Adiabatic lapse rate of non-ideal gases: The role of molecular interactions and vibrations

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We report a formula for the dry adiabatic lapse rate that depends on the compressibility factor and the adiabatic curves. Then, to take into account the non-ideal behavior of the gases, we consider molecules that can move, rotate, vibrate, and the information of molecular interactions through the virial coefficients. We deduce the compressibility factor in its virial expansion form and the adiabatic curves within the virial expansion up to any order. With this information and to illustrate the mentioned formula, we write down the lapse rate for the ideal gas, and the virial expansion up to the second, and up to the third coefficient cases. To figure out the role of the virial coefficients and vibrations, under different atmospheric conditions, we calculate the lapse rate in the Earth, Mars, Venus, Titan, and the exoplanet Gl 581d. Furthermore, for each one we consider three models in the virial expansion: van der Waals, square-well, and hard-sphere. Also, when possible, we compare our results to the experimental data. Finally, we remark that for Venus and Titan, which are under extreme conditions of pressure or temperature, our calculations are in good agreement with the observed values, in some instances.

I. INTRODUCTION

The lapse rate, $\Gamma$, of an astronomic object’s atmosphere is by definition the rate of change of its temperature with respect to height. Its value has been determined for many objects within the solar system.\textsuperscript{2,4} The usual theoretical approach to study this quantity is the so-called dry adiabatic lapse rate (DALR). In this model, each parcel of the atmosphere is considered to be in thermal equilibrium and exchange no heat with its surroundings. Also, it makes use of the hydrostatic equation and the equation of state of the gas. The most elemental estimation of the DALR is obtained by considering the ideal gas model (denoted henceforth as $\Gamma^{IG}$), but this calculation yields a value that is far from experimental data.\textsuperscript{5} This is expected, on one hand, since the atmospheres comprise many other elements (Earth’s atmosphere contains traces of vapor, for example). On the other hand, the molecules of a real gas can vibrate and interact between them (non-ideal gas behavior).

Some authors try to incorporate these non-ideal gas effects of the molecules using experimental information about the gas in the formula of $\Gamma^{IG}$.\textsuperscript{3,4} This is an incorrect procedure because the $\Gamma^{IG}$ strongly depends on the initial assumptions. A derivation of a DALR for real gases is found in Ref.\textsuperscript{4}, where the author applied his formula on Venus, obtaining a good approximation to the experimental value. A limitation of this approach is the availability of experimental data in the range of atmospheric conditions for other astronomic objects. From the theoretical point of view, a shortcoming of this method is the impossibility of quantifying the origin of the correction, namely, the molecular vibrations, or the molecular interactions, or both.

An attempt to quantify the contribution of molecular interactions can be found in Ref.\textsuperscript{4}. There, the authors analyze the effect of the second virial coefficient on the DALR. This means that they include the possibility of pair interaction only. This is quite restrictive, in fact, in some instances, the $n$-particle interactions could be relevant. Nevertheless, they find that in Titan, given its atmospheric conditions, these interactions have a strong effect on the DALR towards the observed value. The purpose of this paper is to incorporate the information of $n$-particle interactions and the possibility of molecular vibrations to the DALR model.

The plan of the paper is the following. In Sec.\textsuperscript{II} we deduce a formula for the DALR that depends on the compressibility factor (for fluids) and the adiabatic curves. Next, from statistical mechanics, in Sec.\textsuperscript{III} we deduce the compressibility factor and the adiabatic curves within the virial expansion up to any order and allowing molecular vibrations. In Sec.\textsuperscript{IV} we combine the results of sections\textsuperscript{II} and\textsuperscript{III} to compute the DALR for some particular cases of the virial expansion for vibrating and non-vibrating molecules. There, we also discuss three instances of virial coefficients related to simple fluid models, namely: van der Waals, square-well, and hard-sphere. As an application of the formulae obtained, we devote Sec.\textsuperscript{V} to calculate the DALR for the Earth, Mars, Venus, Titan, and the exoplanet Gl 581d. Finally, in Sec.\textsuperscript{VI} we compare our results to the observational data and in the case of Venus to those reported in Ref.\textsuperscript{4}, and we present our conclusions.
II. DRY ADIABATIC LAPSE RATE

In this section, we shall determine a general expression for the DALR for non-ideal gases. The mathematical definition of the lapse rate is

\[ \Gamma := -\frac{dT}{dz}, \quad (1) \]

where \( T \) is the temperature and \( z \) the height. We show below that it turns out to be proportional to the well-known DALR of monocomponent ideal gases given by

\[ \Gamma_{IG} = \frac{M_{mol}g}{C_P^f}, \quad (2) \]

where \( M_{mol} \) is the molar mass of the gas of the atmosphere, \( g \) denotes the magnitude of the acceleration due to gravity close to the surface of the astronomical object, and \( C_P^f \) is the specific heat at constant pressure for ideal gases, whose value is \( C_P^f = \frac{R}{2g} \), where \( f_r = 0, 2 \) and 3, for monoatomic, diatomic or linear, and polyatomic molecules, respectively. \( R \) is the gas constant \( (R = 8.31 \text{ J/(mol K)}) \). In the equation above and in what follows, we consider one mole of gas.

