PHYSICAL REVIEW E **89**, 023208 (2014)

Acoustics and precondensation phenomena in gas-vapor saturated mixtures

C. Guianvarc'h[*]
Laboratoire Commun de Métrologie, LNE-Cnam, 61 rue du Landy, 93210 La Plaine Saint Denis, France

M. Bruneau
Laboratoire d'Acoustique de l'Université du Maine, UMR CNRS 6613, av. Olivier Messiaen, 72085 Le Mans Cedex 9, France

R. M. Gavioso
Istituto Nazionale di Ricerca Metrologica, strada delle Cacce 91, 10135 Torino, Italy

(Received 10 October 2013; published 26 February 2014)

Starting from fundamental hydrodynamics and thermodynamics equations for thermoviscous fluids, a new modeling procedure, which is suitable to describe acoustic propagation in gas mixtures, is presented. The model revises the boundary conditions which are appropriate to describe the condensation-evaporation processes taking place on a solid wall when one component of the mixture approaches saturation conditions. The general analytical solutions of these basic equations now give a unified description of acoustic propagation in an infinite, semi-infinite, or finite medium, throughout and beyond the boundary layers. The solutions account for the coupling between acoustic propagation and heat and concentration diffusion processes, including precondensation on the walls. The validity of the model and its predictive capability have been tested by a comparison with the description available in the literature of two particular systems (precondensation of propane and acoustic attenuation in a duct filled with an air-water vapor saturated mixture). The results of this comparison are discussed to clarify the relevance of the various physical phenomena that are involved in these processes. The model proposed here might be useful to develop methods for the acoustic determination of the thermodynamic and transport properties of gas mixtures as well as for practical applications involving gas and gas-vapor mixtures like thermoacoustics and acoustics in wet granular or porous media.

DOI: 10.1103/PhysRevE.89.023208 PACS number(s): 43.20.+g, 64.70.F−, 89.90.+n

I. INTRODUCTION

During the last three decades, important research work has been carried out to improve the description of acoustic fields in binary gas mixtures, pure saturated vapors, and gas-saturated vapor mixtures. On one hand, the analysis of mixture separation phenomena inside the boundary layers (experimentally observed in thermoacoustic engines) led Swift *et al.* to suggest analytical models of acoustic fields coupled to heat and concentration diffusion processes in thermoacoustic cores filled with binary gas mixtures [1–3]. More recently, the experimental work of Gavioso *et al.*, aimed at an accurate measurement of the acoustic fields in a resonant cavity filled with a binary inert gas mixture, indicated the need for advanced acoustic modeling in the bulk of the gas as well as in the boundary layers [4]. Recently, two of us provided a more general and unified analytic procedure whereby the acoustic field in binary gas mixtures can be expressed, throughout and beyond boundary layers, from coupled solutions for the propagative and diffusive fields [5].

On the other hand, the results of accurate speed of sound measurements in cavities filled with a pure saturated vapor (i.e., a gas in static pressure and temperature conditions close to the vapor-liquid equilibrium) led several authors [6–8] to point out and address (Mehl and Moldover [7]) the significant influence of precondensation effects taking place on the walls of the cavity. Indeed, due to the difference between the intermolecular potential in the bulk of the gas and at the vapor-solid interface, an adsorbed liquid film can exist in a thermodynamic equilibrium state, even when the thermodynamic state of the vapor lies below the liquid-gas phase transition line in the phase space (P,T) diagram. The thickness of the liquid film coating the wall is determined by the pressure and temperature of the vapor. Therefore, pressure and temperature variations due to the acoustic cycle, being coupled to heat diffusion processes in the boundary layers, result in liquid-vapor phase changes on the walls, whose effects on the acoustic field involve the liquid film rate of change, the latent heat of vaporization, and the balance of the heat flows at the liquid-vapor interface, as suggested in the analytical model first developed by Mehl and Moldover [7], which predicts the enhancement of the acoustic admittance of a solid wall coated with a liquid film.

Finally, both Mao [9] and Raspet *et al.* [10–13] observed experimentally the relevant influence of humidity on the acoustic attenuation in porous materials and the functional properties of thermoacoustic engines. Following these observations, several attempts were made to improve the existing theory to provide a better understanding of the boundary water evaporation-condensation effects on the acoustic propagation in ducts filled with an air-water vapor mixture [9–13]. These attempts correctly include heat and concentration diffusion processes throughout the boundary layers and their coupling to phase changes on the walls. However, in these models the thickness of the interfacial film is assumed to be null, and the influence of the liquid film rate of change is neglected even though it could be significant, as previously demonstrated [7].

To sum up, previous work has considered either the coupling between heat and concentration diffusion processes

---

[*] cecile.guianvarc_h@cnam.fr

in binary mixtures or the description of the physical processes which determine precondensation in a pure vapor. The quest for a unified coherent acoustic description of all these phenomena was the initial motivation of this work, which deals with acoustic wave propagation in gas-vapor saturated mixtures in an infinite, semi-infinite, or finite medium throughout and beyond the boundary layers. Here, the evaporation-condensation processes take place only on the walls, which are permanently coated with a liquid film of variable thickness.

This study is extensively analytical and relies on a standard formulation based on the classical equations of acoustics in thermoviscous fluids and the formalism developed by Landau and Lifshitz for binary gas mixtures [14] (Sec. II).

In Sec. III, the acoustic behavior of the gas-vapor mixture near the boundaries is modeled as follows: (1) the coupling between the thermal diffusion and the concentration diffusion inside the boundary layers is described using the formulation first suggested by Swift and Spoor [1] and later revised in Ref. [5], (2) the effect of the heat flows related to the vaporization latent heat of the precondensed liquid film and the state of equilibrium of this liquid film are introduced as suggested by Mehl and Moldover [7], and (3) in addition to the classic nonslip conditions on the walls, we make use of the boundary conditions first presented by Mao [9] and later by Raspet *et al.* [10–13] to describe the mass transfers between the vapor and the wet wall. However, we do not use quasi-isothermal boundary conditions as they do not suitably account for the latent heat associated with the condensation-evaporation processes.

Within this rather convoluted framework, complete and tractable solutions expressing the variation of temperature, concentration, and particle velocity are derived in Sec. IV. These solutions are used in Sec. V to deal with two specific acoustic problems, namely, the reflection off the liquid coated wall and the propagation of quasi-plane waves in cylindrical waveguides.

Finally, in Sec. VI, we apply our extended acoustic model and discuss its impact for two particular cases previously considered in the literature, i.e., a determination of the acoustic admittance of the boundary layer in nearly saturated propane and the acoustic attenuation within a duct filled with a mixture of air and saturated water vapor.

II. LINEARIZED FUNDAMENTAL EQUATIONS

The variables describing the dynamic and thermodynamic states of the binary mixture and each of its components (the subscript index $i = 1,2$ refers to the gas and the saturated vapor, respectively) are the pressure variations p and p_i, the particle velocities $\mathbf{v}$ and $\mathbf{v}_i$, the mass density variations ρ' and ρ'_i, the mass fraction variation of the gas c (i.e., $1 - c$ for the vapor), and the temperature variation τ of the mixture.

The parameters specifying the state of the mixture are the total and partial static pressures P_0 and P_i and the mass densities ρ_0 and ρ_i of the mixture and of each component, respectively, and the static temperature T_0.

Finally, the parameters specifying the nature of the mixture are the adiabatic speed of sound a_0, the static mass and mole fractions C_0 and x of the gas ($1 - C_0$ and $1 - x$, respectively, for the vapor), the number of moles per unit volume of the mixture and each component n and n_i, the molar masses M and M_i, the heat capacity ratios of the mixture and each component γ and γ_i, the heat capacities at constant pressure per unit of mass of the mixture and each component C_P and C_{Pi}, the pressure and thermal diffusion ratios $k_P = x(1-x)(M_2 - M_1)/M$ and k_T, respectively, the mutual diffusion coefficient D, the increase in pressure per unit increase in temperature at constant density $\hat{\beta}$, the shear and bulk viscosity coefficients μ and η, respectively, and the thermal conductivity λ_h of the mixture.

The set of linear equations governing acoustic fields in a gas-vapor mixture are the following [5,9,10,14].

(1) The Navier-Stokes equation for the mixture

$$\frac{1}{a_0}\frac{\partial \mathbf{v}}{\partial t} = -\frac{1}{\rho_0 a_0}\nabla p + \ell_v \nabla(\nabla\cdot\mathbf{v}) - \ell'_v \nabla\wedge\nabla\wedge\mathbf{v}, \tag{1}$$

where $\ell_v = (4\mu/3 + \eta)/(\rho_0 a_0)$ and $\ell'_v = \mu/(\rho_0 a_0)$.

(2) The mass conservation equations are

$$\frac{\partial \rho'_i}{\partial t} + \rho_i \nabla\cdot\mathbf{v}_i = 0, \tag{2a}$$

$$\frac{\partial \rho'}{\partial t} + \rho_0 \nabla\cdot\mathbf{v} = 0, \tag{2b}$$

where $\rho_0\mathbf{v} = \rho_1\mathbf{v}_1 + \rho_2\mathbf{v}_2$.

