settings. Fig. 7 shows a typical curve which confirms Maddock's data and is definite evidence that practically all of the photoelectric emission of the bismuth film is due to this line.

Conclusions

1. The curves of Figs. 2 to 6 indicate that the photoelectric emission and the threshold wave-length of bismuth films increase with increasing film thickness until a limiting value is attained.

2. The maximum and minimum values of the threshold wave-length for the four films, given in Table I, are in substantial agreement despite the fact that the first film was "gas contaminated" to a much greater degree than were the other three. It also should be noted that the four maximum threshold wave-lengths do not correspond to films of equal thickness. The minimum values of the threshold wave-lengths obtained are for extremely thin films, barely visible.

The author wishes finally, to express his thanks to the physics department of the University of Pennsylvania for the loan of the Hilger monochromator and to Dr. C. B. Bazzoni of the same laboratories for helpful suggestions and discussions while the work was in progress.

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Reflection of Sound

Karl F. Herzfeld
Catholic University of America, Washington, D. C.
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The losses in the reflection of sound on solids are investigated. The heat conduction of the solid disturbs the temperature distribution in the gas and sets up a temperature wave. The fact that the pressure in the gas near the wall is no longer in phase with the density results in a heating of the gas on the wall. The effect amounts to a few percent for a million cycles. The scattering of the molecules on the wall, the scattering of the sound waves by uneven places, the effect of adsorption are also investigated. They become important only at higher frequencies.

I. Introduction

It has been customary to state that the reflection of a sound wave by a smooth solid wall is almost complete. In support of this it is argued that because of the very large density and hardness of the wall the amplitude of the sound wave propagated into it will be small.

A few years ago, however, measurements by J. C. Hubbard gave ultrasonic reflection coefficients lower than expected and R. W. Curtis[1] reported reflection coefficients as low as 70 percent for 1000 kc in air on brass. The present investigation was undertaken at that time to look for a theoretical explanation for this result. It turned out that the theory leads to losses of a few percent, but that it was impossible to account for losses as high as 30 percent. Recent measurements[2] and computations of Alleman, done under Professor J. C. Hubbard, which include a modification of interferometer theory to take account of the effect discussed in this paper show good agreement of his own and previous measurements with the theory presented here.

To understand how the loss in reflection discussed here arises attention must first be drawn to the periodic temperature variations in the gas due to adiabatic expansion and compression. At the contact with the wall, the heat conduction of which is usually very much greater than that of the gas, heat will be alternately drained and put back into the gas, setting up a "temperature wave" in the solid in addition to the mechanical wave, which was alone considered before. The effect increases with frequency, because with shorter wave-length the temperature gradient increases.[3]

[1] R. W. Curtis, Diss. 1934, Phys. Rev. **46**, 811 (1934).
[2] R. Alleman, to be published.
[3] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).

To put this argument into mathematical form, another reflected wave besides the regular reflected one is introduced. This new wave, a secondary wave due to the temperature conduction of the wall, dies out very rapidly so that at a greater distance only the regularly reflected wave is measured, but with a smaller amplitude than would be calculated otherwise, because at the surface of the reflector the sum of the regularly reflected wave and the new wave must be equal to the incident, instead of the reflected alone.

The elaboration of this idea is contained in Chapter II. Chapter III investigates the influence of the fact that the molecules are not all reflected specularly, but scattered in all directions. This does, however, affect primarily the phase jump; the reflection coefficient is changed only in the second order. Chapter IV discusses the loss due to scattering by the unevenness of the reflector, as far as these eminences are large compared to the mean free path, but small compared with the wave-length. Chapter V investigates the possibility that adsorption of gas molecules on the surface might take place with a finite lifetime of adsorption and therefore delayed reevaporation. This results in a normal velocity component at the wall different from zero and gives a phase difference between velocity and temperature resulting in energy loss.

None of the effects discussed in III to V is, however, large enough to be measurable at present.

