

Influence of Adsorption upon Sound Attenuation in a Tube *

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Sound waves propagating in a tube filled with gas are attenuated because of absorption in bulk, because of viscothermal effects, and possibly because the gas is adsorbed upon the wall. The latter effect is shown to depend upon a thermal relaxation time, the near-equilibrium desorption rate, and a phenomenological coefficient containing the sticking probability. In case of multilayer adsorption, especially upon metals, this data could be deduced from measurements of sound attenuation. An early experiment by Maurer is discussed in this light.

1. Introduction

Sound waves in a gas lose energy in the bulk and at surfaces. For instance, the reflectance of ultrasound from a solid surface is always less than 100% because of heat waves generated in the solid and in the gas [1, 2]. For oblique incidence, shear waves in the gas also play a role. The effect is enhanced if the gas condenses or is adsorbed at the surface, since delays make both processes irreversible at high frequencies. In some cases measurements of acoustic reflectance should give information about condensation and adsorption parameters [3, 4, 5]. Multilayer adsorption upon metals appears promising in this respect.

If the effect is small, one ought to multiply it somehow to obtain significant results. While multiple reflection is hardly practical, attenuation of sound waves propagating in a tube appears a sensible option. The attenuation due to heat and shear waves is well known [2, 6]; it is strongest for high frequencies and narrow tubes. The subsequent analysis will include the influence of adsorption in order to show whether and when measurements of attenuation could provide data about adsorption.

The reasoning will hinge upon the formulation of boundary conditions for the sound wave. For this we need an equation of state linking the surface density ν (adsorbed mass per unit area) to the equilibrium pressure and temperature. Naturally, it will suffice to know the differential form, which

in the notation used previously [5] reads as follows:

$$\frac{\Delta p}{p} = J \frac{\Delta \nu}{\nu} + K \frac{\Delta T}{T}, \quad (1)$$

$$J = \frac{\nu}{p} \left(\frac{\partial p}{\partial \nu} \right)_T, \quad K = \frac{T}{p} \left(\frac{\partial p}{\partial T} \right)_\nu. \quad (2)$$

The specific adsorption enthalpy q determines the “Clausius-Clapeyron” coefficient $K = Mg/k_B T$, which is of the order of 10 for physical adsorption. J equals unity for small pressures and drops to zero when saturation pressure is approached. In this region Frenkel’s theory predicts [7]

$$-\ln(p/p_s) = a(\nu_m/\nu)^3, \quad (3)$$

so that $J = -3 \ln(p/p_s)$. Here p_s is the saturation pressure and ν_m the monomolecular surface density. Typical values of a are between 1 and 10.

2. Boundary Conditions

To connect the temperature, pressure and velocity fields in the gas and in the solid with the surface density we need six boundary conditions. The first three merely state the conservation of energy and mass

$$\lambda_1 \frac{\partial \Delta T_1}{\partial r} - \lambda_2 \frac{\partial \Delta T_2}{\partial r} = \varrho_1 \nu_{r1} q, \quad r = R, \quad (4)$$

$$\varrho_1 \nu_{r1} = \frac{\partial \Delta \nu}{\partial t}, \quad r = R, \quad (5)$$

and the continuity of pressure,

$$p_1 = p_2, \quad r = R. \quad (6)$$

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The subscripts 1 and 2 refer to the gas and the wall of the tube (radius R), respectively, λ is the heat conductance, ϱ the density and v_r the radial velocity component.

Whenever the gas is not in equilibrium with the wall, there is a boundary layer — called the Knudsen layer — which is not even in local equilibrium, so that hydrodynamics does not apply there. However, since the layer is only a few mean free paths thick, the hydrodynamic variables can be extrapolated and hydrodynamic equations used throughout. The modified boundary conditions include various slip and jump coefficients [8].

Velocity slip plays no significant role in the present problem, because the mean free path is small compared to the radius of the tube. It is therefore safe to assume a vanishing tangential velocity at the wall

$$v_{z1} = 0, \quad r = R. \quad (7)$$

Two more boundary conditions relate the deviation of gas pressure from equilibrium, as well as the extrapolated temperature difference, to mass and heat fluxes in the gas at the boundary. Since the deviations are small, the relations are linear [3, 5]:

$$\frac{\Delta p}{p} - \left(J \frac{\Delta v}{v} + K \frac{\Delta T_2}{T} \right) \quad (8)$$

$$= \frac{\gamma_1}{c_1} \left(L_{pp} v_{r1} - L_{pT} \frac{\lambda_1}{p} \frac{\partial \Delta T_1}{\partial r} \right), \quad r = R,$$