(3) The equation describing the mutual diffusion of the mixture components, involving the concentration flux density $\mathbf{i}$, defined as the density flow rate through the unit surface per unit time due to the diffusion process of component 1 of concentration C [$-\mathbf{i}$ for component 2 of concentration $(1-C)$] is

$$\mathbf{i} = -\rho_0 a_0 \ell_D \frac{M_1 M_2}{M^2}\left[\frac{M^2}{M_1 M_2}\nabla c + \frac{k_P}{P_0}\nabla p + \frac{k_T}{T_0}\nabla\tau\right], \tag{3a}$$

with $M = xM_1 + (1-x)M_2$ and $\ell_D = D/a_0$; the concentration flux density is also related to the particle velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ by

$$\mathbf{i} = -\rho_0 x(1-x)\frac{M_1 M_2}{M^2}(\mathbf{v}_2 - \mathbf{v}_1) \tag{3b}$$

and to the expression of the mass fraction field variation c by, neglecting the second order term $\rho_0\mathbf{v}\cdot\nabla c$,

$$\frac{\partial c}{\partial t} \approx -\frac{1}{\rho_0}\nabla\cdot\mathbf{i}. \tag{3c}$$

The fundamental equations may be more conveniently expressed by introducing the variable b, defined as

$$\frac{\partial b}{\partial t} = \frac{M^2}{M_1 M_2}\frac{\partial c}{\partial t} = -\frac{M^2}{M_1 M_2}\frac{1}{\rho_0}\nabla\cdot\mathbf{i}. \tag{4}$$

(4) The entropy continuity for the mixture is

$$\left(\frac{1}{a_0}\frac{\partial}{\partial t} - \ell_h\,\Delta\right)\tau = \frac{\gamma - 1}{\gamma\hat{\beta}}\frac{1}{a_0}\frac{\partial}{\partial t}\left[p + P_0\alpha_T b\right], \tag{5}$$

where $\ell_h = \lambda_h/(\rho_0 a_0 C_P)$ and $\alpha_T = k_T/[x(1-x)]$.

The last term, which involves the normalized mass fraction variation b, arises from the expressions of both the concentration flux density $\mathbf{i}$ [having the same dimension as a heat flux;

see Eq. (3a)] and the heat flux [14, Eq. (58.12)]:

$$\mathbf{q} = \left[k_T \left(\frac{\partial g}{\partial C} \right)_{P,T} - T_0 \left(\frac{\partial g}{\partial T} \right)_{P,C} + g \right] \mathbf{i} - \lambda_h \nabla \tau, \quad (6)$$

where $g = g_1/M_1 - g_2/M_2$ and g_i are the chemical potentials of the mixture and of the component i, respectively.

(5) The equation of state of the mixture (ideal gas, Dalton's law)

$$\frac{1}{\rho_0} \frac{\partial \rho'}{\partial t} = \frac{1}{P_0} \frac{\partial p}{\partial t} - \frac{1}{T_0} \frac{\partial \tau}{\partial t} - \alpha_P \frac{M^2}{M_1 M_2} \frac{\partial c}{\partial t}, \quad (7)$$

where $\alpha_P = k_P/[x(1-x)]$.

Therefore, the set of fundamental equations needed to describe harmonic motion expressed as $e^{j\omega t}$ (with angular frequency ω and adiabatic wave number $k_0 = \omega/a_0$), involving the variables p, $\mathbf{v}$, τ and b, takes the following form [5]:

$$\mathbf{v} = -\frac{1}{j\omega \rho_0} \nabla p + \frac{\ell_v}{jk_0} \nabla(\nabla \cdot \mathbf{v}) + \frac{1}{k_v^2} \nabla \wedge \nabla \wedge \mathbf{v}, \quad (8a)$$

$$\nabla \cdot \mathbf{v} = -\frac{j\omega\gamma}{\rho_0 a_0^2}(p - \hat{\beta}\tau) + j\omega\alpha_P b, \quad (8b)$$

$$\left(1 + \frac{1}{k_h^2}\Delta\right)\tau = \frac{\gamma - 1}{\gamma\hat{\beta}}(p + P_0\alpha_T b), \quad (8c)$$

$$\left(1 + \frac{1}{k_D^2}\Delta\right) b = -\frac{\gamma}{\rho_0 a_0^2}\frac{1}{k_D^2}(k_P \Delta p + \hat{\beta} k_T \Delta\tau), \quad (8d)$$

where the wave numbers, defined as

$$k_v^2 = -\frac{jk_0}{\ell'_v}, \quad k_h^2 = -\frac{jk_0}{\ell_h}, \quad k_D^2 = -\frac{jk_0}{\ell_D}, \quad (8e)$$

are, respectively, related to the shear displacement (significant only within the viscous boundary layer), the thermal diffusion process, and the mutual diffusion process.

In the following, we make the limiting assumption that the evaporation-condensation process may be neglected within the bulk of the fluid, as there the nucleation energy is much higher than close to the wall of the enclosure. Therefore, the appropriate description for the acoustic field is that given in Ref. [5]. In agreement with the approximations made above, terms of order higher than 1 for the characteristic lengths are neglected below (i.e., order 2 of the penetration depths $\delta_{v,h,D} = \sqrt{2}/|k_{v,h,D}|$).

III. EQUATIONS INSIDE BOUNDARY LAYERS AND BOUNDARY CONDITIONS

We consider a rigid solid wall, locally assumed to be a plane, which is coated with a liquid film of variable thickness (Fig. 1). The coordinate normal to the wall inwardly directed is denoted u, with $u = d$ at the interface between the liquid and the gas mixture and $u = 0$ on the solid wall; the coordinate tangent to the wall is denoted $\mathbf{w}$ with components w_1, w_2 on the wall. To simplify the description of the small amplitude acoustic disturbance within the boundary layer and the corresponding formulation, we assume the validity of the following approximations: (1) the component normal to the wall v_u of the acoustic velocity is much lower than the tangential components v_{wi} (mostly within the boundary layers), and (2) the spatial variation of the acoustic velocity and the temperature and concentration variations are much higher in the normal direction u than in the tangential directions (w_1, w_2).

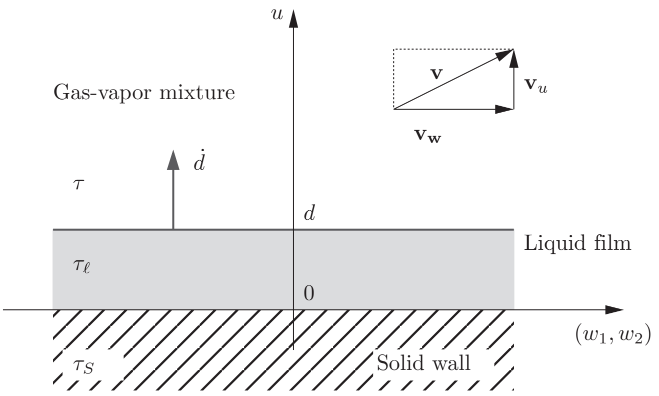

FIG. 1. Temperature and particle velocity fields in a gas-vapor mixture close to a solid wall coated with a liquid film.

Under these assumptions, the normal and tangential components of Navier-Stokes equation (8a) lead to the following relations, using expression (8b) for $\nabla \cdot \mathbf{v}$ and assuming that $\tau \approx (\gamma - 1)/(\gamma\hat{\beta})p$ in the higher order terms:

$$j\omega\rho_0 v_u = -(1 + jk_0\ell_v)\frac{\partial p}{\partial u} + jk_0\ell_v\,\rho_0 a_0^2 \alpha_P \frac{\partial b}{\partial u}, \quad (9a)$$

$$\left(1 + \frac{1}{k_v^2}\frac{\partial^2}{\partial u^2}\right)\mathbf{v_w} = -\frac{1 + jk_0\ell_v}{j\omega\rho_0}\nabla_{\mathbf{w}} p + \ell_v\, a_0 \alpha_P \nabla_{\mathbf{w}} b, \quad (9b)$$

with $\nabla_{\mathbf{w}}$ being the del operator in coordinate system (w_1, w_2) (Fig. 1).

We can note that by substituting the expressions obtained in the following for $\frac{\partial}{\partial u} v_u$ and $\frac{\partial^2}{\partial u^2} b$ (Secs. IV B and IV D) into the derivative of Eq. (9a) with respect to the variable u, we get the propagation equation that governs the pressure variation p.

The tangential particle velocity, the temperature and concentration variations, and the normal particle velocity are then governed by the following set of equations:

$$\frac{\partial}{\partial u} v_u + \nabla_{\mathbf{w}} \cdot \mathbf{v_w} = -\frac{j\omega\gamma}{\rho_0 a_0^2}(p - \hat{\beta}\tau) + j\omega\alpha_P b, \quad (10a)$$

$$\left(1 + \frac{1}{k_v^2}\frac{\partial^2}{\partial u^2}\right)\mathbf{v_w} = -\frac{1 + jk_0\ell_v}{j\omega\rho_0}\nabla_{\mathbf{w}} p + \ell_v\, a_0 \alpha_P \nabla_{\mathbf{w}} b, \quad (10b)$$

$$\left(1 + \frac{1}{k_h^2}\Delta\right)\tau = \frac{\gamma - 1}{\gamma\hat{\beta}}(p + P_0\alpha_T b), \quad (10c)$$

$$\left(1 + \frac{1}{k_D^2}\Delta\right) b = -\frac{\gamma}{\rho_0 a_0^2}\frac{1}{k_D^2}(k_P \Delta p + \hat{\beta} k_T \Delta\tau). \quad (10d)$$

The general solutions of these equations are subjected to the following boundary conditions at the interface $u = d$ between the liquid film and the gas mixture.