We start our derivation from the definition of the compressibility factor, \( Z \),

\[ Z := \frac{PV}{RT}, \quad (3) \]

where \( P \) is the pressure, \( V \) is the volume, and \( T \) is the absolute temperature of the gas. The value of \( Z \) can be determined experimentally (see for example Ref. [11]), obtaining then an equation of state that describes real gases. As we mentioned, a shortcoming of this approach is the availability of data for the conditions of interest in the astronomical objects under study. As an alternative, there exist theoretical models that propose some specific functions for \( Z \), that can be physically interpreted, such as ideal gas \( (Z = 1) \), van der Waals [12], and Redlich-Kwong [10] models, among others. Within the theoretical approaches, we are interested in the virial expansion, which accounts for interactions between successively larger groups of molecules. For completeness, we derive the corresponding \( Z \) in Sec. III from statistical mechanics. At this moment it is sufficient to know that in this approach \( Z \) can be expressed as a function that only depends on \( V \) and \( T \), i.e., \( Z = Z(V,T) \).

Furthermore, we are interested in the analysis of the adiabatic lapse rate. The adiabatic process dictates the specific forms of the curves in the different diagrams, they are called adiabatic curves. We obtain these curves in Sec. III for the general formula that we are getting after, it is enough to use that, in the region we are interested in, the volume can be written as a function of the temperature, \( V = V(T) \), on each adiabatic curve. From now on, for functions that only depend on \( T \) we denote with a prime its derivative respect to the temperature, for example, \( V' \).

According to the general considerations discussed above, from (3) we have

\[ dP = \frac{R}{V} \left( Z + T \frac{\partial Z}{\partial T} - Z T \frac{V'}{V} + T \frac{\partial Z}{\partial V} V' \right) dT. \quad (4) \]

On the other hand, using that the density of the gas, \( \rho \), in the atmosphere is given by \( \rho = \frac{M_{mol}}{V} \) we can write the hydrostatic equation as

\[ dP = -\frac{M_{mol}g}{V} dz. \quad (5) \]

Substituting (3) in (4) and taking into account (1) and (2), we obtain

\[ \Gamma = \Gamma_{IG} \frac{C_P^f}{R} \left( Z + T \frac{\partial Z}{\partial T} - Z T \frac{V'}{V} + T \frac{\partial Z}{\partial V} V' \right)^{-1}. \quad (6) \]

Let us make some remarks about Eq. (6):

1. Regarding the compressibility factor, this equation only makes use of the fact that \( Z \) can be expressed as a function of the volume and temperature. This happens in the virial expansion to any order and this is also true for the compressibility factor obtained from other equations of state, for example, the van der Waals equation.

2. As we have mentioned before, in the virial expansion \( Z \) accounts for interactions between successively larger groups of molecules. However, by itself, it is not sensitive to the vibrational state of the molecules.

3. We must emphasize that this equation is evaluated on an adiabatic curve \( V = V(T) \). We show in Sec. III that the energy, which is used to derive the adiabatic curves, is not only modified by the virial coefficients, but it also takes into account the contribution of molecular vibrations.

4. Of course, equation (6) reproduces (2), because for the ideal gas case \( Z = 1 \), and the adiabatic curves of ideal gases satisfy \( V'/V = -C_{IG}^f / (RT) \), where \( C_{IG}^f \) is the specific heat at constant volume for ideal gases, which fulfills \( C_V^f = C_{IG}^f - R (= \frac{5}{2} R) \). Using this, we have \( \Gamma = \Gamma_{IG} \).

5. Notice that, so far, the consideration of a monocomponent gas in (3) is only explicit in \( \Gamma_{IG} \) and \( C_P^f \) which can be generalized to the case of multicomponent gases. However, in that scenario the compressibility factor and the adiabatic curves are modified in a non-trivial way. In what follows, we restrict ourselves to the monocomponent case, which suffices to understand the atmospheric features of the astronomical objects that we are interested in.
III. EQUATION OF STATE AND ADIABATIC CURVES

We start from the partition function for the non-ideal gases in which we are interested. This allows us to compute the average pressure and the average energy. Then, using the ensemble postulate of Gibbs, we obtain the thermodynamic variables of interest, the pressure and the internal energy. From the pressure expression, we derive the equation of state for this system. Then, we identify the compressibility factor, which corresponds to the well-known functional expression of $Z$ in the virial expansion. On the other hand, we need the internal energy to describe the adiabatic processes, i.e., the adiabatic curves, which we calculate at the end of this section.