Notations

Index 0 indicates quantities in absence of sound, one prime refers (if necessary) to gas, two primes to solid.

The left half-space (x negative) is filled with the solid, the right half-space (x positive) with the gas, the reflecting surface being the $y-z$ plane. The solid is considered infinitely rigid, therefore the mechanical wave propagated in it is neglected.

T', temperature of the gas.
$T'-T_0=\theta$.
R, gas constant, M, molecular weight.
D density $=pM/RT=D_0(1+s)$ where s is the compression.
K', heat conductivity.
C_v, specific heat at constant volume per mole.
C_p, specific heat at constant pressure per mole.
$c=C_p(M/D)$ specific heat at constant pressure per cc.
V, normal sound velocity $=[(C_p/C_v)(RT/M)]^{\frac{1}{2}}$.
u, flow velocity in the x direction.
T'', temperature of solid.
$T''-T_0=\theta''$.
K'', heat conductivity of solid.
C'', specific heat of solid per cc.
k, coefficient of temperature jump at surface of solid, so that $\partial T'/\partial x=(T'-T'')k$.
ω, frequency of sound.

II. Influence of Heat Conduction

The equation for the temperature distribution in a solid is for a one dimensional problem.

$$C''(\partial T''/\partial t)=K''(\partial^2 T''/\partial x^2). \tag{1}$$

If we assume everything to be proportional to $e^{2\pi i\omega t}$, the appropriate solution of (1) is[4]

$$T''-T_0=F\exp\left[2\pi i\omega t+(1+i)(C''\pi\omega/K'')^{\frac{1}{2}}x\right]. \tag{2}$$

The equations of motion for the gas are: the equation of continuity

$$-\partial D/\partial t=D_0\partial u/\partial x$$

or

$$-\partial s/\partial t=\partial u/\partial x; \tag{3}$$

the equation of motion (neglecting friction)

$$\frac{\partial u}{\partial t}=-\frac{1}{D}\frac{\partial p}{\partial x}=-\frac{R}{M}\frac{\partial T'}{\partial x}-\frac{RT_0}{M}\frac{\partial s}{dx} \tag{4}$$

and the equation for the conservation of energy

$$C_v\frac{D}{M}\frac{\partial T}{\partial t}=RT_0\frac{\partial s}{\partial t}\frac{D}{M}+K'\frac{\partial^2 T'}{\partial x} \tag{5}$$

or

$$C_v\frac{\partial T'}{\partial t}=RT_0\frac{\partial s}{\partial t}+\frac{M}{D_0}K'\frac{\partial^2 T'}{\partial x^2}. \tag{5'}$$

Make again everything proportional to $e^{2\pi i\omega t}$ and eliminate s from (4) and (5′) with the help of (3)

$$\frac{\partial^2 u}{\partial x^2}+\frac{4\pi^2\omega^2 M}{RT_0}u=\frac{2\pi i\omega}{T_0}\frac{\partial T'}{\partial x}, \tag{4'}$$

$$\frac{K'M}{D_0RT_0}\frac{\partial^2\theta'}{\partial x^2}-\frac{2\pi i\omega C_v}{RT_0}\theta'=\frac{\partial u}{\partial x}. \tag{5''}$$

[4] See e.g. L. R. Ingersoll and O. J. Zobel, *An Introduction to the Mathematical Theory of Heat Conduction* (New York), Chapter V.

One tries now solutions of the type

$$u=Ue^{2\pi i\omega t+\lambda x},\quad T-T_0=\Theta e^{2\pi i\omega t+\lambda x},$$

which leads to the following secular equation in λ

$$\left(\lambda^2+\frac{4\pi^2\omega^2M}{RT_0}\right)\left(\frac{K'M}{D_0RT_0}\lambda^2-\frac{2\pi i\omega C_v}{RT_0}\right)=\frac{2\pi i\omega}{T_0}\lambda^2$$

or

$$i\frac{K'}{2\pi c\omega}\lambda^4+\left(1+\frac{K'}{c}\frac{2\pi i\omega M}{RT_0}\right)\lambda^2=-\frac{4\pi^2\omega^2}{V^2}. \quad (6)$$

That is a quadratic equation in λ^2; one of the roots, λ_1^2, corresponds to the usual propagation of sound, the other to the newly introduced short range (temperature) wave.