(1) The tangential components v_{wi} of the particle velocity of the mixture vanish (nonslip condition):

$$\mathbf{v_w}(d) = \mathbf{0}. \tag{11}$$

(2) On the surface $u = d$ of the liquid film, the normal component of the gas particle velocity v_{1u} must be equal to the velocity $\dot{d} = \partial d/\partial t$ of the interface between the liquid and the gas-vapor saturated mixture:

$$v_{1u}(d) = \dot{d}. \tag{12a}$$

The thickness of the liquid film is equal to d, and $\dot{d}$ is related to the u component of the vapor particle velocity $v_{2u}(d)$ by

$$\rho_\ell \dot{d} = -\rho_2 v_{2u}(d), \tag{12b}$$

with ρ_ℓ being the density of the liquid. Then, the relation $\rho_0 \mathbf{v} = \rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2$ expressed at $u = d$ leads to the following relationship between the normal component of the particle velocity and the vibration velocity of the liquid film, under the reasonable assumption that $\rho_\ell \gg \rho_1$:

$$\rho_0 v_u(d) = (\rho_1 - \rho_\ell)\dot{d} \approx -\rho_\ell \dot{d}\,. \tag{12c}$$

The particle velocity $v_u(d)$ is related to the first derivative of the acoustic pressure with respect to the u coordinate (9a), leading to

$$\left.\frac{\partial p}{\partial u}\right|_d \approx j\omega\,\rho_\ell \dot{d} \tag{12d}$$

to the lowest order of the characteristic lengths. This result shows that the spatial variation of the acoustic pressure in the direction normal to the wall is nonzero due to the thickness variations of the liquid film.

Also, the concentration density flux is nonzero at the liquid-gas mixture interface since it is related to the vibration velocity of the liquid film $\dot{d}$. Making use of relations (12a), 12(b), and 12(c) in expressions (3a) and 3(b) of the concentration flux density allows us to write, assuming that $\rho_\ell/\rho_2 \gg 1$,

$$\begin{aligned} i_u(d) &= x\frac{M_1}{M}\rho_\ell \dot{d} \\ &= -\rho_0 D\frac{M_1 M_2}{M^2}\left[\frac{\partial b}{\partial u} + \frac{k_P}{P_0}\frac{\partial p}{\partial u} + \frac{k_T}{T_0}\frac{\partial \tau}{\partial u}\right]_d, \end{aligned} \tag{13}$$

and, finally, at the lowest order of the characteristic lengths,

$$x\frac{M}{M_2}\frac{\rho_\ell}{\rho_0}\frac{\dot{d}}{a_0} = -\ell_D\left[\frac{\partial b}{\partial u} + \frac{\hat{\beta}\gamma}{\rho_0 a_0^2}k_T\frac{\partial \tau}{\partial u}\right]_d. \tag{14}$$

Note that when $\dot{d}$ vanishes (no liquid film on the wall), this boundary condition takes the form [1,5]

$$\left.\frac{\partial b}{\partial u}\right|_d = -\frac{\hat{\beta}\gamma}{\rho_0 a_0^2}k_T\left.\frac{\partial \tau}{\partial u}\right|_d.$$

(3) Even though the temperature variation τ on the wall is much lower than the adiabatic temperature variation in the bulk of the fluid, the usual isothermal boundary condition $\tau(d) = 0$ no longer holds, as it would imply that the temperature variations due to the latent heat of vaporization and condensation are negligible. As emphasized in the literature [7], although this latent heat is convected in the liquid layer and the wall, the balance of heat flow at the liquid-vapor interface implies that a slight non-negligible temperature variation occurs on the liquid boundary.

Assuming the conservation of heat flux at the interface between the wall and the liquid film ($u = 0$) and the temperature continuity at both interfaces, wall-liquid film and liquid film-gas mixture ($u = d$), the equations describing the spatial dependence of the temperature waves, created at the liquid-gas mixture interface $u = d$ (by the energy source due to the latent heat), in the wall and in the liquid are respectively given by

$$\tau_S(u) = \frac{\tau(d)}{\cos k_\ell d + j\Theta\sin k_\ell d}e^{jk_S u}, \quad u < 0, \tag{15a}$$

$$\tau_\ell(u) = \tau(d)\frac{\cos k_\ell u + j\Theta\sin k_\ell u}{\cos k_\ell d + j\Theta\sin k_\ell d}, \quad 0 < u < d, \tag{15b}$$

where $k_{S,\ell} = (1-j)\sqrt{\omega\rho_{S,\ell}C_{S,\ell}/(2\lambda_{S,\ell})}$ are the complex propagation constants of thermal waves in the wall and the liquid, respectively, $\lambda_{S,\ell}$ are the thermal conductivities, $C_{S,\ell}$ are the heat capacities, and $\rho_{S,\ell}$ are the densities of the wall and the liquid, respectively, and $\Theta = \sqrt{\rho_S C_S\lambda_S/(\rho_\ell C_\ell\lambda_\ell)}$.

Using the expression, which would strictly hold for an ideal gas [14, Eq. (58.10)],

$$\left(\frac{\partial g}{\partial c}\right)_{P,T} = \frac{P_0}{k_P}\left(\frac{\partial\,(1/\rho)}{\partial c}\right)_{P,T} = \frac{P_0}{\rho_0}\frac{M^2}{M_1 M_2}\frac{1}{x(1-x)},$$

the normal component of the heat flux (6) can be written as

$$q_u(d) = \left[\frac{P_0}{\rho_0}\frac{\alpha_T M^2}{M_1 M_2} + g - T_0\left(\frac{\partial g}{\partial T}\right)_{P,C}\right]i_u(d) - \lambda_h\left.\frac{\partial \tau}{\partial u}\right|_d.$$

The first term of $q_u(d)$ indicates the contribution to the concentration of the heat flux associated with the temperature gradient. This is usually assumed to be much larger than the effects associated with the chemical potentials, namely, $-T_0(\partial g/\partial T)_{P,C}$ and g. Thus one can write here

$$q_u(d) \approx \alpha_T\frac{P_0}{\rho_0}\frac{M^2}{M_1 M_2}i_u(d) - \lambda_h\left.\frac{\partial \tau}{\partial u}\right|_d. \tag{16}$$

Then, the energy balance for heat flow at the liquid-gas mixture interface $u = d$ takes the following form (L being the latent heat of vapor per unit mass of liquid, provided at $u = d$):

$$\rho_\ell L\dot{d} \approx \alpha_T\frac{P_0}{\rho_0}\frac{M^2}{M_1 M_2}i_u(d) - \lambda_h\left.\frac{\partial \tau}{\partial u}\right|_d + \lambda_\ell\left.\frac{\partial \tau_\ell}{\partial u}\right|_d,$$

or, accounting for the first expression in (13) and expression (15b) for i_u and τ_ℓ, respectively,

$$\begin{aligned} &\frac{\gamma-1}{\gamma\hat{\beta}}\left(\frac{\rho_0 L}{P_0} - x\alpha_T\frac{M}{M_2}\right)P_0\frac{\rho_\ell}{\rho_0}\frac{\dot{d}}{a_0} \\ &\quad = jk_h\ell_h\,\Lambda\tau(d) - \ell_h\left.\frac{\partial \tau}{\partial u}\right|_d, \end{aligned} \tag{17a}$$

where

$$\Lambda = \sqrt{\frac{\rho_\ell C_\ell\lambda_\ell}{\rho_0 C_P\lambda_h}}\frac{j\tan k_\ell d + \Theta}{1 + j\Theta\tan k_\ell d}. \tag{17b}$$

The boundary condition in Eqs. (17a) and 17(b) is more realistic than that used by Slaton *et al.* [12, Eq. (3)] as it accounts for the coupling of the nonzero concentration flux density at the liquid-gas interface with the heat flux generated by thermodiffusion effects within the gas mixture.

(4) The boundary conditions that involve the normal component of the gas particle velocity (condition 2) and the temperature variation (condition 3) depend on the time derivative $\dot{d}$ of the liquid film thickness d. Therefore, we need to express $\dot{d}$ as a function of the variables of interest here, namely, p, τ, and b. We achieve this by expressing the thermodynamical equilibrium of the condensation liquid film by an equation of state relating d to the partial pressure of the vapor $P_2 = (1-x)P = P(1-C)M/M_2$ and the temperature T of the gas mixture. The following approximate form was used by Mehl and Moldover:

$$\ln[P_s(T)/P_2] \approx (d_0/d)^{\nu}\,, \tag{18}$$

which considers the saturated vapor pressure $P_s(T)$ of the vapor, with d_0 being approximately equal to 1 nm and ν varying between 3 and 4 depending on the thickness of the liquid film [7].

The validity of this approximate equation is limited by the assumption that the solid wall is perfectly smooth. However, in practice, this condition is hardly reached, and to our knowledge, there is no work available to account for the influence of the roughness of the wall on the molecular interactions between the vapor and the wall surface and then on precondensation.

Making use of Eq. (18), the velocity $\dot{d}$ of the liquid-gas mixture interface ($u = d$) is given by the following differential expression:

$$\dot{d} = \left(\frac{\partial d}{\partial P}\right)_{T,C}\frac{\partial p}{\partial t} + \left(\frac{\partial d}{\partial T}\right)_{P,C}\frac{\partial \tau}{\partial t} + \left(\frac{\partial d}{\partial C}\right)_{T,P}\frac{\partial c}{\partial t}\,,$$

and it can be written as

$$\frac{\dot{d}}{d} = \frac{j\omega}{\nu\ln(P_s/P_2)}\left[\frac{p(d)}{P_0} - \frac{T_0}{P_s}\frac{dP_s}{dT}\frac{\tau(d)}{T_0} - \frac{b(d)}{1-x}\right]. \tag{19}$$

It is worth noting that Eqs. (18) and (19) express the evaporation-condensation process on the interface between the liquid film and the mixture during each acoustic cycle.

