



## Adiabatic lapse rate of real gases

Bogar Díaz <sup>1,2,\*</sup>, Miguel Ángel García-Ariza <sup>3,†</sup> and J. E. Ramírez <sup>4,5,‡</sup>

<sup>1</sup>*Departamento de Matemáticas, Universidad Carlos III de Madrid, Avenida de la Universidad 30, 28911 Leganés, Spain*

<sup>2</sup>*Grupo de Teorías de Campos y Física Estadística, Instituto Gregorio Millán (UC3M), Unidad Asociada al Instituto de Estructura de la Materia, CSIC, Serrano 123, 28006 Madrid, Spain*

<sup>3</sup>*Arkansas State University Campus Querétaro, Carretera Estatal 100, km 17.5, 76270 Colon, Querétaro, Mexico*

<sup>4</sup>*Centro de Agroecología, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, Apartado Postal 165, 72000 Puebla, Mexico*

<sup>5</sup>*Consejo de Ciencia y Tecnología del Estado de Puebla, Privada B Poniente de la 16 de Septiembre 4511, 72534 Puebla, Mexico*



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We derive a formula for the dry adiabatic lapse rate of atmospheres composed of real gases. We restrict our study to those described by a family of two-parameter cubic equations of state and the recent Guevara-Rodríguez noncubic equation. Since our formula depends on the adiabatic curves, we compute them all at once, considering molecules that can move, rotate, and vibrate, for any equation of state. To illustrate our results, we estimate the lapse rate of the troposphere of Titan, obtaining a better approximation to the observed data in some instances, when compared to the estimation provided by the virial expansion up to the third order.

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### I. INTRODUCTION

The *adiabatic lapse rate* of an atmosphere, denoted henceforth by  $\Gamma$ , is defined to be the rate of change of temperature with respect to height, assuming that parcels of atmosphere at constant height are in equilibrium and that there is no heat exchange between any two of them. This number has been computed directly from observations in many objects within the solar system [1]. Nonetheless, its theoretical reproduction is rather involved. This is in part because real atmospheres are composed of gas mixtures containing traces of vapor or pollutants, and also because of the many thermodynamic processes within them.

In this work, we attempt to improve previous theoretical approximations to the adiabatic lapse rate of dry atmospheres (DALR) by incorporating into its computation *complete* equations of state (EOS), rather than truncated virial expansions [2,3]. This is applied to the atmosphere of Titan, whose surface atmospheric conditions are close to the boiling point of  $N_2$  ( $P \approx 101$  kPa,  $T \approx 77$  K).

The first approach to the theoretical computation of the adiabatic lapse rate of atmospheres considers the ideal gas model [4]. As expected, this yields results far from observations [1], because this EOS overlooks molecular vibrations and

interactions within the gas, among other reasons. Some authors have tried to overcome these downturns by considering ideal gases, but experimental data for heat capacities at constant pressure [1,5]. To some extent, this incorporates information on interactions and molecular vibrations. However, from the conceptual point of view this is an incorrect procedure because the used lapse rate formula strongly depends on the adiabatic curves [2,3]. Another method to derive a DALR for real gases consists of considering the experimental values of the compressibility factor [6]. Although this scheme yields a good approximation to the experimental value for Venus, it is limited by the availability of experimental data in the range of atmospheric conditions for other astronomic objects.

The shortcomings of resorting to experimental values, as described above, may be overcome by using a *truncated* virial expansion and modifying the adiabatic curves to incorporate both intermolecular interactions and molecular vibrations [2,3]. This method improves the value of  $\Gamma$  significantly in extreme atmospheric conditions and allows one to identify the origin of the correction, namely, molecular vibrations (like in Venus's atmosphere), molecular interactions (like in Titan's atmosphere), or both [3].

This work extends the procedures described above by considering complete EOS, in order to further understand the relevance of each ingredient that makes up the DALR of an atmosphere. In particular, we are interested in the role of interactions beyond the two- and three-particle ones. These are taken into account by means of the compressibility factor, denoted by  $Z$ .