$$\frac{\Delta T_1 - \Delta T_2}{T} \quad (9)$$

$$= \frac{\gamma_1}{c_1} \left(L_{Tp} v_{r1} - L_{TT} \frac{\lambda_1}{p} \frac{\partial \Delta T_1}{\partial r} \right), \quad r = R,$$

where $c_1 = (\gamma_1 k_B T / m)^{1/2}$ is the adiabatic sound velocity in the gas. Waldmann and Rübsamen [9], who were the first to introduce relations equivalent to (8) and (9), defined their phenomenological coefficients (α, β, γ) differently. The translation is:

$$\alpha = (\gamma_1 / c_1 p T) L_{TT},$$

$$\beta + \frac{1}{2} \alpha q = (\gamma_1 / c_1 \varrho_1 T) L_{Tp},$$

$$\gamma + \beta q + \frac{1}{4} \alpha q^2 = (p \gamma_1 / c_1 \varrho_1^2 T) L_{pp}.$$

The necessarily positive entropy production within the boundary layer (including the surface) is proportional to the determinant,

$$\alpha \gamma - \beta^2 = (\gamma_1 / c_1 \varrho_1 T)^2 (L_{TT} L_{pp} - L_{Tp}^2) > 0.$$

In case of perfect accommodation of the scattered molecules the phenomenological coefficients can be approximated in terms of the evaporation coefficient σ and the specific-heat ratio γ_1 as follows [3, 10]:

$$L_{pp} = \left(\frac{\pi}{2 \gamma_1} \right)^{1/2} \left[\frac{2}{\pi} + \frac{1 + 3 \gamma_1}{4(1 + \gamma_1)} + \frac{2(1 - \sigma)}{\sigma} \right], \quad (10a)$$

$$L_{pT} = \left(\frac{\pi}{2 \gamma_1} \right)^{1/2} \frac{\gamma_1 - 1}{\gamma_1 + 1} = \frac{1}{2} L_{TT}. \quad (10b)$$

3. Attenuation of Sound in a Cylindrical Tube

A sound wave propagating in a cylindrical tube is described similarly as an electromagnetic wave in a wave guide. The axially symmetric solution has the form [6]:

$$\frac{\Delta p}{p} = A J_0(\mu r) \exp(i k_z z - i \omega t), \quad (11a)$$

$$\frac{\Delta T_1}{T} = \left[\Theta_1 J_0((1 + i) \kappa_1 r) + \frac{\gamma_1 - 1}{\gamma_1} A J_0(\mu r) \right] \exp(i k_z z - i \omega t), \quad (11b)$$

$$\frac{v_{z1}}{c_1} = A \frac{k_z}{\gamma_1 k_0} \left[J_0(\mu r) - J_0(\mu R) \frac{J_0((1 + i) \kappa_v r)}{J_0((1 + i) \kappa_v R)} \right] \exp(i k_z z - i \omega t), \quad (11c)$$

$$\begin{aligned} \frac{v_{r1}}{c_1} = & \left\{ A \frac{i}{\gamma_1} \frac{\mu}{k_0} J_1(\mu r) + (1 + i) \left[- \left(\frac{\omega D_1}{2 c_1^2} \right)^{1/2} \Theta_1 J_1((1 + i) \kappa_1 r) \right. \right. \\ & \left. \left. + \frac{1}{\gamma_1} \left(\frac{\omega \eta_1}{2 \varrho_1 c_1^2} \right)^{1/2} A \left(\frac{k_z}{k_0} \right)^2 J_0(\mu R) \frac{J_1((1 + i) \kappa_v r)}{J_0((1 + i) \kappa_v R)} \right] \right\} \exp(i k_z z - i \omega t), \end{aligned} \quad (11d)$$

$$\frac{\Delta T_2}{T} = \Theta_2 (\kappa_2 r)^{-1/2} \exp \{-(1+i)\kappa_2 r\} \exp \{i k_z z - i \omega t\}, \quad (11e)$$

$$\frac{\Delta v}{v} = N \exp(i k_z z - i \omega t), \quad (11f)$$

$$k = \frac{\omega}{c_1} \left\{ 1 + \frac{i \omega}{2 c_1^2} [(\gamma_1 - 1) D_1 + (\eta_1' + 4 \eta_1/3)/\varrho_1] \right\}, \quad (11g)$$

$$k_z^2 = k^2 - \mu^2, \quad k_0 = \omega/c_1,$$

$$\kappa_i = \left(\frac{\omega}{2 D_i} \right)^{1/2}, \quad \kappa_v = \left(\frac{\omega \varrho_1}{2 \eta_1} \right)^{1/2}, \quad D_i = \frac{\lambda_i}{\varrho_i c_{pi}}, \quad i = 1, 2,$$

where η_1 and η_1' are the shear and bulk viscosities of the vapour. We have simplified the presentation by neglecting sound penetration into the wall. Furthermore, $1/\kappa_2$ is small, so that the heat wave in the wall is described as if the wall were infinitely thick. The corresponding Hankel function is replaced by its asymptotic approximation.