The last expression can be rearranged as follows:

$$\frac{\rho_\ell}{\rho_0}\frac{\dot{d}}{a_0} = \frac{jk_0 d_\ell}{P_0}\left[p(d) - \hat{\beta}h_s\tau(d) - \frac{P_0}{1-x}b(d)\right], \tag{20}$$

where $d_\ell = (\rho_\ell/\rho_0)d/[\nu\ln(P_s/P_2)]$ and $h_s = (T_0/P_s)(dP_s/dT)$. The latent heat L and the slope dP_s/dT, related in a first approximation (through the ideal gas law) by the Clausius-Clapeyron law, are numerically expressed separately herein.

Let us notice that this result is somewhat equivalent to those suggested by Slaton *et al.* [12, Eq. (9)] if $\dot{d}/d$ is assumed to be negligible or P_2 is assumed to be equal to P_s (which cannot be achieved in practice and is not consistent with the phase change hypothesis).

Therefore, the velocity $\dot{d}$ is removed, first from Eqs. (17) and (20) and then from Eqs. (20) and (14), leading to the two relationships used below. Then we make use of Eq. (10c) to remove the variable b, and finally, a lengthy but straightforward calculation leads to the two following boundary conditions:

$$\alpha_T\left[jk_h\Lambda\tau(d) - \left.\frac{\partial\tau}{\partial u}\right|_d\right] = \frac{jk_0\delta_\ell}{\ell_h(1-x)}\left[\frac{M_2}{M}h_0 - x\alpha_T\right]\Xi, \tag{21a}$$

$$(1+\epsilon)\left.\frac{\partial\tau}{\partial u}\right|_d + \frac{1}{k_h^2}\left.\frac{\partial^3\tau}{\partial u^3}\right|_d = -\frac{jk_0\delta_\ell x}{\ell_D(1-x)}\Xi\,, \tag{21b}$$

where

$$h_0 = \frac{L\rho_0}{P_0},\quad \delta_\ell = \frac{M}{M_2}d_\ell,\quad \epsilon = \frac{\gamma-1}{\gamma}x(1-x)\alpha_T^2\,, \tag{21c}$$

and

$$\Xi = \frac{\gamma-1}{\gamma\hat{\beta}}[1+(1-x)\alpha_T]p(d) - \left[1+\frac{\gamma-1}{\gamma}h_s\alpha_T(1-x)\right] \times\tau(d) - \frac{1}{k_h^2}\left.\frac{\partial^2\tau}{\partial u^2}\right|_d. \tag{21d}$$

Without condensation-evaporation, both the thickness of the liquid film d and its velocity $\dot{d}$ vanish. As a consequence, the concentration flux density also vanishes at the boundary, and the coefficient Λ simplifies to the ratio $\sqrt{\rho_S C_S\lambda_S/(\rho_0 C_P\lambda_h)}$, where λ_S is much higher than λ_h (the quantities $k_h\tau$ and $\partial\tau/\partial u|_d$ are of the same order of magnitude). The boundary conditions (21a) and (21b) respectively become

$$\tau(d) = 0,\quad (1+\epsilon)\left.\frac{\partial\tau}{\partial u}\right|_d + \frac{1}{k_h^2}\left.\frac{\partial^3\tau}{\partial u^3}\right|_d = 0\,,$$

which are equivalent to those given in Refs. [1,5].

Alternatively, for the case of a pure vapor ($x = 0$), the variable b and the concentration flux density $\mathbf{i}$ vanish. Then, as expected, the second boundary condition (21b) also vanishes, and the first boundary condition (21a) leads to

$$jk_h\Lambda\tau(d) - \left.\frac{\partial\tau}{\partial u}\right|_d = \frac{jk_0 d_\ell h_0}{\ell_h}\frac{\gamma-1}{\gamma\hat{\beta}}[p(d) - \hat{\beta}h_s\tau(d)]\,.$$

Finally, for the study of gas-vapor mixtures, we are left with three boundary conditions: (11), (21a), and (21b).

IV. SOLUTIONS

A. Solutions for the temperature variation

We apply the operator $(1 + \frac{1}{k_D^2}\Delta)$ on the diffusion equation (10c), and we use equation (10d), which leads to the following equation for τ:

$$\left[1 + \left(\frac{1}{k_h^2} + \frac{1+\epsilon}{k_D^2}\right)\Delta + \frac{1}{k_h^2k_D^2}\Delta\Delta\right]\tau \approx \frac{\gamma-1}{\gamma\hat{\beta}}\left[1 + \frac{1}{k_D^2}(1-\alpha_T k_P)\Delta\right]p. \tag{22}$$

Equation (22) may be more conveniently rearranged to highlight the coupling between temperature and concentration variations inside the boundary layers. The appropriate form of the operator on the left hand side is a "product" of two spatial second order operators [1]:

$$\left(1+\frac{1}{k_{hD}^2}\Delta\right)\left(1+\frac{1}{k_{Dh}^2}\Delta\right)\tau \approx \frac{\gamma-1}{\gamma\hat{\beta}}\left[1+\frac{1}{k_D^2}(1-\alpha_T k_P)\Delta\right]p, \tag{23}$$

where

$$\frac{1}{k_{hD,Dh}^2} = -\frac{A\pm\sqrt{\Gamma}}{2jk_0} = -\frac{\ell_{hD,Dh}}{jk_0}, \tag{24}$$

with $A=\ell_h+(1+\epsilon)\ell_D$ and $\Gamma=(\ell_h-\ell_D)^2+2\epsilon\ell_D\,[\ell_h+\ell_D\,(1+\epsilon/2)]$.

Then, the Laplacian Δ may be expressed as the sum $\Delta=\partial^2/\partial u^2+\Delta_{\mathbf{w}}$. Thus, the particle displacement along the direction which is tangent to the wall is nearly coincident with the acoustic displacement [which implies $\Delta_{\mathbf{w}}\tau\approx(\gamma-1)/(\hat{\beta}\gamma)\Delta_{\mathbf{w}}p$], and the terms of order greater than 1 for the characteristic lengths ℓ_{hD} and ℓ_{Dh} are neglected. Finally, Eq. (23) takes the following form [1,5]:

$$\left(1+\frac{1}{k_{hD}^2}\frac{\partial^2}{\partial u^2}\right)\left(1+\frac{1}{k_{Dh}^2}\frac{\partial^2}{\partial u^2}\right)\tau \approx \frac{\gamma-1}{\gamma\hat{\beta}}p_\tau\,, \tag{25a}$$

with (Δp is identified with $-k_a^2 p$)

$$p_\tau(\mathbf{w}) \approx \left[1+\frac{k_a^2}{k_D^2}x(1-x)\alpha_T\alpha+\frac{k_a^2}{k_h^2}\right]p\,, \tag{25b}$$

where $k_a^2=k_0^2(1+jk_0\ell_{vhd})$ is the acoustic wave number accounting for viscous, thermal, and mutual diffusion effects in the bulk and $\alpha=\alpha_T(\gamma-1)/\gamma+\alpha_P$.

Equations (25a) and 25(b) show that the temperature variation within the boundary layer is determined by the superposition of two diffusion processes, labeled hD and Dh, due to the complex interaction of concentration and thermal gradients. Note that the following relations can be readily obtained:

$$\frac{1}{k_{hD}^2}+\frac{1}{k_{Dh}^2}=\frac{1}{k_h^2}+\frac{1+\epsilon}{k_D^2},\quad k_{hD}^2k_{Dh}^2=k_h^2k_D^2, \tag{26}$$

with the thicknesses of the boundary layers associated with these diffusion processes respectively given by $\delta_{hD}=\sqrt{2}/|k_{hD}|$ and $\delta_{Dh}=\sqrt{2}/|k_{Dh}|$.

In Eqs. (25a) and (25b), the pressure variation p is assumed to be quasi-uniform along the u direction inside the boundary layers. The solution for the temperature variation τ, subjected to the boundary conditions (21a) and (21b), then takes the following form:

$$\tau(u,\mathbf{w}) = \frac{\gamma-1}{\hat{\beta}\gamma}p_\tau(\mathbf{w})\,[1-A_\tau\varphi_{hD}(u)-B_\tau\varphi_{Dh}(u)] = \frac{\gamma-1}{\hat{\beta}\gamma}p_\tau(\mathbf{w})[1-\psi_\tau(u)]\,, \tag{27}$$

where functions $\varphi_X(u)$ (the subscript X in the following stands for subscripts v, hD, and Dh indifferently) are the normalized solutions of the homogeneous equations associated with Eqs. (25a) and (25b) and the integration constants A_τ and B_τ are given by boundary conditions (21a) and (21b).

Functions $\varphi_X(u)$ and integration constants A_τ and B_τ depend on the geometry of the wall surface and of the propagation domain (see examples in Sec. V).