By introducing the abbreviation

$$\epsilon^2=K'/2\pi c;$$

and using numerical values for an estimate, one has for air under normal conditions

$$\epsilon^2=0.041\text{ cm}^2\text{ sec.}^{-1}$$

One finds as solution for (6)

$$\lambda^2=-\frac{\omega}{2\epsilon^2 i}\left(1+\epsilon^2\frac{4\pi^2 i\omega M}{RT_0}\right)\pm\frac{\omega}{2\epsilon^2 i}\left\{\left(1+\epsilon^2\frac{4\pi^2 i\omega M}{RT_0}\right)^2-4\epsilon^2 i\frac{4\pi^2\omega}{V^2}\right\}^{\frac{1}{2}}. \quad (7)$$

As V^2 is for air approximately 10^9 the $4\epsilon^2\cdot 4\pi^2\omega/V^2$ is approximately $6.5\cdot 10^{-9}\omega$ and will therefore be small compared to 1 when the experimental frequency range ω is $<10^7$. Therefore, the square root can be developed and gives

$$\lambda_1^2=-\frac{4\pi^2\omega^2}{V^2}\frac{1}{1+4\pi^2 i\omega MR\epsilon^2/RC_pT_0}, \quad (8)$$

$$\lambda_2^2=i\omega/\epsilon^2.$$

λ_1^2 corresponds, as mentioned before, to the usual propagation of sound. The second fraction takes care of the absorption of sound due to heat conduction in the gas. We are, however, going to neglect that. Otherwise[3] we would have to take into account also the effect of friction, which is similar to that of heat conduction, and of the internal degrees of freedom, which are even more important. However, the absorption of sound in the gas and on the wall seem separate phenomena, and a formula taking both into account would be rather long. In λ_2^2, we have neglected

$$4\pi^2\omega M\epsilon^2/RT_0=4\pi^2\omega\epsilon^2C_p/V^2C_v$$

compared with 1. We attempt now a solution in the form

$$u=Ae^{\lambda_1 x}-Be^{-\lambda_1 x}+Ge^{-\lambda_2 x}. \quad (9)$$

The first member is the incident wave, the second the usual reflected wave, the third the newly introduced ("temperature") wave. From (4′) follows

$$T'-T_0=\frac{T_0}{2\pi i\omega}\left\{(Ae^{\lambda_1 x}+Be^{-\lambda_1 x})\frac{1}{\lambda_1}\left(\lambda_1^2+\frac{4\pi^2\omega^2M}{RT_0}\right)-Ge^{-\lambda_2 x}\frac{1}{\lambda_2}\left(\lambda_2^2+\frac{4\pi^2\omega^2M}{RT_0}\right)\right\}. \quad (10)$$

The surface conditions are, for $x=0$,

$$u=0\quad\text{or}\quad A-B+G=0. \quad (11)$$

Continuity of heat flow is given by

$$K'\partial T'/\partial x=K''\partial T''/\partial x \quad (12)$$

and a possible temperature jump at the surface by

$$k(T'-T'')=\partial T'/\partial x. \quad (13)$$

From this follows exactly

$$\frac{B}{A}=1+2\frac{\lambda_1}{\lambda_2-\lambda_1}\left(1+\frac{4\pi^2\omega^2M}{RT_0\lambda_1^2}\right)\left\{1-\frac{4\pi^2\omega^2M}{RT_0\lambda_1\lambda_2}+(\lambda_1+\lambda_2)\left[\frac{1}{k}+\frac{K'}{K''(1+i)}\left(\frac{K''}{\pi\omega C''}\right)^{\frac{1}{2}}\right]\right\}^{-1}. \quad (14)$$

For $K''=0$ (nonconducting wall) or $k=0$ we have, as must be, $A=B$.