The partition function, in the Mayer’s representation, of a gas constituted by $N$ indistinguishable particles is given by

$$ Q = Q_{MI} \left( \frac{q_{\text{trans}} q_{\text{rot}} q_{\text{vib}}}{N!} \right)^N, \quad (7) $$

where $Q_{MI}$ is the partition function that codifies the molecular interactions, while the other factors are the partition functions corresponding to the fact that the particles move in a three-dimensional space ($q_{\text{trans}}$), rotate ($q_{\text{rot}}$), and vibrate ($q_{\text{vib}}$). These partition functions are given by

$$ Q_{\text{Mi}} = \exp \left( -N \sum_{k=1}^{\infty} \frac{B_{k+1}}{k V^k} \right), \quad (8a) $$

$$ q_{\text{trans}} = \left( \frac{2\pi M k_B T}{\hbar^2} \right)^{3/2} V, \quad (8b) $$

$$ q_{\text{rot}} = \frac{T^{j/2}}{\theta_{\text{rot}}}, \quad (8c) $$

$$ q_{\text{vib}} = \prod_{j=1}^{m} \exp \left( -\frac{\theta_j}{2T} \right) \exp \left( -\frac{\theta_j}{T} \right), \quad (8d) $$

where in (8a), $B_{k+1}$ are the so-called virial coefficients, which represent the $(k+1)$-particle interactions. They are, by construction, functions that can only depend on the temperature $T$. In (8b), $M$, $k_B$, and $\hbar$ are the mass of the molecule, the Boltzmann constant, and the Planck constant, respectively. In (8c), $\theta_{\text{rot}}$ is a constant related to the characteristic rotational temperatures. Finally, in (8d), $m$ is the number of natural vibrational frequencies, $\nu_j$, and $\theta_j := h\nu_j/k_B$ are known as vibrational temperatures. Concerning $q_{\text{vib}}$, notice that a) Its value is gas-dependent. b) For models where there is no need to incorporate the molecular vibration information, it is enough to set $q_{\text{vib}} = 1$. This allows us to turn off the vibrational modes, and c) It is a function that only depends on $T$.

Now, the average pressure and average energy, in the canonical ensemble, are calculated as

$$ \langle P \rangle = k_B T \left( \frac{\partial}{\partial V} \ln Q \right)_{N,T}, \quad (9a) $$

$$ \langle E \rangle = k_B T^2 \left( \frac{\partial}{\partial T} \ln Q \right)_{N,V}. \quad (9b) $$

Therefore, using (8d) and the partition function (7), for one mole, we obtain

$$ \frac{\langle P \rangle V}{RT} = 1 + \sum_{k=1}^{\infty} \frac{B_{k+1}}{k V^k}, \quad (10a) $$

$$ \langle E \rangle = C_V T + RT^2 \Phi - RT^2 \sum_{k=1}^{\infty} \frac{B_{k+1}}{k V^k}, \quad (10b) $$

where $\Phi := q'_{\text{vib}}/q_{\text{vib}}$. Furthermore, through the ensemble postulate of Gibbs, we have that the average pressure and average energy coincide with the pressure and internal energy of the system in the thermodynamic context, i.e., $\langle P \rangle = P$ and $\langle E \rangle = U$. Using the latter result, (10a), and comparing with (9), we have that

$$ Z = 1 + \sum_{k=1}^{\infty} \frac{B_{k+1}}{V^k}. \quad (11) $$

In this way, we have obtained the compressibility factor $Z$ for the well-known virial expansion. This is the function needed in (9) to compute the lapse rate.

Notice that the expression of $Z$ confirms the remark 2 which says that the vibrations do not modify the equation of state and that the energy (10b) takes into account not only the molecular interactions but also the vibrational state of the molecules (through $\Phi$), which confirms the claim we made in remark 3.

Additionally, for (10) we need the adiabatic curves. From the first law of thermodynamics, if we consider an adiabatic process we have

$$ dU + P dV = 0. \quad (12) $$

Plugging the equation of state (10a) and the energy (10b) in (12), we obtain that the adiabatic curves in the $V$-$T$ diagram are given by

$$ T \left[ V q_{\text{vib}} \exp \left( T \Phi - \sum_{k=1}^{\infty} \frac{B_{k+1}}{k V^k} \right) \right]^{R/C_V T} = \varepsilon_0, \quad (13) $$

where $B_{k+1} := TB'_{k+1} + B_{k+1}$ and $\varepsilon_0$ is a constant, that can be determined by the atmospheric conditions on the surface of the astronomical object. However, to be able to use (13) in (9), we need to solve for the volume in terms of the temperature. This last step can not be analytically done for an arbitrary order of the virial expansion. We remark that it strongly depends on the order considered of the virial expansion and that, in the other hand, the vibrations pose no difficulty.
IV. PHYSICAL MODELS AND THEIR DALR

Here, we discuss the following models: ideal gas, the virial expansion up to the second coefficient (both with and without vibrations), and the virial expansion up to the third coefficient with vibrations. We use these models in the Sec.