B. Expression of the concentration variation

We may solve Eq. (10c) to express the variation of the normalized concentration on the wall, using the general form (27) for the temperature τ,

$$b(u,\mathbf{w}) = \frac{p}{P_0}x(1-x)\left\{\frac{k_a^2}{k_D^2}\alpha[1-\psi_\tau(u)]-\frac{1}{k_T}\psi_b(u)\right\}, \tag{28}$$

with

$$\psi_b(u) = A_\tau\left[1-\frac{\ell_h}{\ell_{hD}}\right]\varphi_{hD}(u)+B_\tau\left[1-\frac{\ell_h}{\ell_{Dh}}\right]\varphi_{Dh}(u)\,. \tag{29}$$

C. Solutions for the tangential particle velocity

We next consider a simplified form of Eq. (10b) by neglecting the rightmost term $a_0\alpha_P\ell_v\,\nabla_{\mathbf{w}}b$, which would lead to a second order function of the characteristic lengths. Thus, imposing the boundary condition (11), the particle velocity on the wall is given by

$$\mathbf{v}_{\mathbf{w}}(u,\mathbf{w}) \approx -\frac{1}{j\omega\rho_0}(1+jk_0\ell_v)\nabla_{\mathbf{w}}p(\mathbf{w})[1-\varphi_v(u)]\,, \tag{30}$$

where $\varphi_v(u)$ is a solution of Eq. (10b) and depends on the particular geometry of the wall surface and of the propagation domain.

D. Relation between the particle velocity normal to the wall and the pressure variation

Together, solutions (27), (28), and (30), which define the temperature and concentration variations and the tangential particle velocity, are used in Eq. (10a), leading to the final relation between the normal component v_u of the particle velocity $\mathbf{v}$ and the acoustic pressure p, at first order in the characteristic lengths:

$$\begin{aligned} j\omega\rho_0\frac{\partial}{\partial u}v_u = {} & [1-\varphi_v(u)]\Delta_{\mathbf{w}}p+k_0^2 \\ & \times\Big\{1-jk_0\ell_{vhd}+\gamma\frac{k_P}{k_T}\psi_b(u) \\ & +(\gamma-1)\psi_\tau(u)+jk_0\ell_v\,\varphi_v(u) \\ & +jk_0[(\gamma-1)\ell_h+\ell_D\,\gamma x(1-x)\alpha^2]\psi_\tau(u)\Big\}p, \end{aligned} \tag{31}$$

where $\ell_{vhd}=\ell_v+(\gamma-1)\ell_h+\gamma x(1-x)\alpha^2\ell_D$ accounts for the energy dissipation in the bulk of the mixture.

Depending on the geometry of the solid boundary, the propagation domain, and accuracy requirement, simplified versions of Eq. (31) may hold, as discussed below for two cases of practical interest.

Finally, the pressure variation is governed by the second order differential equation obtained from the derivative of Eq. (9a) with respect to the variable u, accounting for the expression of $\frac{\partial}{\partial u}v_u$ [Eq. (31)].

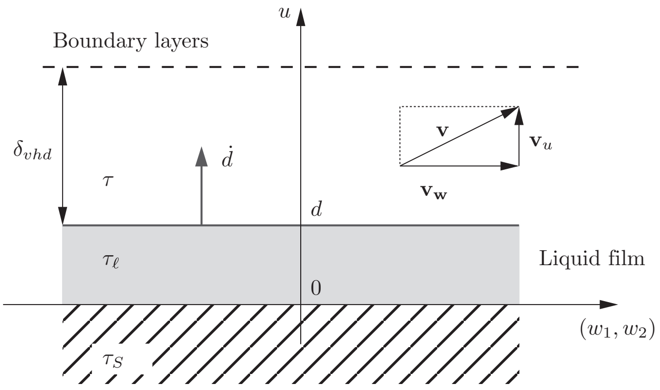

FIG. 2. Quasi-plane rigid wall coated with a liquid film: temperature and particle velocity fields within the boundary layers.

V. SPECIFIC APPLICATIONS

A. Reflection on a quasi-plane rigid wall

Within the boundary layers, the acoustic pressure p is nearly uniform. It is then appropriate here to identify $\Delta_w p$ with $-k_w^2 p$ (Δ_w and k_w are, respectively, the components of the Laplacian and of the acoustic wave number tangent to the wall) and to substitute the following terms in Eq. (31) with their mean values:

$$\int_d^u \frac{\partial}{\partial y} v_u dy = v_u(u) - v_u(d), \tag{32a}$$

$$\int_d^u \Delta_{\mathbf{w}}[1 - \varphi_v(y)] p dy \approx -k_{\mathbf{w}}^2 p \left(\delta - \int_d^u \varphi_v(y) dy \right), \tag{32b}$$

where $\delta = (u - d)$ has the same order of magnitude as the boundary layer thickness and the relative variations of the functions φ_X in the boundary layers are much larger than those of p.

Considering the reflection on a wall in a semi-infinite domain (Fig. 2), we may express the functions $\varphi_X(u)$ as exponential functions $e^{-jk_X(u-d)}$, which rapidly vanish when $\delta \approx \delta_X$ (evanescent waves associated with diffusion processes from the wall), leading to

$$\int_d^u \varphi_X(y) dy \approx \frac{1-j}{\sqrt{2}} \sqrt{\frac{\ell_X}{k_0}}, \quad \left. \frac{\partial \varphi_X}{\partial u} \right|_d = \frac{1+j}{\sqrt{2}} \sqrt{\frac{k_0}{\ell_X}}.$$

Therefore, expressions (27), (28), and (30) for τ, b, and $\mathbf{v_w}$ are used in Eq. (31); then we integrate it from d to u, and we use expression (20) for $\dot{d}$ in relation (12c). It turns out, with a lengthy but straightforward calculation, that

$$\begin{aligned} -\rho_0 a_0 \frac{v_u}{p} &\approx \frac{1+j}{\sqrt{2}} \sqrt{k_0} \left[\frac{k_w^2}{k_0^2} \sqrt{\ell'_v} + (\gamma - 1) \frac{\sqrt{\ell_h}}{q_{hD}} \right] \\ &\quad + \frac{jk_0 \delta_\ell \gamma}{q_{hD}} \left[\left(1 - \frac{\gamma - 1}{\gamma} h_2 \right) \frac{\zeta_s}{\Lambda} + \frac{f_{hD}}{\sqrt{\ell_{hD}} + \sqrt{\ell_{Dh}}} \right], \end{aligned} \tag{33a}$$

where $h_2 = h_0 M_2/M$, $\zeta_s = 1 - h_s(\gamma - 1)/\gamma$, and

$$\begin{aligned} q_{hD} &= \frac{\sqrt{\ell_h} + \sqrt{\ell_D}}{\sqrt{\ell_{hD}} + \sqrt{\ell_{Dh}}} \left[1 + \frac{jk_h \delta_\ell}{\Lambda} \left(\frac{\gamma - 1}{\gamma} h_s h_2 + \zeta \right) \right] \\ &\quad + \frac{1}{\Lambda} + jk_h \delta_\ell \, \zeta + \frac{jk_h \delta_\ell \sqrt{\ell_D} \, x \alpha_T}{\Lambda(\sqrt{\ell_{hD}} + \sqrt{\ell_{Dh}})} \frac{\gamma - 1}{\gamma} \\ &\quad \times (x\alpha_T - h_2 - h_s), \end{aligned} \tag{33b}$$

$$\begin{aligned} f_{hD} &= \left(1 + \frac{\gamma - 1}{\gamma} \zeta \right) (\sqrt{\ell_h} + \sqrt{\ell_D}) \\ &\quad - \frac{\gamma - 1}{\gamma} x \alpha_T \left(1 - \frac{\gamma - 1}{\gamma} x \alpha_T \right) \sqrt{\ell_D}, \end{aligned} \tag{33c}$$

with $\zeta = \sqrt{\ell_h / \ell_D} \, x/(1 - x)$.

In a gas mixture or a pure gas without evaporation-condensation ($d_\ell = 0$, or $x = 1$), expressions (33a)–(33c) coincide with the results previously obtained in [5,15].

Equations (33a)–(33c) show that the two components of the mixture do not symmetrically contribute to the diffusion phenomena due to the combined effect of evaporation and condensation within the boundary and the variations of the film thickness (effects expressed by the terms factor of d_ℓ).

On the other hand, for a pure saturated vapor ($x = 0$ and $M = M_2$), expression (33a) gives

$$-\rho_0 a_0 \frac{v_u}{p} \approx \frac{1+j}{\sqrt{2}} \sqrt{k_0} \left[\frac{k_w^2}{k_0^2} \sqrt{\ell'_v} + (\gamma - 1) \frac{\sqrt{\ell_h}}{q_h} \right] + \beta_f \,, \tag{34a}$$

where $q_h = 1 + [1 + jk_h d_\ell h_0 h_s (\gamma - 1)/\gamma]/\Lambda$ and

$$\beta_f = \frac{jk_0 d_\ell \gamma}{q_h} \left[1 + \left(1 - \frac{\gamma - 1}{\gamma} h_0 \right) \frac{\zeta_s}{\Lambda} \right]. \tag{34b}$$

Equation (34b), which expresses the specific acoustic admittance of the liquid film, differs from the result previously obtained by Mehl and Moldover [7, Eq. (21)]:

$$-\rho_0 a_0 \frac{v_u(d)}{p} = \frac{jk_0 d_\ell \gamma}{q_h} \left(1 + \frac{\zeta_s}{\Lambda} \right), \tag{34c}$$

as adapted to the notation used in this work. In fact, while both expressions account for the acoustic effects of the variation of the film thickness, Eqs. (34a) and (34b) additionally take into account the influence on the rate of evaporation and condensation due to thermal diffusion in the boundary layers. The quantitative influence of this additional contribution is further discussed below in Sec. VI A.