If we use the values (8), we find

$$\frac{B}{A}=1-2\frac{R}{C_v}\frac{\lambda_1}{\lambda_2-\lambda_1}\left\{1+\frac{C_p}{C_v}\frac{\lambda_1}{\lambda_2}+(\lambda_1+\lambda_2)\left[\frac{1}{k}+\frac{K'}{K''(1+i)}\left(\frac{K''}{C''\pi\omega}\right)^{\frac{1}{2}}\right]\right\}^{-1}. \quad (15)$$

Now

$$\frac{\lambda_1}{\lambda_2}=2\pi\frac{1-i}{V}\epsilon\left(\frac{\omega}{2}\right)^{\frac{1}{2}}\sim 1.5\cdot 10^{-5}\omega^{\frac{1}{2}}$$

in air, therefore small for experimental frequencies. The last term in the bracket can be written

$$\lambda_2\frac{1}{k}+\frac{K'\lambda_2}{\epsilon(2\pi K''C'')^{\frac{1}{2}}}\left(\frac{K'c'}{K'C''}\right)^{\frac{1}{2}}$$

$$=\frac{1+i}{\epsilon}\left(\frac{\omega}{2}\right)^{\frac{1}{2}}\frac{2-\gamma}{\gamma}\Lambda+\left(\frac{K'c'}{K''C''}\right)^{\frac{1}{2}}.$$

Here Λ is the mean free path, and γ the accommodation coefficient for energy.

$(K'c'/K''C'')^{\frac{1}{2}}=1.5\cdot 10^{-4}$ for air and copper, and is therefore entirely negligible; copper can be treated as an infinitely good conductor. Even for paraffin the expression is small. The first term is also small, except for very low pressures. Therefore we have with sufficient accuracy[5]

$$\left(\frac{B}{A}\right)^2=1-4\frac{R}{C_v}\frac{\lambda_1}{\lambda_2}=1-4\pi\frac{R}{C_v}\frac{\epsilon(2\omega)^{\frac{1}{2}}}{V}. \quad (16)$$

That gives for $(B/A)^2$ in air,

$1-4.4\cdot 10^{-5}(\omega)^{\frac{1}{2}}$ or 0.96 for 1 megacycle,

in helium,

$1-9.5\cdot 10^{-5}(\omega)^{\frac{1}{2}}$ or 0.90 for 1 megacycle.

Other terms will be found in III.

The loss on the wall is, however, not due to heat being conducted away in the solid. The temperature distribution in the wall is periodic in time so that all the heat that enters the solid comes out again. Instead the loss is due to a heating of the gas by adiabatic compression. In normal sound propagation, the temperature is in phase with the density changes and therefore the amount of work done on the gas during one period of the sound is zero.

$$\oint p\,dV=R\oint\frac{T}{V}dV=0.$$

The temperature wave, however, which exists at the wall gives to the pressure an out-of-phase (watt) component so that the work integral over a period is positive. The result is a progressive heating of the gas near the wall which extends over a distance of about

real part of $1/\lambda_2=(2/\omega)^{\frac{1}{2}}\epsilon$.

In the physical laboratory at Johns Hopkins University experiments are in progress to investigate this heating.

III. Influence of Scattering of Molecules

We shall see next whether the details of the molecular reflection on the solid surface affect the result. The method for this problem has been developed elsewhere.[6]

We assume that the heat conductivity of the reflector is infinite, that a fraction $1-\alpha$ of the impinging molecules is reflected specularly, α diffusely according to the cosine law.