A. Ideal gas with vibrational modes

Let us consider the case of an ideal gas with and incorporate the effect of vibrational modes. Physically, this case represents a gas composed of non-interacting molecules that can move, rotate, and vibrate. Under these circumstances \( B_k = 0 \) for all \( k \). Then (13) reduces to

\[
TV^{R/C_{IG}V} [q_{vib} \exp(T\Phi)]^{R/C_{IG}V} = \varepsilon_0.
\]  

(14)

The volume as a function of the temperature is

\[
V = \left(\frac{\varepsilon_0}{T}\right)^{C_{IG}V/R} \exp\left(-\frac{RT}{q_{vib}}\right).
\]  

(15)

Then,

\[
\frac{V'}{V} = -\frac{C_{IG}V}{RT} - T\Phi' - 2\Phi.
\]  

(16)

Using (15), (16), and \( Z = 1 \) in (6), we obtain that the DALR is given by

\[
\Gamma = \Gamma_{IG} \frac{C_{IG}V}{C_{IG}P + RT^2\Phi' + 2RT\Phi}.
\]  

(17)

Notice that the corresponding value of \( \varepsilon_0 \) is not needed in (17).

Ideal gas case without vibrations

As we have mentioned, if we do not want to consider the contributions of molecular vibrations it suffices to set \( q_{vib} = 1 \), then \( \Phi = 0 \). Using this in (16) and (17), we find

\[
\frac{V'}{V} = -\frac{C_{IG}V}{RT},
\]  

(18a)

\[
\Gamma = \Gamma_{IG}.
\]  

(18b)

This proves the claim we made in remark 4.

B. Virial expansion up to second order including vibrations

Now, we add to the case IV A the possibility of pair interaction between the molecules. Mathematically, this means we consider the virial expansion up to second order, i.e., \( B_k = 0 \) for \( k > 2 \), therefore (13) reduces to

\[
TV^{R/C_{IG}V} [q_{vib} \exp(T\Phi)]^{R/C_{IG}V} = \varepsilon_0.
\]  

(19)

From which,

\[
V(T) = \frac{B_2}{W(x)},
\]  

(20)

where \( x := B_2 q_{vib} \exp(T\Phi) \left(\frac{2}{\varepsilon_0}\right)^{C_{IG}V/R} \) and \( W(x) \) is the Lambert function. In (20), we obtain the following DALR

\[
\Gamma = \Gamma_{IG} \frac{C_{IG}P}{RT^2\Phi' + 2RT\Phi} \left\{1 + W(x) - T \left[1 + 2B_2 W(x) \right] \left[ \frac{B_2}{B_2} - \frac{1}{1 + W(x)} \right] \right\}^{-1},
\]  

(21)

where the quotient \( x'/x \) is explicitly given by

\[
\frac{x'}{x} = \frac{B_2'}{B_2} + \frac{C_{IG}V}{RT} + 2\Phi + T\Phi'.
\]  

(22)

Notice that the corresponding value of \( \varepsilon_0 \) is needed in (21) because \( x \) depends on it.

Virial expansion up to second order without vibrations

We can directly obtain the case without vibrations from the analysis in Subsec. IV B. The formula for the DALR looks like (21). By setting \( q_{vib} = 1 \), now we have

\[
x = B_2 \left(\frac{T}{\varepsilon_0}\right)^{C_{IG}V/R},
\]  

(23a)

\[
\frac{x'}{x} = \frac{B_2'}{B_2} + \frac{C_{IG}V}{RT}.
\]  

(23b)
It is worth mentioning that this case was studied in Ref. [8] by the authors and collaborators. There, the following formula for the DALR was obtained

\[ \Gamma = \frac{M_{\text{mol}} g}{2 B_2 P'} \left( \sqrt{1 + \frac{4P}{RT} B_2 - 1} \right), \]  

(24)

where \( P \) is the pressure on the adiabatic curve. Equation \( 24 \) looks different from \( 21 \), the reason is that in Ref. [8] the adiabatic curves were used in the \( P-T \) diagram. The equivalence between \( 21 \) and \( 24 \) can be proved in the following way. We need the equation of state over the adiabatic curve, this is,

\[ \left( \frac{P}{RT} \right) \left( \frac{B_2}{W(x)} \right) = 1 + B_2 \left( \frac{W(x)}{B_2} \right), \]  

(25)

We have used \( 20 \), with \( x \) given by \( 23a \), to substitute the volume. From \( 25 \), we obtain \( P \) and \( P' \), and plugging them in \( 24 \) we obtain \( 21 \).

We believe that the derivation presented here is conceptually clearer and shorter than the one appearing in Ref. [8]. Moreover, here we have obtained a formula for the DALR to any order in the virial expansion, not only up to the second one as in Ref. [8].