B. Quasi-plane waves in cylindrical waveguides

We consider a waveguide with perfectly rigid walls (Fig. 3). By calculating the mean value of Eq. (31) over the section S of the guide, we derive the wave equation which governs the pressure variation of quasi-plane waves. To achieve this, we initially remark that the mean value of the normal velocity v_u over the waveguide section is null:

$$\langle \partial v_u / \partial u \rangle_S = 0.$$

Then, in Eq. (31), the mean values of the variables τ, b, and $\mathbf{v_w}$ are substituted by the mean values of their respective expressions, Eqs. (27), (28), and (30). Here, the functions

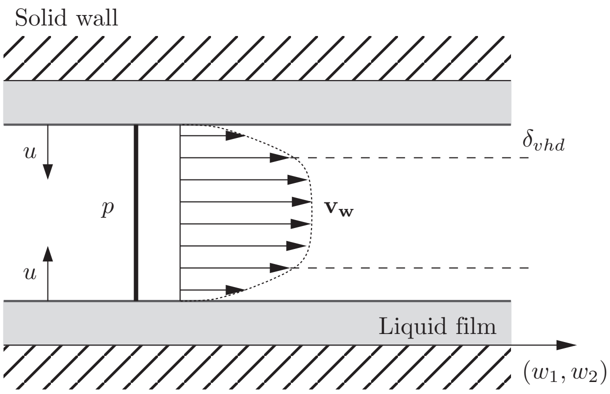

FIG. 3. Acoustic pressure and particle velocity fields across a section of a waveguide.

$\varphi_X(u)$ are a linear combination of calculable Bessel or trigonometric functions, depending on the geometry of the waveguide. Finally, by denoting $K_X = \langle \varphi_X(u) \rangle_S$ and using V/A as the volume to surface ratio of the waveguide, we have

$$\left.\frac{\partial \varphi_X}{\partial u}\right|_d = \frac{V}{A} k_X^2 K_X,$$

and the mean value of Eq. (31) corresponds to the propagation equation

$$\left(\Delta_{\mathrm{w}} + k_w^2\right) p = 0, \tag{35}$$

where terms of order greater than 1 for the characteristic lengths are neglected and the wave number k_w takes the following form:

$$\frac{k_w^2}{k_0^2} \approx \frac{1}{1-K_v} \left\{ 1 + \frac{\ell_{Dh} - \ell_{hD}}{\ell_D} \frac{K_{hD} K_{Dh}}{Q_{hD}} \left[\gamma - 1 - \frac{j k_h \delta_\ell \gamma}{\Lambda} \zeta_s \left(\frac{\gamma - 1}{\gamma} h_2 + x \alpha_P \right) \right] \right.$$
$$\left. - \frac{A}{V} \frac{\delta_\ell \gamma x}{Q_{hD}} \left[\alpha_P \Xi_{hD} + \frac{\gamma - 1}{\gamma} \left(\frac{\Xi_{Dh}}{1-x} + \frac{x \alpha_T M_2}{M} (K_{Dh} - K_{hD}) \right) \right] \right\} - j k_0 \ell_{vhd} \,, \tag{36a}$$

with

$$\Xi_{hD} = \left(1 - \frac{\ell_h}{\ell_{Dh}}\right) K_{Dh} - \left(1 - \frac{\ell_h}{\ell_{hD}}\right) K_{hD}, \tag{36b}$$

$$\Xi_{Dh} = \left(1 - \frac{\ell_{Dh}}{\ell_D}\right) K_{Dh} - \left(1 - \frac{\ell_{hD}}{\ell_D}\right) K_{hD}, \tag{36c}$$

and

$$Q_{hD} = \left(1 + \frac{j k_h \delta_\ell}{\Lambda} \frac{\gamma - 1}{\gamma} h_2 h_s\right) \Xi_{hD} - \frac{j k_h \delta_\ell x}{\Lambda (1-x)} \Xi_{Dh}$$
$$+ \frac{\ell_{Dh} - \ell_{hD}}{\ell_D} \left(\frac{A}{V} \frac{\delta_\ell x}{1-x} + \frac{j k_h V}{\Lambda A} K_{hD} K_{Dh} \right)$$
$$- \frac{j k_h \delta_\ell x}{\Lambda} \frac{\gamma - 1}{\gamma} \alpha_T (h_2 - h_s)(K_{Dh} - K_{hD}). \tag{36d}$$

We remark that the terms of order 1 for the characteristic lengths ℓ_v, ℓ_h, and ℓ_D are included in the formalism, and the bulk effects are included in the same model by the term ℓ_{vhd}.

For a gas mixture without evaporation-saturation ($d_\ell = 0$), this expression is consistent with the one obtained from the model presented in Ref. [5]. For the case of a pure saturated vapor, the wave number k_w reduces to

$$\frac{k_w^2}{k_0^2} \approx \frac{1}{1-K_v}$$
$$\times \left[1 + (\gamma - 1) K_h \frac{1 - j k_h d_\ell h_0 \zeta_s / \Lambda}{1 + j k_h \left(\frac{V}{A} K_h + \frac{\gamma - 1}{\gamma} h_0 h_s d_\ell \right) / \Lambda} \right]$$
$$- j k_0 \ell_{vhd}. \tag{37}$$

VI. SPECIFIC RESULTS IN PURE VAPORS AND GAS-VAPOR MIXTURES

A. Reflection on a quasi-plane rigid wall in pure propane saturated vapor

As a first application of the model discussed above, we compare its prediction of the acoustic admittance of a wall in contact with saturated propane with the theoretical results obtained by Mehl and Moldover [7] to account for the observed anomalous decrease of the speed of sound in precondensation conditions.

For this comparison $T_0 = 287.65$ K and P_0 is varied near the nominal saturation pressure $P_s = 0.72$ MPa so that $1.0 \times 10^{-12} < (P_s - P_0)/P_s < 0.6$, with a corresponding variation [based on the assumption that $\nu = 3$ in Eq. (18)] of the thickness d of the condensed liquid film coating the wall between 5×10^{-10} (a few molecular layers) and 1.0×10^{-5}. The thermophysical properties of propane used as input data in the model are the same as tabulated in Table 1 in Ref. [7], while the sensitive dependence on static pressure of the vapor density, speed of sound, and heat capacity were taken from the equation of state of propane of Younglove and Ely [16].

For a normal incident wave ($k_w = 0$), the expression of the total specific admittance describing the "classical" thermal effects in the boundary layers and the effects of the adsorbed liquid film on the acoustic field as previously modeled by Mehl and Moldover [7, Eq. (21)] takes the following form [see Eq. (34c)]:

$$j \beta_{\mathrm{tot}}^{MM} = \frac{j-1}{\sqrt{2}} (\gamma - 1) \sqrt{k_0 \ell_h} - \frac{k_0 d_\ell \gamma}{q_h} \left(1 + \frac{\zeta_s}{\Lambda} \right). \tag{38}$$

The real and imaginary parts of the total acoustic admittance calculated using Eq. (38) (dotted lines) are compared in Fig. 4 to the same quantities as predicted by Eq. (33) in this work

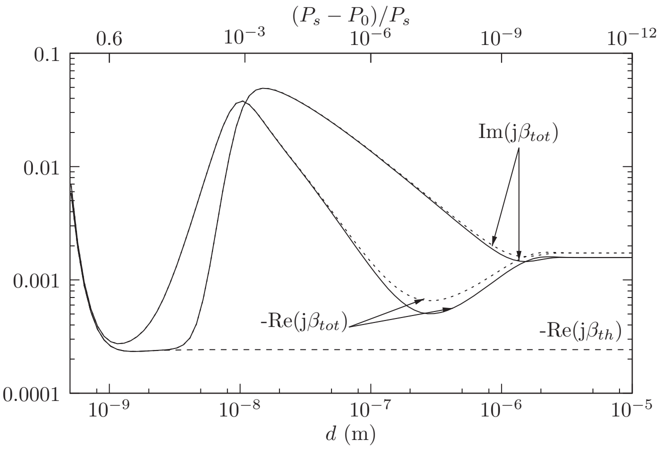

FIG. 4. Real and imaginary parts of the specific total admittances $j\beta_{\text{tot}}$ [Eq. (33), solid lines] and $j\beta_{\text{tot}}^{MM}$ [Eq. (38), dotted lines] and thermal admittance $j\beta_{\text{th}}$ [Eq. (39), dashed line, with equal real and imaginary parts] of a plane rigid wall coated with a liquid film of depth d, in propane near saturation for $f = 24$ kHz.

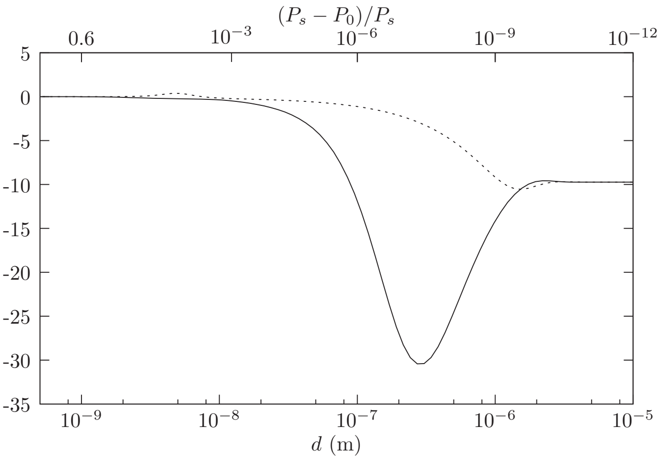

FIG. 5. Relative differences (percent) between the real parts (solid line) and imaginary parts (dotted line) of the specific total admittances $j\beta_{\text{tot}}$ [Eq. (33)] and $j\beta_{\text{tot}}^{MM}$ [Eq. (38)] in propane near saturation for $f = 24$ kHz.

