 0)=-(T_0/\rho_0)S_0. \tag{30}$$

Eliminating $\bar{u}(x, p)$, the Laplace transformed velocity perturbation, leads to the following coupled equations for $\bar{\rho}(x, p)$ and $\bar{T}(x, p)$:

$$\lambda_T\bar{T}''-\tfrac{3}{2}R\rho_0 p\bar{T}+pRT_0\bar{\rho}=-\tfrac{1}{2}RT_0S_0 \tag{31}$$

$$\left(RT_0+\frac{4}{3}\frac{\mu_v}{\rho_0}p\right)\bar{\rho}''-p^2\bar{\rho}+R\rho_0\bar{T}''=-pS_0. \tag{32}$$

The general solutions of these two equations are readily found to be

$$\bar{T}(x, p)=A_0\cosh s_1x+A_2\cosh s_2x+\frac{T_0S_0}{\rho_0 p} \tag{33}$$

$$\bar{\rho}(x, p)=A_3\cosh s_1x+A_4\cosh s_2x+\frac{S_0}{p} \tag{34}$$

where

$$A_3=\frac{1}{pRT_0}\left(\tfrac{3}{2}R\rho_0 p-\lambda_T s_1^2\right)A_0 \tag{35}$$

$$A_4=\frac{1}{pRT_0}(\tfrac{3}{2}R\rho_0 p-\lambda_T s_2^2)A_2 \tag{36}$$

and s_1^2 and s_2^2 are the roots of

$$\lambda_T\left(RT_0+\frac{4}{3}\frac{\mu_v}{\rho_0}p\right)s^4-(\lambda_T p^2+\tfrac{5}{2}R^2T_0\rho_0 p+2R\mu_v p^2)s^2+\tfrac{3}{2}R\rho_0 p^3=0. \tag{37}$$

Similarly, the velocity perturbation is given by

$$\bar{u}(x,p) = -\frac{A_0}{\rho_0 s_1 R T_0}(\tfrac{3}{2}R\rho_0 p - \lambda_T s_1^2)\sinh s_1 x - \frac{A_2}{\rho_0 s_2 R T_0}(\tfrac{3}{2}R\rho_o p - \lambda_T s_2^2)\sinh s_2 x. \tag{38}$$

The remaining unknowns A_0 and A_2 are obtained by using boundary conditions (26) and (27), whence we can write complete expressions for $\bar{T}(x,p)$, $\bar{\rho}(x,p)$ and $\bar{u}(x,p)$. The expressions are rather lengthy and we shall therefore consider only $\bar{T}(x,p)$ which takes the form:

$$\bar{T}(x,p) = \frac{T_0 S_0}{\rho_0 p}\left(1 + \frac{\Phi_1(p)}{\Delta(p)}\cosh s_1 x + \frac{\Phi_2(p)}{\Delta(p)}\cosh s_2 x\right) \tag{40}$$

where

$$\Phi_1(p) = (\tfrac{3}{2}R\rho_0 p - \lambda_T s_2^2)\left[\frac{1}{s_2}\sinh\left(\frac{s_2 d}{2}\right) + \zeta\cosh\left(\frac{s_2 d}{2}\right)\right] \tag{41}$$

$$\Phi_2(p) = (\tfrac{3}{2}R\rho_0 p - \lambda_T s_1^2)\left[\frac{1}{s_1}\sinh\left(\frac{s_1 d}{2}\right) + \zeta\cosh\left(\frac{s_1 d}{2}\right)\right] \tag{42}$$

$$\begin{aligned}\Delta(p) = (\tfrac{3}{2}R\rho_0 p - \lambda_T s_1^2)&\left[\cosh\left(\frac{s_2 d}{2}\right) + s_2\mathscr{G}\sinh\left(\frac{s_2 d}{2}\right)\right]\left[\frac{1}{s_1}\sinh\left(\frac{s_1 d}{2}\right) + \zeta\cosh\left(\frac{s_1 d}{2}\right)\right]\\ &- (\tfrac{3}{2}R\rho_0 p - \lambda_T s_2^2)\left[\cosh\left(\frac{s_1 d}{2}\right) + s_1\mathscr{G}\sinh\left(\frac{s_1 d}{2}\right)\right]\\ &\times\left[\frac{1}{s_2}\sinh\left(\frac{s_2 d}{2}\right) + \zeta\cosh\left(\frac{s_2 d}{2}\right)\right].\end{aligned} \tag{43}$$