We abbreviate by F_0 the Maxwell distribution function

$$F_0=\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}}\exp\left[-\frac{M}{2RT}(\xi^2+\eta^2+\zeta^2)\right],$$

where ξ, η, ζ are the molecular velocity components. Then the distribution function can be written for the present case:

$$F=(1+s)F_0+(T-T_0)\frac{\partial F_0}{\partial T}-\frac{\partial F_0}{\partial \xi}u+\rho f_1\frac{\partial T}{\partial x}+\rho f_2\frac{\partial u}{\partial x}, \quad (17)$$

[5] The last term in (16) is of the order of magnitude, 10 (time between collisions/period of sound)$^{\frac{1}{2}}$.

[6] K. F. Herzfeld, Ann. d. Physik **23**, 476 (1935).

where ρf, $\rho f'$ are functions of ξ, η, ζ, T_0 proportional to the small quantity ρ which in turn is proportional to the mean free path.

Equation (17) is to hold everywhere in the gas and on the wall. Now on the wall, there are molecules going toward the wall $0>\xi>-\infty$, and molecules coming from the wall, $0<\xi<\infty$. The distribution of the former is given by (17) for negative ξ; that of the latter by (17) with positive ξ. But this latter distribution must also be made up by $(1-\alpha)$ specularly reflected molecules and α diffusely reflected ones. The distribution of the latter is $\alpha(1+s')F_0$, their temperature corresponding to that of the wall where s' is to be calculated. Therefore the distribution of the departing molecules is[7]

$$(1-\alpha)\left\{(1+s)F_0+(T-T_0)\frac{\partial F_0}{\partial T}-\rho f\frac{\partial T}{\partial x}+\rho f'\frac{\partial u}{\partial x}\right\}+\alpha(1+s')F_0,$$

when u is zero. This must equal (17) for $\xi>0$. With the approximation taken here this is impossible. Instead we take the difference:

$$\alpha\Delta F=(1+s)F_0+(T-T_0)\frac{\partial F_0}{\partial T}+\rho f_1\frac{\partial T}{\partial x}+\rho f_2\frac{\partial u}{\partial x}$$

$$-(1-\alpha)\left\{(1+s)F_0+(T-T_0)\frac{\partial F_0}{\partial T}-\rho f_1\frac{\partial T}{\partial x}+\rho f_2\frac{\partial u}{\partial x}\right\}-\alpha(1+s')F_0 \quad (18)$$

and make $(\Delta f)^2$, integrated over all positive values of ξ and all values of η and ζ minimum. This integration will be abbreviated $\int\cdots d\Omega$. In addition we must give expression to the fact that the total number of impinging and departing molecules is equal. Introduced in (18), this condition gives:

$$\Delta f=\frac{T-T_0}{T_0}\left(T_0\frac{\partial F_0}{\partial T}-\frac{F_0}{2}\right)+\rho\frac{2-\alpha}{\alpha}f_1\frac{\partial T}{\partial x}+\rho\frac{\partial u}{\partial x}\left[f_2-F_0\left(\frac{2\pi M}{RT_0}\right)^{\frac{1}{2}}\int_0^\infty \xi f_2 d\Omega\right]. \quad (18')$$

If we now make use of (9), (10), (11) and write the following abbreviations

$$\gamma=-4\pi^2\omega^2M/RT_0\lambda_1^2=C_p/C_v, \quad (19)$$

$$\phi=\left(1+\gamma\frac{\lambda_1}{\lambda_2}\right)\left(T_0\frac{\partial F_0}{\partial T_0}-\frac{F_0}{2}\right)-\rho\frac{2-\alpha}{\alpha}f_1(\lambda_1+\lambda_2)T_0+2\pi i\omega\rho\left[f_2-\left(\frac{2\pi M}{RT_0}\right)^{\frac{1}{2}}F_0\int_0^\infty \xi f_2 d\Omega\right], \quad (19')$$

we find:

$$\Delta f=\frac{\lambda_2-\lambda_1}{2\pi i\omega}\phi A\left\{\frac{\lambda_2+\lambda_1}{\lambda_2-\lambda_1}\left[1-2\Phi^{-1}\gamma\frac{\lambda_1}{\lambda_2}\left(T_0\frac{\partial F_0}{\partial T}-\frac{F_0}{2}\right)+2\rho\frac{2-\alpha}{\alpha}T_0\lambda_1\Phi^{-1}f_1\right]-\frac{B}{A}\right\}. \quad (19'')$$