(solid lines) as functions of the liquid film thickness d (the equivalent relative pressure scale is also represented in Fig. 4).

Also represented in Fig. 4 (dashed line) is the specific admittance

$$j\beta_{\text{th}} = (j-1)/\sqrt{2}(\gamma - 1)\sqrt{k_0 \ell_h}\,, \tag{39}$$

expressing the "classical" thermal effects in the boundary layers [15].

When the thickness of the liquid film is at its minimum (i.e., $d \leqslant 10^{-9}$ m), the specific admittance tends to the "classical" thermal admittance β_{th} as expected. However, we shall notice that the relative difference between the total specific admittance of the wall β_{tot} and its thermal admittance β_{th} starts to be relevant from $d = 10^{-9}$ and $P_0 \approx 0.37 P_s$ since it is at least 10% there and could be even more when considering nonsmooth walls.

For a "thin" liquid film, when 10^{-9} m $\leqslant d \leqslant 10^{-8}$ m [i.e., $0.632 \geqslant (P_s - P_0)/P_s \geqslant 10^{-3}$], the expression of Λ in Eq. (17b) is reduced to its limit for small values of d because the effect of thermal diffusion inside the liquid film is negligible. As a consequence, in this range of static pressures, the expression of the total specific admittance β_{tot} simplifies to

$$j\beta_{\text{thin}} \approx \frac{j-1}{\sqrt{2}}(\gamma - 1)\sqrt{k_0 \ell_h} - k_0 d_\ell \gamma\,, \tag{40}$$

showing that precondensation effects within the boundary layer are purely reactive with the corresponding contributions to the total admittance of the boundary layer which have the same order of magnitude.

Finally, for $d \geqslant 10^{-8}$ m [i.e., $(P_s - P_0)/P_s \leqslant 10^{-3}$], namely, for a "thick" liquid film, the multiplying factors in the term including d_ℓ prevail, leading to, for the specific admittance of the wall,

$$j\beta_{\text{thick}} \approx \frac{j-1}{\sqrt{2}}\sqrt{k_0 \ell_h}\,\frac{\Lambda\gamma}{h_0 h_s(\gamma - 1)/\gamma}\,. \tag{41}$$

In Eq. (41), "classical" thermal effects may be neglected as they have the same order of magnitude of the characteristic thermal length ℓ_h. In fact, the acoustic and thermal fields within the boundary are governed by the combined effect of precondensation and thermal diffusion, expressed by the h_s and h_0 factors.

The relative influence of the latter contribution, which is accounted for in this work but not in Ref. [7], is evident in Fig. 5, which displays the relative differences of the specific total admittance as predicted by these alternative models.

We next consider the relevance of the perturbing effect of boundary layer precondensation and thermal phenomena on the complex resonance frequencies measured in a spherical acoustic cavity. As an example, the induced shift Δf_{0n} to the unperturbed resonance frequency f_{0n} and the corresponding contribution to the half width g_{0n} of the nth radial mode of the resonator used in Ref. [7] (radius $R = 6.35$ cm) to measure these effects in nearly saturated propane is

$$(\Delta f_{0n} + j g_{0n})/f_{0n} = j\beta_{\text{tot}}/z_{0n}\,, \tag{42}$$

with z_{0n} being the nth zero of the spherical Bessel function of first order j_0.

The model discussed above for the specific admittance β_{tot} can be used to predict the contribution of precondensation effects to the total energy loss that takes place within the boundary layer of the resonator. When this is done, it is found that the contribution of precondensation to the half width g_{0n} of a radial mode can be as high as 4.5×10^{-3} when scaled to the corresponding resonance frequency f_{0n}.

Thus, the predictions of the theoretical model presented in this work may be subject to accurate verification with this type of instrument, which has a demonstrated agreement between experiment and theory on the order of a few parts per million [17]. When available, these experimental data may lead to a more realistic equation describing the influence of the wall surface roughness on the minimum pressure at which the presence of the liquid film is detectable.

B. Attenuation in a cylindrical duct filled with a mixture of air and saturated water vapor

In this section, we consider the acoustic propagation in a cylindrical duct of 1 mm in diameter made of different materials and filled with an air-water vapor mixture. This case has been previously considered by Raspet *et al.* [10,12] to test their models of acoustic propagation in wet porous materials. There, the composition and total static pressure of the air-water vapor mixture vary as a function of the temperature with the partial pressure of air P_1 remaining constant at 101.325 kPa and the partial pressure of water P_2 being equal to the vapor pressure $P_s(T)$. With this rule, when temperature T_0 is varied from 0.1 °C to 100 °C, the molar fraction of water vapor $x_w = 1 - x$ varies between 6.0×10^{-3} and 0.506, and the static pressure of the mixture $P_0 = P_1 + P_2$ varies from about 101.959 to 202.74 kPa.

The thermophysical properties of air and water, which are needed as input data to model acoustic propagation within the bulk of the mixture and in the boundary layer, are retrieved from the following sources: the thermodynamic and transport properties of dry air from correlations worked out by Lemmon and coworkers [18,19]; the thermodynamic properties of liquid and gaseous water, including the saturated vapor pressure, from the International Association for the Properties of Water and Steam (IAPWS) equation of state of Wagner and Pruß [20]; the transport properties of water from the correlation of Kestin *et al.* [21]; the enhancement factor of humid air from the pioneering work of Hyland [22]; the density of humid air from a virial expansion truncated at second order using recent correlations of the second virial coefficient of water [23] and the interaction virial coefficient of the air-water system [24]; the speed of sound in the mixture, including relaxation effects, using the method of Zuckerwar and references therein [25]; the transport properties of the humid mixture, namely, the diffusion coefficient, the thermal diffusion ratio, shear viscosity, and thermal conductivity, with the methods and the data discussed and tabulated for a mixture of nonpolar and polar components by Hirschfelder *et al.* [26].

For the sake of the comparison between the acoustic models discussed below, it should be noted that the agreement of our estimate of the mixture properties with those reported by Raspet *et al.* [10] is in every case satisfactory, with the exception of the thermal conductivity of gaseous water and the thermal diffusion ratio of the mixture, which show relative differences up to 25% and 50%, respectively, originating from the different estimate of the thermal conductivity of water vapor.

Finally, the physical properties of the duct material (steel or cork) are the same as those tabulated by Slaton *et al.* [12].

The quantity of interest here is the attenuation coefficient of the duct (as a function of the temperature in the interval 0 °C to 100 °C at 10 kHz), which is proportional to the imaginary part of the wave number k_w given by Eq. (36) in the present work or by Eq. (30) in the work of Slaton *et al.* [12].

As shown in Fig. 6, the theoretical duct attenuation obtained herein is comparable in magnitude but shows a rather different trend from that of Slaton *et al.* [12, Fig. 2].

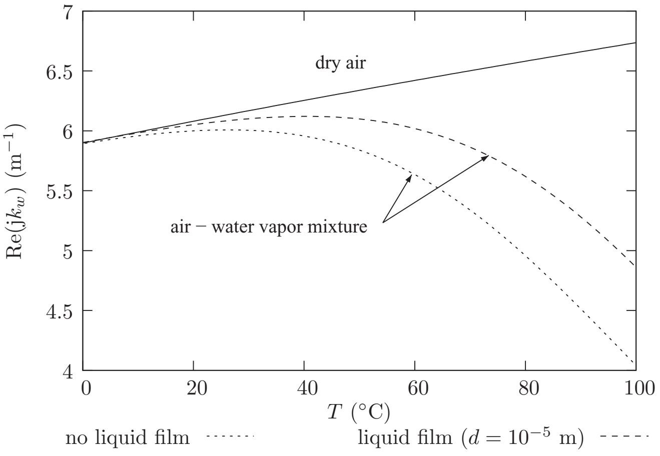

FIG. 6. Attenuation coefficient of a cylindrical duct (diameter 1 mm) filled with dry air (solid line) or an air-water vapor mixture, in the presence or absence of a boundary liquid film (dashed and dotted lines, respectively) at 10 kHz as a function of the temperature.