We work with two-parameter cubic EOS and an extension of this family, known as the Guevara-Rodríguez noncubic EOS. Our choice of EOS relies on the fact that the family we pick is relatively simple and, at the same time, correctly reproduces certain experimental data on the behavior of real fluids [7]. An advantage of our approach is, however, that the

\*bodiazj@math.uc3m.es

†mgarciaariza@astate.edu

‡jhony.ramirezcancino@viep.com.mx

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formula we obtain for the DALR can be used with any EOS, regardless of the motivation underlying its choice.

We have organized this paper as follows. In Sec. II, we review the formula for the lapse rate in terms of  $Z$ , as obtained in Ref. [3], and apply it to the EOS of interest. The resulting expressions depend on the adiabatic curves of each model, which are computed in Sec. III. In Sec. IV, we plug into our formulas the information to calculate the lapse rate of Titan and compare the theoretical  $\Gamma$  of each EOS with observed data and with the prediction of the virial expansion up to the third order. We wrap up this work with our concluding remarks in Sec. V.

## II. DRY ADIABATIC LAPSE RATE

In this section, we discuss the derivation of the DALR formula presented in Ref. [3] and its application to a family of cubic EOS and the noncubic Guevara-Rodríguez EOS.

As we said before, the lapse rate of the atmosphere is defined as

$$\Gamma = \frac{dT}{dz}, \quad (1)$$

where  $T$  is the temperature and  $z$  is the height ranging within the troposphere of the planet. To obtain the formula for  $\Gamma$  as in Ref. [3], it is necessary to relate the derivatives of the compressibility factor  $Z = PV/(RT)$  on adiabatic curves to the hydrostatic equation  $dP/dz = -M_{\text{mol}}g/V$ . Here,  $P$  is the pressure at height  $z$ ,  $V$  is the volume corresponding to given values of temperature and pressure,  $M_{\text{mol}}$  is the molar mass of the atmosphere,  $g$  is the magnitude of the acceleration near to the planet surface (its variation across the troposphere is usually less than 1%), and  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$  is the gas constant. We assume atmospheres to be homogeneous mono-component simple fluids (consisting of the most abundant gas), whence the compressibility factor depends on volume and temperature only. On adiabatic curves,  $Z$  can be expressed solely in terms of the temperature. As usual, we consider that neither the temperature nor the lapse rate itself depends on latitude.

From the definition of the compressibility factor, we obtain that, on adiabatic curves,

$$dP = \frac{R}{V} \left( Z + T \frac{\partial Z}{\partial T} - ZT \frac{V'}{V} + TV' \frac{\partial Z}{\partial V} \right) dT. \quad (2)$$

In what follows, we denote the adiabatic volume and the adiabatic compressibility factor as  $V_{\text{ad}}$  and  $Z_{\text{ad}}$ , respectively. In addition, primed variables denote their derivative with respect to temperature, for example,  $V' = dV/dT$ . Using Eq. (2) and the hydrostatic equation, we have that the adiabatic lapse rate can be computed as

$$\Gamma = \Gamma^{\text{IG}} \frac{C_P^{\text{IG}}}{R} \left( Z_{\text{ad}} + T \frac{\partial Z}{\partial T} \Big|_{V_{\text{ad}}} - Z_{\text{ad}} T \frac{V'_{\text{ad}}}{V_{\text{ad}}} + TV'_{\text{ad}} \frac{\partial Z}{\partial V} \Big|_{V_{\text{ad}}} \right)^{-1}, \quad (3)$$

where  $\Gamma^{\text{IG}} = M_{\text{mol}}g/C_P^{\text{IG}}$  is the adiabatic lapse rate for ideal gases and  $C_P^{\text{IG}}$  is the heat capacity at constant pressure, expressed as  $(5 + f_r)R/2$ , with  $f_r$  being the rotational degrees of freedom of the gas molecules, which takes the values 0,

2, and 3 for monoatomic, diatomic or linear, and polyatomic molecules, respectively. We must mention that an alternative to Eq. (3) is presented in Ref. [8]. In the latter, the heat capacity at constant pressure obtained from the EOS is an input to obtain  $\Gamma$ , whereas in Eq. (3), only the  $C_p$  of the ideal gas is required. This is an advantage, due to its simple form. Besides,  $Z$  is more common than the correcting factor of temperature used in Ref. [8].