The result of the minimization is:

$$\frac{B}{A}=\frac{\lambda_2+\lambda_1}{\lambda_2-\lambda_1}\left\{1-2\left[\int\phi^2d\Omega\right]^{-1}\left[\gamma\frac{\lambda_1}{\lambda_2}\int\phi\left(T_0\frac{\partial F_0}{\partial T_0}-\frac{F_0}{2}\right)d\Omega-\rho\frac{2-\alpha}{\alpha}\lambda_1T_0\int\phi f_1 d\Omega\right]\right\}.$$

If we now keep no terms ρ^2 or $\rho\lambda_1/\lambda_2$, we get

$$\frac{B}{A}=1-\frac{\lambda_1}{\lambda_2-\lambda_1}\frac{\gamma-1}{1+\gamma(\lambda_1/\lambda_2)}+\frac{256}{7}\frac{2-\alpha}{\alpha}\rho T_0\lambda_1\left(\frac{\pi RT_0}{M}\right)^{\frac{3}{2}}\int f_1\left(T_0\frac{\partial F_0}{\partial T}-\frac{F_0}{2}\right)d\Omega. \quad (20)$$

[7] Because f_1 is odd in ξ, $f_1(-\xi)$, which is the function for the incoming molecules, is equal to $-f_1(\xi)$.

The connection between f_1 and the coefficient of heat conduction shows that

$$\rho\int \xi^3 f_1 d\Omega \sim C_v \Lambda V/M,$$

where Λ is the mean free path. The last expression can therefore be written

$$\frac{2-\alpha}{\alpha}\phi i\frac{\omega}{V}\Lambda,$$

where ϕ is a function of T of the order of magnitude 200 and V/ω the acoustical wave-lengths. This term, which is purely imaginary and small, contributes to the reflection coefficient only to the second order and will be neglected; it does, however, affect the phase jump in the first order. The first terms are identical with the corresponding terms in (15). Therefore, the detailed law of reflection of the molecules does not affect the reflection coefficient in the first order. The phase jump in units of the acoustical wave-lengths is:

$$-\frac{R}{C_v}\frac{\epsilon(2\omega)^{\frac{1}{2}}}{V}-\frac{\phi}{2\pi}\frac{2-\alpha}{\alpha}\frac{\omega}{V}\Lambda. \tag{20'}$$

IV. Effect of Unevenness of the Surface

We want to investigate whether the presence of uneven spots on the reflector could scatter so much sound that the regularly reflected intensity is measurably decreased.

Take a plane in the $y-z$ plane with a half-spherical boss of radius a at the origin, on which a plane sound wave falls at right angles. The problem of the scattering of sound waves by a full sphere has often been treated. We shall follow the treatment given by Lamb.[8] A progressive wave of unit amplitude can be represented by

$$e^{ikx}=\Sigma(2n+1)\psi(kr)(ikr)^nP_n(\cos\theta), \tag{21}$$

which gives a scattered wave

$$\Sigma B_n' f_n(kr)r^nP_n\cos\theta. \tag{21'}$$

If we now add a reflected wave to the incoming wave

$$e^{-ikx}=\Sigma(2n+1)\psi_n(kr)(ikr)^n(-1)^nP_n; \tag{21''}$$

we simply cut out all odd-numbered terms in the scattered wave and multiply the even numbered ones by 2, and get a solution (incoming, reflected, and scattered waves) which disappears properly at the surface of the sphere and its equatorial plane, i.e., the $y-z$ plane.