Regarding the case in which precondensation effects are neglected (i.e., no liquid film and isothermal boundary conditions on the solid wall), according to the model presented here, the effects of mutual diffusion on the attenuation are very small. Indeed, in this case, when we use the well-known simple expression of k_w in a duct filled with a thermoviscous gas available in Refs. [5,15] (mutual diffusion effects neglected), the final results for the duct attenuation are very close to those shown in Fig. 6 (dotted line), which lead to approximately 4 m^{-1} at $T = 100$ °C. These results are coherent with those found by Slaton *et al.* when the same kind of expression is used to calculate the duct attenuation (case denoted "effective fluid" in [12, Fig. 2]), even though the method used here for calculating the properties of humid air differs from those used by Slaton *et al.*

However, still neglecting precondensation effects, Slaton *et al.* also found that taking into account mutual diffusion effects in the gas-vapor mixture makes duct attenuation reach

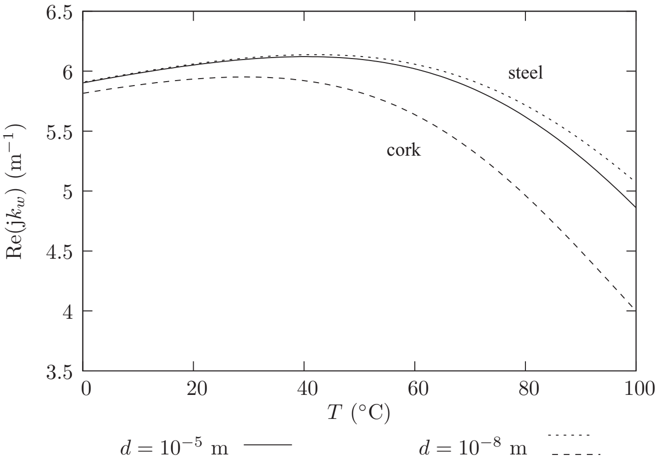

FIG. 7. Attenuation coefficient of a cylindrical duct (diameter 1 mm) of different materials, steel (dotted line) and cork (dashed line), filled with an air-water saturated vapor mixture, with a boundary liquid film of different thicknesses d (10^{-5} m for solid line and 10^{-8} m for dotted and dashed lines), at 10 kHz as functions of the temperature.

nearly 9 m^{-1} at $T = 100$ °C (case denoted "no temperature fluctuation" in [12, Fig. 2]). Also, the model of Slaton *et al.* predicts total attenuation in the air-water vapor mixture which is larger or smaller than that in dry air, depending on the material of the duct, whereas in the present work, the predicted attenuation is always smaller in the mixture with respect to dry air (see Fig. 7 and explanation below). These discrepancies reflect the different assumptions made by the different models to justify their approximations of the boundary conditions.

In agreement with our previous model of mutual diffusion effects in binary gaseous mixtures away from saturation [5], the results in Fig. 6 show that mutual diffusion effects in the gas, which do not involve the exchange of molecules between the gas and the liquid [expressed by the terms which contain the parameter δ_ℓ, Eq. (36a)], give a very small contribution to the total attenuation (less than 0.1% at approximately 0 °C to 10 °C). On the other hand, we can see in Fig. 6 that the thermal and concentration diffusion effects related to the liquid film and to the phase changes on the boundaries are significant since they have a relative contribution up to 17% at 100 °C.

It is worth noticing that for a thick film [i.e., $d \geqslant 10^{-8}$ m and $(P_s - P_2)/P_s \leqslant 10^{-3}$], the expression of the wave number k_w [Eqs. (36a)–(36c)] is mostly governed by the terms which contain the parameter δ_ℓ and reduces to

$$\frac{k_w^2}{k_0^2} \approx \frac{1}{1-K_v}\left\{1 - \frac{jk_h\gamma}{\Lambda}\zeta_s\left(\frac{\gamma-1}{\gamma}h_2 + x\alpha_P\right)\frac{\ell_{Dh} - \ell_{hD}}{\ell_D}\frac{K_{hD}K_{Dh}}{Q_{hD}} - \frac{A}{V}\frac{\gamma x}{Q_{hD}}\left[\alpha_P\Xi_{hD} + \frac{\gamma-1}{\gamma}\left(\frac{\Xi_{Dh}}{x_w} + \frac{x\alpha_T M_2}{M}(K_{Dh} - K_{hD})\right)\right]\right\},$$

with

$$Q_{hD} = \frac{A}{V}\frac{x}{x_w}\frac{\ell_{Dh} - \ell_{hD}}{\ell_D} + \frac{jk_h}{\Lambda}\left[\frac{\gamma-1}{\gamma}h_2 h_s\Xi_{hD} - \frac{x}{x_w}\Xi_{Dh}\right].$$

Slaton *et al.* noted important discrepancies between the results for acoustic attenuation depending on the material of the duct [12]. In Fig. 7, we also note this effect, but with a rather different trend. So we next consider the influence of the solid material of the duct, choosing steel and cork to represent radically different physical properties. In spite of this difference, the calculated acoustic attenuation for these two materials when the wall is coated with a 10^{-5} m depth liquid film displays negligible differences (relatively less than 1.5×10^{-6}, with the solid line in Fig. 7 standing for both a steel and a cork duct). For this case, in fact, the thermal diffusion processes inside the liquid film and the wall, as expressed by the boundary condition (21a), which involves Λ and Θ, take place almost completely within the thick liquid film, where the major part of the thermal wave is dissipated.

On the contrary, if we consider a 10^{-8} m depth liquid film [i.e., for $(P_s - P_2)/P_s \approx 10^{-3}$], the thermal diffusion in the solid wall and its thermodynamic behavior are significant, and the physical properties of the solid material have great influence on the total acoustic attenuation, as shown in Fig. 7 (dashed and dotted lines). When we compare these results with those calculated for a 10^{-5} m depth adsorbed liquid film (solid line), the relative discrepancies in the behavior of the mixture are 4% for the steel duct and 18% for the cork duct. Therefore, it is evident that correct estimates of the thickness d of the liquid film and of the quantity $(P_s - P_2)/P_s$ are necessary to a reliable calculation of the total acoustic attenuation within the duct.

VII. CONCLUSION AND PROSPECTS

An analytical model for acoustic propagation has been worked out which accounts for the coupled effects of heat and mutual diffusion processes and phase changes at the vapor-liquid interface coating a solid wall. The model is suited for application to a gaseous mixture when the thermodynamic state of one of its constituents approaches saturation. Therefore, its predictions should be useful to improve the description of acoustic phenomena encountered in a variety of applications, including the metrology of the thermophysical properties of gaseous mixtures, the estimate of acoustic attenuation in porous media, and thermoacoustics.

As a preliminary test of the effectiveness of the model, it was used to predict salient acoustic properties of two systems, which were previously described in the literature, namely, the variation of the boundary layer acoustic impedance of an acoustic resonator and the total attenuation in a small duct coated with a liquid film. In both cases an overall satisfactory agreement was found between the results presented here and those calculated with more simplified models, increasing confidence in the correctness of the derived solutions and their implementation. Minor differences highlighted by this comparison were used to quantify the relevance of diffusion processes.

So far, no experimental attempt has been carried out to validate the prediction capability of the model, and this is likely to be the subject of future investigation. Such experimental activity might improve our knowledge of the acoustic effects of an adsorbed liquid film at low pressure. Acoustic quasi-spherical resonators are the most suitable experimental technique for this aim because of the accuracy demonstrated in the determination of the speed of sound and boundary layer losses.

[1] G. W. Swift and P. S. Spoor, J. Acoust. Soc. Am. **106**, 1794 (1999).

[2] R. A. Hiller and G. W. Swift, J. Acoust. Soc. Am. **108**, 1521 (2000).

[3] D. A. Geller and G. W. Swift, J. Acoust. Soc. Am. **111**, 1675 (2002).

[4] R. M. Gavioso, D. Madonna Ripa, C. Guianvarc'h, G. Benedetto, P. A. Giuliano Albo, R. Cuccaro, L. Pitre, and D. Truong, Int. J. Thermophys. **31**, 1739 (2010).

[5] C. Guianvarc'h and M. Bruneau, J. Acoust. Soc. Am. **131**, 4252 (2012).

[6] B. A. Younglove and R. D. McCarty, J. Chem. Thermodyn. **12**, 1121 (1980).

[7] J. B. Mehl and M. R. Moldover, J. Chem. Phys. **77**, 455 (1982).

[8] S. E. Turner and D. R. Dowling, J. Acoust. Soc. Am. **97**, 1014 (1995).

[9] Y. Mao, J. Acoust. Soc. Am. **104**, 664 (1998).

[10] R. Raspet, C. J. Hickey, and J. M. Sabatier, J. Acoust. Soc. Am. **105**, 65 (1999).

[11] R. Raspet, W. V. Slaton, and C. J. Hickey, J. Acoust. Soc. Am. **112**, 1414 (2002).

[12] W. V. Slaton, R. Raspet, and C. J. Hickey, J. Acoust. Soc. Am. **108**, 2120 (2000).

[13] C. J. Hickey, R. Raspet, and W. V. Slaton, J. Acoust. Soc. Am. **107**, 1126 (2000).

[14] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, Oxford, 1982).

[15] M. Bruneau, *Fundamentals of Acoustics*, translated by T. Scelo (ISTE, London, 2006).

[16] B. A. Younglove and J. F. Ely, J. Phys. Chem. Ref. Data **16**, 577 (1987).

[17] R. M. Gavioso, G. Benedetto, P. A. Giuliano Albo, D. Madonna Ripa, A. Merlone, C. Guianvarc'h, F. Moro, and R. Cuccaro, Metrologia **47**, 387 (2010).

[18] E. Lemmon, R. Jacobsen, S. Penoncello, and D. Friend, J. Phys. Chem. Ref. Data **29**, 331 (2000).

[19] E. Lemmon and R. Jacobsen, Int. J. Thermophys. **25**, 21 (2004).

[20] W. Wagner and A. Pruß, J. Phys. Chem. Ref. Data **31**, 387 (2002).

[21] J. Kestin, J. Sengers, B. Kamgar-Parsi, and J. Levelt Sengers, J. Phys. Chem. Ref. Data **13**, 175 (1984).

[22] R. Hyland, J. Res. Natl. Bur. Stand. **79A**, 551 (1975).

[23] A. H. Harvey and E. W. Lemmon, J. Phys. Chem. Ref. Data **33**, 369 (2004).

[24] A. H. Harvey and P. H. Huang, Int. J. Thermophys. **28**, 556 (2007).

[25] A. J. Zuckerwar, *Handbook of Speed of Sound in Real Gases* (Academic, San Diego, 2002), Vols. 1 and 3 .

[26] J. V. Hirschfelder, C. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).