**C. Third order virial expansion including vibrations**

The last model that we want to analyze considers that the molecules can also have interactions between three of them. This case corresponds to the third order virial expansion, \( B_k = 0 \) for \( k > 3 \). For the adiabatic curves, \( 16 \) reduces to

\[ T \left[ V \exp \left( \frac{B_2}{V} - \frac{B_3}{2V^2} \right) q_{\text{vib}} \exp(T\Phi) \right] \frac{d\Phi}{dT} = \varepsilon_0. \]  

(26)

Unfortunately, from \( 26 \) we can not write the volume as a function of the temperature in closed form. However, we can use numerical methods to obtain the volume in the region of interest. To be precise, we search for a solution of \( 26 \) using Newton methods (starting in the ideal gas volume with or without vibration, accordingly), starting with the temperature at the surface of the astronomical object and decreasing it in steps of \( \Delta T = 0.01 \text{K} \) until reaching the value of the temperature that corresponds to the highest part of the troposphere. Moreover, the derivative is computed by using the five-point stencil method (with a spacing between points of 0.001). Both, the volume and its derivative are interpolated with cubic splines.

Finally, under these circumstances and using \( Z = 1 + B_2/V + B_3/V^2 \), the DALR is given by

\[ \Gamma = \Gamma^{IG} C_{P'}^{IG} \left[ 1 + \frac{B_2}{V} + \frac{B_3}{V^2} \right] \]  

\[ - \frac{T V''}{V} \left( 1 + 2 \frac{B_2}{V} + 3 \frac{B_3}{V^2} \right)^{-1}. \]  

(27)

**D. Virial coefficients**

As we have mentioned \( B_2 \) and \( B_3 \) take into account two-molecule and three-molecule interactions, respectively. Their explicit functional form is dictated by the molecular interaction model. For the analysis of the lapse rate in the astronomical objects of interest, we have chosen three models: van der Waals, square-well, and hard-sphere. Their second virial coefficients are given by

\[ B_2^{vdW} = a + \frac{b}{T}, \]  

(28a)

\[ B_2^{sw} = b[1 - (d^3 - 1)f], \]  

(28b)

\[ B_2^{hs} = b, \]  

(28c)

respectively \[ 17 \; 20 \]. The function \( f \) in \( 28b \) is \( f = \exp(c/T) - 1 \). The parameters \( a, b, c, \) and \( d \) have a physical interpretation and their values are gas-dependent.

As it is well known, the van der Waals model takes into account the volume of the molecules and the molecular interactions. In \( 28a \), \( a \) represents the average excluded volume and \( b \) is associated with the attractive interaction. The square-well model also considers the volume of the molecules and an attractive interaction. In \( 28b \), \( b \) is the volume of the molecules, considered as hard spheres, while \( d \) and \( c \) are related to the range and amplitude of the attractive interaction potential. Therefore, the square well is a generalization of the hard-sphere model, which only considers the volume \( b \) in \( 28c \).

Using the parameters introduced in \( 28 \), we can write the third virial coefficient \[ 17 \; 20 \] as

\[ B_3^{vdW} = a^2, \]  

(29a)

\[ B_3^{sw} = \frac{b^2}{8} \left[ 5 - (d^6 - 18d^4 + 32d^3 - 15)f \right. \]  

\[ + \left. (-2d^6 + 36d^4 - 32d^3 - 18d^2 + 16)f^2 \right] \text{if} \; d < 2, \]  

(29b)

\[ B_3^{hs} = \frac{5b^2}{8}. \]  

(29c)

Notice that \( 29b \) is valid only if \( d < 2 \), for the case \( d \geq 2 \) the corresponding formula is reported in Ref. [19]. For the gases that we consider below \( 29b \) suffices.

The parameters that appear in \( 28 \) can be obtained by fitting these equations to the experimental data for the second virial coefficient of the gas of interest. In our case, we are interested in \( \text{N}_2 \) and \( \text{CO}_2 \) (see Sec. V). We show in Table 1 the values obtained for the parameters and in Fig. 1 the curves fitting the experimental data (see Ref. [22]) for the three models considered.

**V. RESULTS**

Here, we present an application of the formulae developed in Sec. IV. As we want to illustrate the role of the
For the astronomical objects under discussion, these gases are $N_2$ and $CO_2$. The microscopic information required for the calculations is the following: the rotational degrees of freedom are $f_r = 2$ due to the linearity of these molecules. For the vibrational temperatures, $\theta_j$, we use the wave numbers: i) for $CO_2$, $667.3 \text{ cm}^{-1}$ (with degeneracy two), $1341.5 \text{ cm}^{-1}$ and $2349.3 \text{ cm}^{-1}$ [29], and ii) for $N_2$, $2328.72 \text{ cm}^{-1}$ [27].