The velocity potential of the scattered wave is therefore, if the radius of the boss is small compared with the wave-length,

$$\tfrac{2}{3}(ka)^3e^{-ikr}/r \tag{22}$$

and the scattered energy (the intensity is 4 times that for progressive waves, but over a hemisphere)

$$\frac{128}{9}\pi^5\frac{\omega^4}{V^4}a^6. \tag{23}$$

If we assume the action of several bosses additive and half the surface covered with bosses, i.e., their number per cm² $\frac{1}{2}(\pi a^2)^{-1}$, we find[9] as the scattered fraction of the incoming energy

$$\frac{64\pi^4}{9}\left(\frac{a}{\text{wave-length}}\right)^4\sim 700\left(\frac{a}{\text{wave-length}}\right)^4. \tag{23'}$$

If we have $\omega=3\cdot 10^5$ and $a=1/20$ mm, the loss is $\frac{1}{2}$ percent but mounts rapidly with the frequency.

[8] Lamb, *Hydrodynamics*, fifth edition (Cambridge, 1930), pp. 486–487.

[9] This number is too large. Multiplication of the scattering of one boss by the number of bosses is only justified if the arrangement is completely irregular, while a completely regular arrangement would give regular reflection and no scattering. To get the correct value one would have to multiply the expression for the completely irregular arrangement with the ratio of the compressibility of a surface gas whose molecules are rigid spheres of the diameter of the bosses to the compressibility of an ideal gas.

V. Adsorption

In the discussion of this effect, we assume again that the wall is an infinitely good heat conductor, so that the heat of adsorption does not change the temperature of the gas, but we also assume that the different effects are additive, so that we need not now consider the effects already calculated. We will follow Langmuir in the assumptions concerning adsorption.

Let the number of adsorbed molecules per cm² of (macroscopic) surface of the reflector be N. Call furthermore N_s the number of adsorbing spots or the saturation value of N, so that N_s-N is the number of free places. Let τ be the average time an adsorbed molecule stays at the wall. The number of molecules which hit the wall is then

$$n_0(1+s)\left(W_0+\frac{\partial W}{\partial T}\Delta T\right)=n_0W_0\left(1+s+\frac{1}{2}\frac{\Delta T}{T_0}\right), \tag{24}$$

where n_0 is the number of molecules in 1 cc of the gas and W_0 the thermal velocity normal to the wall. It seems, however, doubtful, whether the term $\frac{1}{2}\Delta T/T_0$ should be there, i.e. whether the temperature at the wall is actually the temperature $T_0+\Delta T$ calculated from the equation of motion or whether the cooling effect of the wall keeps the gas at the wall at $\Delta T=0$. Not wishing to spend too much time on that question, we are going to write instead

$$\tfrac{1}{2}\beta\Delta T/T_0, \quad 0<\beta<1, \text{ probably } \beta=0.$$

The equation for the molecules at the wall is then

$$\frac{dN}{dt}=\frac{N_s-N}{N_s}n_0W_0\left(1+s+\tfrac{1}{2}\beta\frac{\Delta T}{T_0}\right)-\frac{N}{\tau}. \tag{25}$$

Call N_0 the number of adsorbed particles at the given temperature and pressure in equilibrium, i.e.

$$\frac{N_s-N_0}{N_s}n_0W_0=\frac{N_0}{\tau} \tag{25'}$$

or

$$\frac{N_0}{N_s}=\frac{n_0W_0}{n_0W_0+N_s/\tau} \quad \text{(Langmuir's adsorption isotherm)} \tag{25''}$$

and call the deviations $N'=N-N_0$

$$\frac{dN'}{dt}=\frac{N_s-N_0}{N_s}n_0W_0\left(s+\tfrac{1}{2}\beta\frac{\Delta T}{T_0}\right)-\left(\frac{n_0W_0}{N_s}+\frac{1}{\tau}\right)N', \tag{26}$$

keeping only first-order terms. If we write now everything proportional to $e^{2\pi i\omega t}$ and remember

$$-RT_0\frac{\partial s}{\partial t}+C_v\frac{\partial T}{\partial t}=0 \quad \text{or} \quad \frac{\Delta T}{T_0}=\frac{R}{C_v}s,$$

we find

$$\left\{1+\frac{1}{2\pi i\omega}\left(\frac{n_0W_0}{N_s}+\frac{1}{\tau}\right)\right\}\frac{dN'}{dt}=\frac{N_s-N_0}{N_s}n_0W_0\left(1+\frac{\beta}{2}\frac{R}{C_v}\right)s. \tag{27}$$