As we mentioned before, for Eq. (3), the compressibility factor can be found from tabulated experimental data. This procedure yields a lapse rate that incorporates all the information of the molecules within the gas, including interactions and vibrations. Nevertheless, a shortcoming of this approach is the availability of data for the atmospheric conditions of the astronomical objects under study.

A theoretical alternative is considering a particular model for the EOS, namely, ideal gas ( $Z = 1$ ), van der Waals, Redlich-Kwong, etc. This is the path we follow in the present paper. As we stated in the Introduction, we are interested in the well-known family of two-parameter cubic EOS. These equations of state are relevant because they incorporate information about molecular interactions and their ranges. Moreover, they predict phase transitions. This last feature could be of significant importance in the computation of lapse rates for astronomical objects having atmospheres under conditions near to critical points, as is the case of Titan, whose surface atmospheric conditions are close to the nitrogen boiling point.

The general two-parameter cubic EOS is [9]

$$P = \frac{RT}{V - b} - \frac{a(T)}{V^2 + uV + wb^2}. \quad (4)$$

Several cubic equations of state can be reproduced by setting the adequate values of  $u$  and  $w$  and the functional form for  $a(T)$ . In this work, we are interested in the van der Waals, Redlich-Kwong, and Peng-Robinson models. We also include other interesting cubic EOS, developed by Guevara-Rodríguez in Ref. [10], wherein the author constructs a square-well-type fluid model whose reduced EOS fulfills the corresponding-states principle. Remarkably, Guevara-Rodríguez cubic EOS reproduces very well the coexistence diagram for simple fluids, even water. We use the fact that all these equations of state can be written as

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V - c)(V - d)}. \quad (5)$$

In Table I we show the information concerning the mentioned equations of state.

Recently, Guevara-Rodríguez also developed a noncubic extension of his cubic EOS (denoted here by  $P_0$ ) given by

$$P_G = P_0 - \frac{fT}{(V - e)^v}, \quad (6)$$

where  $e$ ,  $f$ , and  $v$  are additional parameters that are adjusted according to the substance to be studied [11]. This noncubic EOS predicts phase diagrams for simple fluids that are in agreement with the experimental data, which renders it particularly suited for the lapse rate computation in situations where the tropospheric conditions are close to boiling or sublimation points, like in Titan's atmosphere, as we show below.

TABLE I. Parameters of the EOS. Some of these admit a physical interpretation:  $b$  corresponds to the excluded volume,  $a_c$  is the magnitude of the intermolecular repulsive force,  $T_r$  denotes the reduced temperature,  $\kappa$  is related to the acentric factor, and  $\lambda$  and  $\varepsilon$  are the range and the amplitude of the attractive interaction of the square-well potential.

EOS	$u$	$w$	$c$	$d$	$a(T)$
van der Waals	0	0	0	0	$a_c$
Redlich-Kwong	1	0	$-b$	0	$a_c T^{-1/2}$
Peng-Robinson	2	$-1$	$(-1 + \sqrt{2})b$	$(-1 - \sqrt{2})b$	$a_c [1 + \kappa(1 - T_r^{1/2})]^2$
Guevara-Rodríguez	$-(a_1 + a_2)/b$	$a_1 a_2 / b^2$	$a_1$	$a_2$	$RTb(\lambda^3 - 1)(\exp[\varepsilon/(k_B T)] - 1)$