The inversion of $\bar{T}(x,p)$ leads to $\delta T(x,t)$, namely

$$\delta T(x,t) = \frac{1}{2\pi \mathrm{i}}\int_L e^{pt}\bar{T}(x,p)\,\mathrm{d}p. \tag{44}$$

It is readily shown that the apparent pole at $p=0$ has zero residue so that the singularities of the integrand are determined by the zeros of $\Delta(p)$. This function has in general an infinite number of complex conjugate roots $p_n = -\beta_n \pm \mathrm{i}\alpha_n$, so that $\delta T(x,t)$ takes the form

$$\begin{aligned}\delta T(x,t) = \sum_{n=0}^{\infty}\frac{T_0 S_0\,e^{-p_n t}}{\rho_0 p_n \Delta'(p_n)}(\Phi_1(p_n)\cosh s_1(p_n)x + \Phi_2(p_n)\cosh s_2(p_n)x)&\\ +\text{complex conjugate}.&\end{aligned} \tag{45}$$

If this general form is correct, and hydrodynamic approximations are usually accurate indicators of asymptotic behaviour (i.e. $n=0$ term), it suggests the transport theory asymptotic solution given by (20*a*) has associated with it an additional spatial term with a different value of B, possibly related to the diffusive mode.

We also note from the relation between p and s_2, i.e. equation (37), that the two roots s_1 and s_2 can, for small p, be written

$$s_1 \simeq \frac{p}{V_0} + \frac{p^2}{\rho_0 V_0^3}\left(\frac{2}{3}\mu_v + \frac{2\lambda_T}{15R}\right) \tag{46}$$

and

$$s_2 \simeq (2\rho_0 p/3\mu_v)^{1/2} \tag{47}$$

or

$$p = -V_0 s_1 + \frac{s_1^2}{\rho_0}\left(\frac{2}{3}\mu_v + \frac{2\lambda_T}{15R}\right) \tag{48}$$

and

$$p = \frac{3\mu_v}{2\rho_0} s_2^2. \tag{49}$$

Since the values of p have negative real parts we can set $s_1 = \mathrm{i}B$ and $s_2 = \mathrm{i}\xi$ thereby leading to

$$p \simeq -\mathrm{i}BV_0 - \frac{B^2}{\rho_0}\left(\frac{2}{3}\mu_v + \frac{2\lambda_T}{15R}\right) \tag{50}$$

$$p \simeq -\frac{3\mu_v}{2\rho_0}\xi^2 \tag{51}$$

which are equivalent to the first two terms of the perturbation theory approximation of the full transport equation. It is not to be inferred that B and ξ are necessarily real; however, they will certainly have small imaginary parts.

The actual computation of the p_n depends upon a thorough study of the roots of $\Delta(p) = 0$. This may be best achieved by writing it in the form

$$\frac{\frac{3}{2}R\rho_0 p - \lambda_T s_1^2}{\frac{3}{2}R\rho_0 p - \lambda_T s_2^2} = \left(\frac{1 + s_1\mathcal{G}\tanh(s_1 d/2)}{s_1^{-1}\tanh(s_1 d/2) + \zeta}\right)\left(\frac{s_2^{-1}\tanh(s_2 d/2) + \zeta}{1 + s_2\mathcal{G}\tanh(s_2 d/2)}\right). \tag{52}$$

The special case of $\mathcal{G} = \zeta = \infty$ leads to Φ_1/Δ and Φ_2/Δ both tending to zero and thereby predicts $\delta T(x, t)$ to be independent of space as expected. On the other hand, $\mathcal{G} = \zeta = 0$ corresponds to no slip at the walls and (52) becomes the classical expression (Rayleigh 1896).