Now it is clear that dN'/dt, the change in adsorption, gives the resultant flow towards the wall, i.e.

$$un_0=-dN'/dt$$

and we find the border condition

$$-u\left\{1+\frac{1}{2\pi i\omega}\left(\frac{n_0W_0}{N_s}+\frac{1}{\tau}\right)\right\}=\frac{N_s-N_0}{N_0}n_0W_0\left(1+\frac{\beta}{2}\frac{R}{C_v}\right)s. \quad (28)$$

Putting now

$$u=e^{2\pi i\omega t}(Ae^{2\pi i\omega x/V}-Be^{-2\pi i\omega x/V}) \text{ and correspondingly } s=-(1/V)e^{2\pi i\omega t}(Ae^{2\pi i\omega x/V}+Be^{-2\pi i\omega x/V}) \quad (29)$$

one can solve and find

$$\frac{B}{A}=1-\frac{2}{\tau}\frac{N_0}{n_0W}\left(1+\frac{\beta R}{2C_v}\right)\left\{1+\frac{1}{\tau}\frac{N_0}{n_0V}\left(1+\frac{\beta R}{2C_v}\right)+\frac{1}{2\pi i\omega}\frac{n_0W}{N_0}\right\}^{-1} \quad (30)$$

or

$$\left|\frac{B}{A}\right|^2=1-\left[\frac{2N_0^2}{\tau n_0^2W_0}\left(1+\frac{\beta R}{2C_v}\right)\frac{2\pi\omega}{V}\right]^2\left\{1+\left[2\pi\omega\frac{N_0}{n_0W_0}\left(1+\frac{N_0}{\tau n_0V}\left(1+\frac{\beta R}{2C_v}\right)\right)\right]^2\right\}^{-1}. \quad (30')$$

If the reflection coefficient is not much different from 1, { } can be replaced by one. It is possible to transform the equation somewhat with the help of (25′) and write

$$\left|\frac{B}{A}\right|^2=1-\left[\frac{4\pi\omega}{V}\frac{N_0}{n_0}\left(1-\frac{N_0}{N_s}\right)\left(1+\frac{\beta R}{2C_v}\right)\right]^2. \quad (31)$$

N_0/n_0 would be the height of a cylinder of the gas of 1 cm² base containing just the number of adsorbed molecules at the density of the gas. Another way of writing this would be

$$\left|\frac{B}{A}\right|^2=1-\left[\frac{4\pi\omega}{V}\frac{1}{\tau W_0}\left(\frac{1}{\tau W_0}+\frac{n_0}{N_s}\right)^{-2}\left(1+\frac{\beta R}{2C_v}\right)\right]^2 \quad (31')$$

or finally

$$\left|\frac{B}{A}\right|^2=1-\frac{8\pi C_v}{C_p}(\omega\tau)^2\left(1+\frac{n_0}{n_s}\right)^{-4}, \quad (31'')$$

where n_s is the value of the gas density that would be necessary to have N_s adsorbed if the low pressure linear law would hold.

To get a numerical estimate, take $N_s=10^{15}$, $N_0=\frac{1}{2}\,10^{15}$ so that half of the available places are taken, $n_0=2.7\cdot10^{19}$, $C_v=5R/2$ and $\beta=0$,

$$B/A=1-2\cdot10^{-16}\omega^2.$$

Only at frequencies above 10^7 is the effect appreciable.