As we mentioned before, we aim at studying the effect that complete equations of state have on the computation of the lapse rate, compared to the results obtained with a truncated virial expansion. To this end, we recall that the virial expansion of an equation of state is

$$P_v = \frac{RT}{V} \left( 1 + \sum_{k=1} \frac{B_{k+1}}{V^k} \right), \quad (7)$$

where  $B_{k+1}$  are the so-called virial coefficients. These functions are generically sums of the cluster integrals involving the  $(k+1)$ -particle interactions [12]. By construction, they *only* depend on temperature [13] in states sufficiently far from the boiling point [14]. In Sec. IV, we also compare results for the Eqs. (5) and (6) with its corresponding virial expansion up to the third coefficient. In particular, the virial coefficients of Eq. (5) are

$$B_k(T) = b^{k-1} - \frac{a(T)}{RT} (c+d)^{k-2}, \quad (8)$$

for  $k > 2$ . In the case of the van der Waals EOS ( $k = 2$ ), we have  $B_2(T) = b - a_c/(RT)$ . The first 12 virial coefficients of the noncubic and cubic Guevara-Rodríguez EOS coincide. Notice that the truncated virial expansions also depend on the same parameters ( $a_c$ ,  $b$ ,  $c$ , etc.) of the original EOS, but they *only* contain information on  $k$ -particle interactions. This is an important physical difference between truncated virial expansions and complete EOS.

The compressibility factor for the cubic equations of state (5), Guevara-Rodríguez's noncubic equation (6), and the virial expansion (7) are

$$Z = \frac{V}{V-b} - \frac{a(T)V}{RT(V-c)(V-d)}, \quad (9a)$$

$$Z_G = Z_0 - \frac{fV}{R(V-e)^v}, \quad (9b)$$

$$Z_v = 1 + \sum_{k=1} \frac{B_{k+1}}{V^k}, \quad (9c)$$

respectively, where  $Z_0$  represents the compressibility factor of Guevara-Rodríguez's cubic EOS. Then, the lapse rates in these cases are

$$\Gamma = \Gamma^{\text{IG}} \frac{C_P^{\text{IG}}}{R} \left[ \frac{V_{\text{ad}}}{V_{\text{ad}} - b} - \frac{a'(T)V_{\text{ad}}}{R(V_{\text{ad}} - c)(V_{\text{ad}} - d)} + V_{\text{ad}} V_{\text{ad}}' \left( \frac{a(T)(2V_{\text{ad}} - c - d)}{R(V_{\text{ad}} - c)^2(V_{\text{ad}} - d)^2} - \frac{T}{(V_{\text{ad}} - b)^2} \right) \right]^{-1}, \quad (10a)$$

$$\Gamma_G = \Gamma_0 \left[ 1 + \frac{\Gamma_0 R}{\Gamma^{\text{IG}} C_P^{\text{IG}}} \left( V_{\text{ad}} V_{\text{ad}}' \frac{T f v}{R(V_{\text{ad}} - e)^{v+1}} - \frac{f V_{\text{ad}}}{R(V_{\text{ad}} - e)^v} \right) \right]^{-1}, \quad (10b)$$

$$\Gamma_v = \Gamma^{\text{IG}} \frac{C_P^{\text{IG}}}{R} \left( 1 + \sum_{k=1} \frac{B_{k+1}}{V_{\text{ad}}^k} - T \frac{V_{\text{ad}}'}{V_{\text{ad}}} \sum_{k=1} \frac{(k+1)B_{k+1}}{V_{\text{ad}}^k} \right)^{-1}, \quad (10c)$$

with  $B_{k+1} = T B'_{k+1} + B_{k+1}$  and  $\Gamma_0$  denoting the lapse rate corresponding to the Guevara-Rodríguez cubic EOS. Notice that  $V_{\text{ad}}$  is the adiabatic volume for the corresponding EOS, which we derive in the next section.

### III. ADIABATIC CURVES

As we have stated, to calculate the DALR we need the adiabatic curves corresponding to the EOS under consideration. In this section, we show in a general framework that it is possible to obtain, at least in quadratures, the equation of the adiabatic curves of *any* equation of state.