The boundary condition (7) has already been taken into account in (11c), while condition (6) has become superfluous. The remaining conditions (4), (5), (8) and (9) yield a homogeneous system of four linear equations for the amplitudes A , Θ_1 , Θ_2 and N . By requiring that the determinant vanishes, we obtain an equation for the eigenvalues of μ .

It is to be noted that μ only appears within one column of the determinant. The equation has the form

$$i k_0 J_0(\mu R) + \zeta \mu J_1(\mu R) = 0, \quad (12)$$

and it obviously admits a discrete set of roots $\mu = \mu_0, \mu_1, \mu_2, \dots$. The coefficient ζ coincides with the acoustic impedance of the tube wall [6],

$$\zeta = i k_0 \Delta p \left(\frac{\partial \Delta p}{\partial r} \right)_{r=R}^{-1}. \quad (13)$$

A rough approximation for ζ , to be called ζ_0 , is obtained by neglecting heat and shear waves in the gas. Naturally, the result

$$\zeta_0 = L_{pp} + \frac{1}{(1-i)(\omega \tau_{th})^{1/2}} + \frac{i}{\omega \tau}, \quad (14)$$

is the same as for a plane surface and perpendicular incidence [5]. The relaxation times

$$\tau_{th} = \frac{1}{2} \lambda_2 \varrho_2 c_{p2} \left(\frac{c_1 T}{K p q} \right)^2, \quad (15)$$

$$\tau = \frac{v c_1}{J p} = c_1 \left(\frac{\partial v}{\partial p} \right)_T, \quad (16)$$

are characteristic of the adsorbed layer.

Dissipation in bulk is represented by the so called viscothermal impedance

$$\zeta_{vt} = \frac{(1+i)}{2} \left[(\gamma_1 - 1) \left(\frac{\omega D_1}{2 c_1^2} \right)^{1/2} + \left(\frac{k_z}{k} \right)^2 \left(\frac{\omega \eta}{2 c_1^2 \varrho} \right)^{1/2} \right]^{-1}. \quad (17)$$

Following Morse and Ingard [6] we sum reciprocal impedances:

$$\zeta^{-1} = \zeta_0^{-1} + \zeta_{vt}^{-1}. \quad (18)$$

For large ζ_0 the result roughly agrees with one derived by iteration [3, 5].

For waves with $\mu > k$ we see that k_z becomes almost purely imaginary. Hence for a given mode m , below the cut-off frequency

$$\omega_m = \mu_m c_1 \quad (19)$$

we are left with strongly attenuated standing waves, just as in an electromagnetic wave guide. They also resemble the solution of the Schrödinger equation in a classically forbidden region.

When looking for an easy approximation for μ_m we note that the impedance of the wall is usually very large. Therefore the solution of (12) does not differ much from that for a rigid wall ($\zeta^{-1} = 0$). For $(kR/\zeta)^{1/2} \ll 1$ we take a linear approximation around $\tilde{\mu}_m$ defined by

$$J_1(\tilde{\mu}_m R) = 0, \quad \tilde{\mu}_0 = 0, \quad \tilde{\mu}_1 = 3.8, \dots \quad (20)$$

After some algebra (12) yields [6]:

$$\mu_0 = \left(\frac{-2 i k_0}{R \zeta} \right)^{1/2}, \quad (21a)$$

$$\mu_m = -\frac{ik_0}{R\zeta\tilde{\mu}_m} + \tilde{\mu}_m, \quad m = 1, 2, \dots \quad (21b)$$

Here we neglect the dependence of ζ upon μ , which means that $k_z^2 = k^2 - \mu^2$ in (17) is replaced by $k^2 - \tilde{\mu}^2$.

The quantity measured in an experiment is the attenuation factor $\beta = \text{Im}(k_z)$. The value corresponding to (21a, b) is

$$\beta_m = \text{Im}(k) + \frac{1}{R} \text{Re}(\zeta^{-1}) \left[1 - \frac{\tilde{\mu}_m^2}{k_0^2} \right]^{-1/2}. \quad (22)$$

The first term on the right, cf. (11g), represents absorption in the bulk and is usually negligible. Indeed, the ratio of the attenuation factors due to absorption and to viscothermal effects near the wall is

$$\text{Im}(k)/\beta_{vt} = \frac{1}{2} k_0 R (\omega \tau_{rel})^{1/2}, \quad (23)$$

where $\beta_{vt} = R^{-1} \text{Re}(\zeta_{vt}^{-1})$ and τ_{rel} is a molecular relaxation time related to the ratio of the bracketed expressions in (11g) and (17).