In order to improve notation, we will denote the different models in Sec. IV as follows: ideal gases with (without) vibrations by I. G.+ vib (I.G), virial expansion up to the second order with (without) vibrations by $B_2$ + vib ($B_2$), and virial expansion up to the third order with vibrations by $B_3$ + vib.

### A. Adiabatic curves

The adiabatic curves, given in the general case by [13], require the information of at least one point lying on the curve to calculate the constant $\varepsilon_0$. We choose to take the atmospheric conditions at the surface of the astronomical object in question. This information is provided in Table II in terms of the temperature $T_0$ and the pressure $P_0$, but [13] is defined in the $V-T$ diagram. For our calculations, it is necessary to compute the corresponding volume of one mole of the gas under these pressure and temperature conditions. To do this, we substitute $T_0$ and $P_0$ in the equation of state and then solve for $V$. In particular, for the virial expansion up to $B_2$ and $B_3$, we obtain two and three $V_0$ values, respectively. Then, we discard complex or negative solutions, and also those that do not reduce to the ideal gas case when $B_2$ and $B_3$ are equal to zero and there are no vibrations. In Table III, we summarize the values of $\varepsilon_0$ for all the models discussed in Sec. IV.

As an example, and to illustrate the effect of the interactions and vibrations, we show in Fig. 2 the adiabatic curves for the third order virial expansion with vibrations together with the I. G. and I. G.+vib cases for the Earth, Titan, Mars, and Venus. Those of the exoplanet GL 581d, under the three atmospheric conditions showed in Table II are depicted in Fig. 3. Let us make some comments: a) The major deviation due to the molecular vibrations occurs in Venus. This is to be expected as a consequence of the high atmospheric temperatures. b) On the other hand, the deviations on Titan are primarily due to the molecular interactions, since its atmospheric conditions are close to the boiling point of $N_2$ (ca. 77 K at 101 kPa), and c) The different atmospheric conditions in the exoplanet are such to avoid phase transitions, as we illustrate in Fig. 3.

### B. Lapse rate

Here, we show the DALR under the conditions described in Sec. IV together the values obtained in Subsec. VA for the astronomical objects in Table II.

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Table I. Values of the parameters in [28] obtained by fitting these equations to the experimental data for the second virial coefficient.

| Model | Parameters | $N_2$ | $CO_2$ |
|-------|------------|-------|--------|
| vDW   | $a$ [cm$^3$/mol] | 63.6 ± 0.9 | 125 ± 3 |
|       | $b$ [cm$^3$/mol]  | −20786 ± 266 | −74780 ± 1281 |
| SW    | $b$ [cm$^3$/mol]  | 44.5 ± 0.2 | 50.4 ± 0.3 |
|       | $c$ [K]        | 1.619 ± 0.003 | 1.400 ± 0.002 |
|       | $\varepsilon_0$ | 87.8 ± 0.7 | 324 ± 2 |
| HS    | $b$ [cm$^3$/mol]  | 44.5 ± 0.2 | 50.4 ± 0.3 |

![Figure 1](image.png)

Figure 1. Experimental data (points) of the virial coefficients $B_2$ (a) and $B_3$ (b) for $N_2$ (squares) and $CO_2$ (circles). In (a), blue and yellow lines correspond to the curve fits to the $B_2$ data for the interaction molecular models of van der Waals and square-well, respectively. Green lines are the $B_2$ value for the hard-sphere interaction. Solid and dot-dashed lines denote the environment of the gas $N_2$ and $CO_2$, correspondingly. In (b), color lines are the closed form expressions of $B_3$ in [29] using the corresponding fit parameters of $B_2$. Virial coefficients and vibrations, we pick out astronomical objects having diverse atmospheric conditions. Our selection is the Earth, Mars, Venus, Titan, and the exoplanet GL 581d. In Table II, we present the relevant information for each astronomical object, namely: the most abundant gas in its atmosphere (major constituent), $\Gamma^{IG}$, the experimental lapse rate (denoted by $\Gamma^{Obs}$), the atmospheric conditions on the surface (for the exoplanet GL 581d there is a wide range of pressures and temperatures allowing the presence of liquid water [28 [23]), and their corresponding g-value. In the computation of the DALR, the atmosphere constitution is considered as monocomponent, composed of the most abundant gas.
Table II. Information about the astronomical objects under consideration.