Given the equation of state  $P = P(V, T)$ , the corresponding Helmholtz free energy  $A$  is calculated as [15,16]

$$A = - \int P dV + \phi(T), \quad (11)$$

with [17]

$$\phi(T) = k_B T \ln N! - N k_B T \ln \left( \frac{q_{\text{tras}}}{V} q_{\text{rot}} q_{\text{vib}} \right), \quad (12)$$

where

$$\frac{q_{\text{tras}}}{V} = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2}, \quad (13a)$$

$$q_{\text{rot}} = \frac{T^{f_r/2}}{\theta_{\text{rot}}}, \quad (13b)$$

$$q_{\text{vib}} = \prod_{j=1}^m \frac{\exp[-h\nu_j/(2k_B T)]}{1 - \exp[-h\nu_j/(k_B T)]}, \quad (13c)$$

represent the partition functions corresponding to translations, rotations, and vibrations, respectively [18–20]. In the equations above,  $M$  is the molecular mass,  $h$  is the Planck constant,  $\theta_{\text{rot}}$  and  $\nu_1, \dots, \nu_m$  are the characteristic rotational temperatures and the natural vibrational frequencies of the gas molecules, respectively. As is well known, for molecules with  $n$  atoms,  $m = 3n - 1$  (linear molecules) or  $m = 3n - 6$  (nonlinear molecules) [18]. Notice that  $q_{\text{vib}}$  is a function that depends on  $T$  and on the vibrational properties of the gas under consideration.

On the other hand, from statistical mechanics we have that the Helmholtz energy is calculated by  $A = -k_B T \ln Q$ , where  $Q$  is the canonical partition function of the system. Comparing this with Eq. (11), we get

$$\ln Q = \frac{1}{k_B T} \int P dV - \tilde{\phi}(T), \quad (14)$$

with  $\tilde{\phi}(T) = \phi(T)/(k_B T)$ . With this information we can calculate the internal energy  $U$  as

$$\begin{aligned} U &= k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V \\ &= \int \left( T \frac{\partial P}{\partial T} - P \right) dV - k_B T^2 \tilde{\phi}'(T). \end{aligned} \quad (15)$$

Integrating the adiabatic curves,  $dU + PdV = 0$ , of the system in the  $T$ - $V$  representation yields

$$\int \frac{\partial P}{\partial T} dV - \int \frac{1}{T} \frac{d}{dT} (k_B T^2 \tilde{\phi}'(T)) dT = \text{const.} \quad (16)$$

Making use of Eq. (12), Eq. (16) for 1 mol of gas is

$$\int \frac{\partial P}{\partial T} dV + C_V^{\text{IG}} \ln T + \frac{RT q'_{\text{vib}}}{q_{\text{vib}}} + R \ln(q_{\text{vib}}) = \epsilon_0, \quad (17)$$

where we have identified the heat capacity of ideal gases at constant volume, given by  $C_V^{\text{IG}} = (3 + f_r)R/2$ , and all constants are grouped in  $\epsilon_0$ . We remark that the heat capacity  $C_V$  corresponding to the EOS does not necessarily coincide with that of the ideal gas. It is, rather, obtained by differentiating  $U$  with respect to  $T$  at constant volume, which is in general not constant.

Equation (17) is the general expression in quadratures of the adiabatic curves of 1 mol of gas. This expression coincides with others that have been reported before [21] up to an arbitrary function of temperature. The latter has been fixed herein by considering the microscopic degrees of freedom of the molecules.

Using Eq. (17), we have that the adiabatic curves for the cubic (5), virial (7), and Guevara-Rodríguez noncubic (6) EOS can be written respectively as

$$\left( \frac{V-d}{V-c} \right)^{d(T)R/(c-d)C_V^{\text{IG}}} W(V, T) = \epsilon_0, \quad (18a)$$

$$T \left[ V q_{\text{vib}} \exp \left( \frac{T q'_{\text{vib}}}{q_{\text{vib}}} - \sum_{k=1} \frac{B_{k+1}}{kV^k} \right) \right]^{R/C_V^{\text{IG}}} = \epsilon_0, \quad (18b)$$

$$\mathcal{V}_0(V, T) \exp \left( \frac{f}{(v-1)(V-e)^{(v-1)}} \right) = \epsilon_0, \quad (18c)$$