4. Experimental Options

The preceding results may be studied graphically (Fig. 1), similarly as was done in the previous paper [5]. We plot the factor $e^{-2\beta L}$ representing the attenuation of sound energy in a tube of length L as a function of $\omega \tau$, for several values of the param-

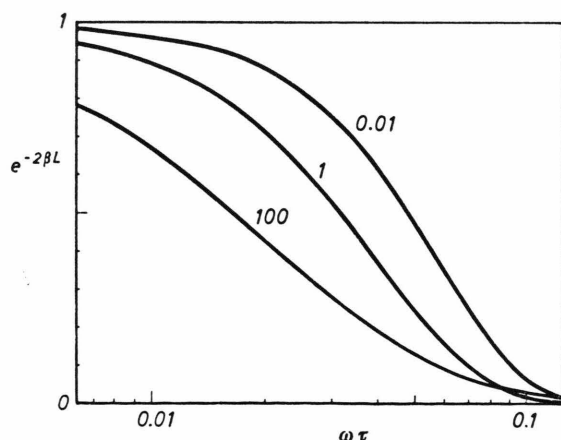


Fig. 1. Attenuation of sound energy for the lowest mode ($m=0$) in a tube with adsorbing walls, evaluated from Eqs. (14) and (22) for $L_{pp}=1.27$ (value for water vapour with $\sigma=1$). The numbers attached to the curves are values of the ratio τ/τ_{th} . The ratio tube length to tube radius is fixed at $L/R=100$.

eter τ/τ_{th} and for fixed $L/R=100$. Within the range of strong variation, say

$$0.1 < e^{-2\beta L} < 0.9, \quad (24)$$

measurements of attenuation could lead to useful information about adsorption parameters, via (22) and (14–16).

We may think of observing either travelling waves in an open-ended tube, or standing waves if the tube is closed. In either case, difficulties with a mixture of several eigenmodes must be avoided by choosing a frequency below the cut-off for the first higher mode ($m=1$), i.e.

$$\omega < 3.8 c_1/R,$$

so that only the fundamental mode ($m=0$) remains. For sensible tube diameters, this prevents much exceeding audible frequencies. As a consequence, ζ_0 will be large, so that in case of $\tau_{th} \gg \tau$, (14) and (22) yield easy order-of-magnitude estimates.

The exclusion of higher frequencies makes the method less promising than expected beforehand. It turns out that the effect of adsorption is overwhelmed by the viscothermal contribution, unless $\omega \tau$ is sufficiently large. As an example we consider a tube of diameter $2R=1$ cm filled with water vapour at 100°C . For the highest permissible frequency $\omega=3 \cdot 10^5 \text{ s}^{-1}$ the lower bound of measurable relaxation times is about the same as with observations of reflectance (Fig. 1 in [5]). Hence, just as there, meaningful experiments can primarily be expected with multilayer adsorption upon metal surfaces.

The feasibility of the proposed method is demonstrated by experiments carried out by Maurer some time ago [11]. He chose to measure the attenuation by observing the width of standing-wave resonances in a brass tube of length $\frac{1}{2}L \approx 60$ cm and radius $R=2.5$ cm. The tube was closed by the sound generator on top and by boiling water below. Most of the tube wall was overheated to about 101°C . The observed strong attenuation was explained as being due to interaction at the interface between bulk water and vapour. To test this, Maurer dropped a small amount of paraffin upon the water, whereupon the resonance curve rose to the level previously observed with air in the tube.

According to the analysis of Robnik et al. [3], the frequency (3.5 kHz) employed by Maurer was much too low for such an explanation. We can only

suppose that moisture on the tube wall was the dominant cause of attenuation. The described test does not rule out this possibility, since liquid paraffin may easily have crept up the wall, covering any water layer attached there.

Because of the proximity to saturation ($p/p_s = 0.97$) under Maurer's conditions, multilayer adsorption must have occurred. However, an estimate based upon Frenkel's isotherm (3) and upon (18) and (22) still falls below the attenuation actually observed, so that further clarification is called for. The first suspect is the temperature of the wall, which according to the description of Maurer's set-up may have been quite close to 100 °C in the lower portion of the tube. As a result, adsorption and thereby sound attenuation must have been enhanced there. In fact, if a few centimeters of the tube wall above

the water surface are assumed as having been covered with more than fifty molecular layers of condensed water, we can easily match the theoretical and experimental results. It may perhaps seem contradictory that such a small piece of wet surface could have produced a significant effect, while a comparably large surface of bulk water could not. The explanation is hidden in the large ratio of heat conductivities of brass and water which enter through (14, 15).

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