| Astronomical object | Major constituent | Composition | \( \Gamma_{\text{IG}} \) [K/km] | \( \Gamma_{\text{Obs}} \) [K/km] | \( P_0 \) [kPa] | \( T_0 \) [K] | \( g \) [m/s^2] |
|---------------------|-----------------|-------------|-----------------|-----------------|----------------|-------------|-------------|
| Earth               | N\(_2\)         | 78\%        | 9.44            | 6.5             | 101            | 288         | 9.80        |
| Titan               | N\(_2\)         | 94.2\%      | 1.30            | 1.38            | 150            | 94          | 1.35        |
| Mars                | CO\(_2\)        | 96\%        | 5.61            | 2.5             | 6              | 215         | 3.71        |
| Venus               | CO\(_2\)        | 96.5\%      | 13.42           | 8.4             | 9200           | 737         | 8.87        |
| Gl 581d (A)         | CO\(_2\)        | 96\%        | 30.70           | —               | 100            | 217         | 20.30       |
| Gl 581d (B)         | CO\(_2\)        | 96\%        | 30.70           | —               | 2000           | 343         | 20.30       |
| Gl 581d (C)         | CO\(_2\)        | 96\%        | 30.70           | —               | 5000           | 375         | 20.30       |

Table III. Values of \( \varepsilon_0 \).

| I. G. | I. G.+vib | \( B_2 \) | \( B_2+\text{vib} \) | \( B_3+\text{vib} \) | \( B_2 \) | \( B_2+\text{vib} \) | \( B_3+\text{vib} \) |
|-------|-----------|---------|-----------------|-----------------|---------|-----------------|-----------------|
| Earth | 64.3729   | 64.4586 | 64.2973         | 64.2973         | 64.2971 | 64.2973         | 64.3076         |
| Titan | 11.5267   | 11.5267 | 11.3274         | 11.3274         | 11.3274 | 11.3274         | 11.3274         |
| Mars  | 332.655   | 350.177 | 332.639         | 332.639         | 332.639 | 332.639         | 332.639         |
| Venus | 39.742    | 86.9272 | 37.4769         | 82.5694         | 82.5694 | 82.5694         | 82.5694         |
| Gl 581d (A)     | 43.5396   | 45.9154 | 43.2026         | 43.2026         | 43.2026 | 43.2026         | 43.2026         |
| Gl 581d (B)     | 24.9368   | 30.6176 | 23.3244         | 28.6379         | 28.6379 | 28.6379         | 28.6379         |
| Gl 581d (C)     | 19.5838   | 25.1675 | 16.8087         | 21.6012         | 21.6012 | 21.6012         | 21.6012         |

Figure 2. Adiabatic curves obtained by considering the third order virial expansion and molecular vibrations for Earth (a), Titan (b), Venus (c), and Mars (d). The colors of the lines are the same as in Fig. 1. The ideal gas prediction with vibrations and without vibrations are represented by a black solid and a red dotted lines, respectively.

Notice that the DALR is a function of the temperature \( T \) only. It is possible to express \( \Gamma \) in terms of the height \( z \). To do this, we solve the differential equation for the corresponding DALR by the 4th order Runge-Kutta method. In this way, we write \( T = T(z) \), and thus, \( \Gamma = \Gamma(T(z)) \).

In order to enhance the exposition, we divide the presentation into three groups: astronomical objects with atmospheres close to ideal gases (The Earth and Mars), atmospheres in extreme conditions of temperature or pressure (Venus and Titan), and the exoplanet Gl 581d under the considered three atmospheric conditions (see Table III).

1. Atmospheres under conditions close to the ideal gas

There are two circumstances in which a gas shows an ideal-gas behavior: i) If its temperature is close to the Boyle temperature \( T_{\text{Boyle}} \), and ii) If it is a diluted gas \( T_{\text{dil}} \). The atmospheres of the Earth and Mars are examples of these conditions, respectively.

In the case of the Earth, neither the molecular inter-
actions nor the molecular vibrations have a significant contribution to the DALR, as we show in Fig. 4. On one hand, the vibration temperature of N$_2$ is $\sim$ 3349 K, which is much higher than the temperature on the Earth's surface, 288 K (see Table II). The molecular vibrations contribution to the heat capacity is 0.00005-0.01 J/K in the troposphere, which is negligible. On the other hand, Earth’s temperature is close to the Boyle’s temperature ($\sim$ 326.65 K and $\sim$ 327.51 K for van der Waals and the square-well models, respectively). This means that attractive and repulsive interaction forces are almost balanced [29]. This makes the total molecular interactions negligible.

In Fig. 5 we show the DALR of Mars. Notice that the dominant contribution to the deviation of the lapse rate with respect to the ideal-gas prediction towards the observational value comes from the molecular vibrations. The reason for the negligible contribution from the virial coefficients is the low probability of observing molecular interactions since the atmosphere is diluted. This fact is consistent with the effects observed in the adiabatic curves (see Fig. 2(d)).

2. Atmospheres under extreme conditions of pressure or temperature

We call extreme conditions those that are close to conditions that allow phase transitions or to the vibrational temperatures, near the surface of the body. For example, comparing Titan’s atmospheric conditions (see Table II) with the boiling point of N$_2$ (ca. 77 K at 101 kPa) and its vibrational temperature ($\sim$ 3349 K), we expect that molecular interactions play a more important role than molecular vibrations in the resulting DALR. This is shown in Fig. 6. This fact is also observed in the adiabatic curves (see Fig. 2(b)). Notice that virial coefficients that also model attractive interactions (van der Waals and square-well) give values of DALR closer to the observational value. On the other hand, the Hard sphere model, which represents a repulsive force only, gives a DALR that is worse than the ideal gas prediction.