where

$$W(V, T) = T \left[ (V-b) q_{\text{vib}} \exp \left( \frac{T q'_{\text{vib}}}{q_{\text{vib}}} \right) \right]^{R/C_V^{\text{IG}}} \quad (19)$$

for all but van der Waals' EOS, for which  $W(V, T) = \epsilon_0$ , and  $\mathcal{V}_0(V, T)$  is the functional form of the adiabatic curves for the Guevara-Rodríguez cubic EOS. Equation (18b) coincides with the result reported in Ref. [3]. We point out that, in the equations above, we incur an abuse of notation, since the parameter  $b$  and the constant  $\epsilon_0$  depend on the equation of state.

To close this section, we emphasize that translations, vibrations, and rotations of molecules contribute to the internal energy and the heat capacity of the gas and hence shape the adiabatic curves accordingly. This can be seen explicitly in Eq. (17). However, the relevance of each kind of motion depends on the given atmospheric conditions. In particular, the contribution of vibrations becomes relevant when the temperature is comparable to one of the vibrational temperatures of the gas. For instance, in Venus' atmosphere, vibrations are the principal correcting factor for the lapse rate, even when considering truncated virial expansions, as was shown in Ref. [3]. This is true because the surface temperature of Venus (737 K) is close to one of the vibrational temperatures of  $\text{CO}_2$  ( $\sim 960$  K). In contrast, the vibrational temperature of  $\text{N}_2$  is 3349 K, which is 2 orders of magnitude above Titan's surface temperature (94 K). Under such circumstances, molecular vibrations are negligible in the computation of the lapse rate of Titan's atmosphere [3]. This is not the case for molecular interactions, as we illustrate below.

#### IV. ESTIMATIONS FOR TITAN

As was shown before [3], the contribution to the DALR from molecular interactions becomes relevant in atmospheric conditions close to phase transitions. For this reason, we have chosen the atmosphere of Titan, which is close to the boiling point, to illustrate how the estimation of the DALR obtained from a complete EOS compares to that provided by its corresponding third-order virial expansion, in reference to the observed value. To this end, we discuss the procedure to compute the parameters of the EOS, the adiabatic curves, and the lapse rate of Titan's atmosphere, considered to be composed exclusively of  $\text{N}_2$  (the actual concentration thereof is 92% [1]). It is important to remark that contributions from the consideration of mixtures are expected to be negligible in this case. For instance, from the point of view of virial expansions, the second virial coefficient of a binary mixture may be written as  $B = y_1^2 B_1 + y_1 y_2 B_{12} + y_2^2 B_2$ , where the  $y_i$ 's and the  $B_i$ 's are molar fractions and the second virial coefficients of the  $i$ th component, respectively, and  $B_{12}$  is an interaction coefficient [22]. Small molar fractions amount to even smaller second and third terms in this expression. The same holds for higher-order virial coefficients, which involve higher-order dependencies on molar fractions. The latter is not exclusive to Titan, but is the case of other celestial bodies like Venus (96.5%  $\text{CO}_2$ ) and Mars (96%  $\text{CO}_2$ ), where a monocomponent approach is not only reasonable but also sufficient. On the other hand, however, mixtures may be relevant in objects like Saturn (88%  $\text{H}_2$  vs 12% He).

TABLE II. Values of the EOS parameters calculated from the critical point.

EOS	Parameters	Values
van der Waals	$a_c = 27bRT_c/8$ $b = V_c/3$	0.104 759 m <sup>6</sup> Pa 0.000 029 6 m <sup>3</sup>
Redlich-Kwong	$a_c = 0.427 48R^2T_c^{2.5}/P_c$ $b = 0.086 64RT_c/P_c$	1.5541 m <sup>6</sup> Pa K <sup>0.5</sup> 0.000 026 7 m <sup>3</sup>
Peng-Robinson	$a_c = 0.457 24R^2T_c^2/P_c$ $b = 0.0778RT_c/P_c$	0.147 978 m <sup>6</sup> Pa 0.000 024 m <sup>3</sup>
Guevara-Rodríguez	$b = (Z_c - 1 + \alpha_c)V_c/Z_c$ $a_1 = (Z_c - 0.5\alpha_c + \alpha_c\sqrt{\alpha_c - 0.75})V_c/Z_c$ $a_2 = (Z_c - 0.5\alpha_c - \alpha_c\sqrt{\alpha_c - 0.75})V_c/Z_c$ $Z_c = P_cV_c/RT_c$ $\alpha_c^3 = a(T_c)P_c/R^2T_c^2$	0.000 033 m <sup>3</sup> 0.000 028 6 m <sup>3</sup> -0.000 103 1 m <sup>3</sup> 0.288 37 0.7863