For convenience in numerical work, we define the dimensionless parameters:

$$p_0 = \mu_0 p/V_0^2, \qquad s_0 = \mu_0 s/V_0, \qquad d_0 = \mathrm{d}V_0/\mu_0$$
$$\zeta_0 = V_0\zeta/\mu_0, \qquad \mathcal{G}_0 = V_0\mathcal{G}/\mu_0,$$

where $\mu_0 = \mu_v/\rho_0$ and $RT_0 = 3V_0^2/5$. Now (52) becomes

$$\frac{\frac{2}{5}p_0 - s_{01}^2}{\frac{2}{5}p_0 - s_{02}^2} = \frac{[1 + s_{01}\mathcal{G}_0\tanh(s_{01}d_0/2)][\zeta_0 + s_{02}^{-1}\tanh(s_{02}d_0/2)]}{[1 + s_{02}\mathcal{G}_0\tanh(s_{02}d_0/2)][\zeta_0 + s_{01}^{-1}\tanh(s_{01}d_0/2)]} \tag{53}$$

where p_0 and s_0 are related by the equation,

$$(1 + \tfrac{20}{9}p_0)s_0^4 - \tfrac{2}{3}p_0(1 + \tfrac{23}{6}p_0)s_0^2 + \tfrac{2}{3}p_0^3 = 0. \tag{54}$$

No detailed numerical results are yet available for p_o. We can, however, note that they occur in complex conjugate pairs and are infinite in number. Moreover, they will depend on the nature of the gas through the viscosity μ_v and also on the boundary conditions through ζ_0 and $\mathcal{G}_0$. It is clear, however, that the hydrodynamic method does not predict any limit-point behaviour and will therefore only be valid for long times and slowly varying spatial conditions: this of course is not unexpected since such conditions are built into the hydrodynamic approximations.

6. The effects of the boundaries on the zero eigenvalues

As we mentioned earlier, the presence of boundaries reduces the fivefold degenerate zero eigenvalue, $\lambda = 0$, to a single one corresponding to the Maxwellian eigenfunction. It is of some interest, however, to examine the way in which the boundary removes the degeneracy. To this end we construct the integral transport equation for this problem directly from the integro-differential form and thereby include implicitly the boundary conditions.

Changing equation (5) to polar coordinates and writing out the kernel $K(\boldsymbol{v}' \to \boldsymbol{v})$ explicitly we note that for parallel-plate geometry the transport equation becomes:

$$\left(\mu c\frac{\partial}{\partial x} + V(c) - \lambda\right)h(c, \mu, \chi, x) = F(c, \mu, \chi, x) \tag{55}$$

where

$$F(\ldots) = \int_0^\infty \mathrm{d}c' c'^2 \,\mathrm{e}^{-c'^2} \int_{-1}^1 \mathrm{d}\mu' \int_0^{2\pi} \mathrm{d}\chi' \, K(c, c', \mu, \mu', \chi, \chi')h(c', \mu', \chi', x) \tag{56}$$

and we have inserted the elementary solution $\exp(-\lambda t)$ and converted to the dimensionless speed variable $c^2 = mv^2/2kT$.

Subject to the boundary condition

$$h(c, \mu, \chi, \tfrac{1}{2}d) = \frac{2}{\pi}\beta \int_0^1 \mathrm{d}\mu'\mu' \int_0^{2\pi} \mathrm{d}c' \, c'^3 \,\mathrm{e}^{-c'^2} h(c', \mu', \chi', \tfrac{1}{2}d) + (1-\beta)h(c, -\mu, \chi, \tfrac{1}{2}d) \tag{57}$$

where β is the amount of diffuse reflection, we convert equation (55), for $\mu > 0$ to the integral form:

$$\begin{aligned} h(c, \mu, \chi, x) = {} & \frac{2}{\pi}\beta \exp\left[-\frac{\bar{V}}{\mu c}\left(\frac{d}{2}+x\right)\right] \frac{1+(1-\beta)\exp(-\bar{V}d/\mu c)}{1-(1-\beta)^2\exp(-2\bar{V}d/\mu c)} \\ & \times \int_0^1 \mathrm{d}\mu' \, \mu' \int_0^{2\pi} \mathrm{d}\chi' \int_0^\infty \mathrm{d}c' \, c'^3 \,\mathrm{e}^{-c'^2} h(c', \mu', \chi', \tfrac{1}{2}d) \\ & + \frac{(1-\beta)^2 \exp[-\bar{V}(2d+x)/\mu c]}{1-(1-\beta)^2\exp(-2\bar{V}d/\mu c)} \frac{1}{\mu c} \\ & \times \int_{-d/2}^{d/2} \mathrm{d}x'[(1-\beta)\,\mathrm{e}^{-\bar{V}(x'+d)/\mu c} F(c, -\mu, \chi, x') + \mathrm{e}^{\bar{V}x'/\mu c} F(c, \mu, \chi, x')] \\ & + (1-\beta)\exp\left[-\frac{\bar{V}}{\mu c}\left(\frac{d}{2}+x\right)\right]\frac{1}{\mu c}\int_{-d/2}^{d/2} \mathrm{d}x' \,\mathrm{e}^{-\bar{V}(x'+\frac{1}{2}d)/\mu c} F(c, -\mu, \chi, x) \\ & + \frac{1}{\mu c}\int_{-d/2}^{x} \mathrm{d}x' \,\mathrm{e}^{-\bar{V}(x-x')/\mu c} F(c, \mu, \chi, x') \end{aligned} \tag{58}$$

with an analogous expression for $\mu < 0$ and where $\bar{V} = V - \lambda$.

We may easily verify that h = constant is a solution of this equation corresponding to $\lambda = 0$. However, if we insert $h = c^2$ on the right-hand side of equation (58) we find that the left-hand side, for $\lambda = 0$, is given by

$$h(c, \mu, \chi, x) \sim c^2 + \frac{(2-c^2)\beta \exp[-V(\frac{1}{2}d+x)/\mu c]}{1-(1-\beta)\exp(-Vd/\mu c)}. \tag{59}$$

Similarly with $h = c(1-\mu^2)^{1/2}\cos\chi$ on the right-hand side, we get for the left-hand side

$$h(c,\mu,\chi,x) \sim c(1-\mu^2)^{1/2}\cos\chi\left(1-\frac{\beta\exp[-V(\frac{1}{2}d+x)/c\mu]}{1-(1-\beta)\exp(-Vd/\mu c)}\right). \qquad (60)$$

Equations (59) and (60) demonstrate the absence of momentum and energy eigenfunctions corresponding to $\lambda = 0$, i.e. equilibrium. They also show what features of the problem are responsible and how sensitive the degeneracy at $\lambda = 0$ is to the physical phenomena. For example, the amplitude of the 'non-eigenfunction' contamination is proportional to β the amount of diffuse reflection. For $\beta = 0$ i.e. a specularly reflecting body, we regain our momentum and energy eigenfunctions. This is not surprising since such a boundary condition is equivalent to an infinite medium. Thus we also regain the additional eigenfunctions when $d \to \infty$, i.e. the boundaries are absent. In general, however, the effect of degeneracy decays rapidly as we move away from the boundary and it is likely that, in systems which are five or more mean free paths in thickness, momentum and energy are 'almost' eigenfunctions. This conclusion is further substantiated if we consider the problem of a sound wave propagating along the axis of a cylindrical tube (Williams 1968b). Here we can also construct an integral equation for $h(\ldots)$ and show that momentum and energy are no longer eigenfunctions for zero frequency. However, the discrepancy is again a surface effect and in view of experimental evidence regarding the attenuation length of sound waves in the tube, it is clear that the energy and momentum conservation conditions continue to play an important role over the main portion of the gas in the interior of the tube.

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