Venus is another planetary body under extreme conditions. In Fig. 7 we show the value obtained for the DALRs. Notice that Venus’ surface temperature is close to the first vibration temperature of CO$_2$ ($\sim$ 960 K). Therefore, the molecular vibrations have a more important effect in the DALR than the virial coefficients (we already observed this effect in the adiabatic curves in Fig. 2(c)). Remarkably, in those cases considering molecular vibrations, we obtain a DALR that is in a good agreement with the observed value.
VI. DISCUSSION AND CONCLUSIONS

In this paper, we obtain a formula for the DALR that depends on the compressibility factor and the adiabatic curves. As our interest is to study the non-ideal behavior of atmospheric gases, we take into account the translation, rotation and vibration of molecules as well as interactions between them. We consider the virial expansion for three models, namely, van der Waals, square-well, and hard-sphere. We analyze in detail the following cases: ideal gas, virial expansion up the second order and both with and without vibrations. We also consider third order contributions together with vibrational modes. We study the DALR for the Earth, Mars, Venus, Titan, and the exoplanet Gl 581d under the previous circumstances.

Notice that in all these cases the contribution of the molecular interactions to the DALR becomes negligible as the height increases. The reason is the decrease in the density, pressure, and temperature. In these conditions the ideal gas behavior is recovered. Regarding the observed value, $\Gamma_{\text{Obs}}$, we show it in the figures of Sec. VI except for the exoplanet Gl 581d whose $\Gamma_{\text{Obs}}$ is unknown.

To quantify how much our DALR approaches to $\Gamma_{\text{Obs}}$, we define the following auxiliary function

$$\eta = \frac{\Gamma\text{IG} - \Gamma}{\Gamma\text{IG} - \Gamma_{\text{Obs}}},$$

here $\Gamma$ denotes the quotient of $\Delta T$, the temperature difference between the surface and the top of the troposphere (calculated with $\Gamma$), over the corresponding $\Delta z$.

In this way, we obtain a mean-type value for the DALR. In Fig. 6 we show the values of $\eta$ for the cases analyzed in Sec. VI.

The interpretation of $\eta$ is straightforward, if $\eta$ takes values around 0 then $\Gamma$ is close to $\Gamma\text{IG}$. The Earth and Mars are examples of this. We conclude that in these cases there are other contributions to the DALR that are more important than the molecular vibrations and interactions. For the Earth, it is known that the atmosphere contains traces of vapors, then we must use the moist lapse rate approach, which gives 6-7 K/km in the middle layer of the troposphere [3], that is a better approximation to $\Gamma_{\text{Obs}}$. On Mars, we observe an improvement of 20% by including molecular vibrations in the computation of the DALR, but it also has additional heating.
that comes from the absorption of solar radiation by suspended dust particles [4].

On the other hand, $\eta \sim 1$ means that $\Gamma$ is a very good approximation to $\Gamma_{\text{Obs}}$. This is the case for astronomical objects under extreme conditions for some models. In Titan, we have that the contributions of the interactions are more important than that of the vibrational ones, as we explain in Subsec. V B 2. Conversely, for Venus, the vibrations are more important than molecular interactions (see Subsec. V B 2).

Let us compare our approach to the results reported in Ref. [2], where the author analyzes Venus considering an atmosphere of 100% CO$_2$ and using experimental data for the compressibility factor and heat capacity. Staley obtains a DALR of 7.8486 K/km at 10100 kPa and 750 K. Under the same conditions, we obtain for the third order virial expansion and including vibrations the following values: 7.670 24 K/km, 8.078 06 K/km, and 7.183 84 K/km, for van der Waals, square-well and hard-sphere models, respectively. The hard-sphere model gives the worst prediction. Notice that the difference between the first two models and the Staley prediction is less than ±0.24 K/km. It is worth mentioning that the square-well model gives the closest value to $\Gamma_{\text{Obs}}$.

Finally, as we state in Sec. II our approach can be applied for the compressibility factor of other equations of state, not only in the virial expansion, to incorporate the molecular interactions. We intend to analyze this in a future work. Furthermore, a feasible extension to this work, is to take into account that atmospheres are composed of several gases (mixed gases). This modifies the molecular mass, the heat capacity, and the virial coefficients $B_k^{\text{mix}}$, that now take into account all possible interactions into the mixed gases [5]. A step forward in the understanding of the lapse rate is to include the molecular vibrations and interactions in other approaches to the computation of the lapse rate, for instance, the moist lapse rate. However, to be applied, these generalizations could face the problem of data availability.

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