### A. Parameters of the EOS

We obtain the values of some of the parameters appearing in the EOS (5) and (6). We use the equations established for the temperature, pressure, and volume at the critical point for N<sub>2</sub>, considering 1 mol of gas. Correspondingly, we take  $T_c = 126.19$  K,  $P_c = 3.3978$  MPa, and  $1/v_c = 11.177$  mol/dm<sup>3</sup> [23]. We report in Table II all the EOS parameters obtained with these data.

The value of  $\kappa$  in the Peng-Robinson EOS is 0.4324, using that  $\kappa = 0.374 64 + 1.542 26\omega - 0.269 92\omega^2$  and that  $\omega = 0.037 72$  for N<sub>2</sub> [11,24]. Guevara-Rodríguez's cubic EOS requires the computation of the parameters of  $a(T)$ , which coincide by construction with those of the square-well potential, i.e.,  $\lambda = 2.716 22$  and  $\varepsilon/k_B = 30.0625$  K<sup>-1</sup> [10]. For the noncubic term in Eq. (6), we take  $e = 2.986 23 \times 10^{-5}$  m<sup>3</sup>,  $f = 5.959 05 \times 10^{-67}$  Pa (m<sup>3</sup>/mol)<sup>12</sup> K<sup>-1</sup>, and  $\nu = 12$ , as reported in Ref. [11].

### B. Computation of the adiabatic curves

To calculate the values of  $\varepsilon_0$  in each case and thus obtain the adiabatic curves, we use the surface atmospheric conditions of Titan,  $T_S = 94$  K and  $P_S = 146.7$  kPa. These are reported in Table III. We also consider that the wave number associated with the vibrational frequencies of N<sub>2</sub> is 2328.72 cm<sup>-1</sup> [25].

The values of  $V_S$  are determined by finding physically admissible solutions (real and greater than the excluded volume  $b$ ) for  $P_S = P(V, T_S)$  considering 1 mol of gas.

 TABLE III. Values of  $\varepsilon_0$ .

EOS	$\varepsilon_0$
van der Waals	11.4591
Virial-van der Waals	11.4605
Redlich-Kwong	11.3029
Virial-Redlich-Kwong	11.3029
Peng-Robinson	11.3209
Virial-Peng-Robinson	11.3209
Guevara-Rodríguez	11.1833
Virial-Guevara-Rodríguez	11.3305
nc-Guevara-Rodríguez	11.0777

Notice that the only model in which  $V = V(T)$  can be written in a closed form is the van der Waals EOS. For the remaining EOS, we use Newton's method with  $\Delta T = 0.01$ . The corresponding derivative is computed by means of the five-point stencil method, with spacing  $h = 0.001$ . The resulting numerical data are implemented into the lapse rate by fitting  $V(T)$  and  $V'(T)$  to cubic splines. Thereby, we obtain continuous expressions for the DALR.

### C. Lapse rate

With the results of the previous sections, we may now obtain the DALR of Titan as a function of height. Indeed, substituting in Eq. (10) the information of the adiabatic curves obtained in Sec. IV B, we find  $\Gamma$  as a function of  $T$ . By solving  $dT/dz = \Gamma$  for  $T$  using the fourth-order Runge-Kutta method, we may write  $T = T(z)$  and thus express the DALR in terms of the height. We present our results in Fig. 1, where we use  $g = 1.35$  m/s<sup>2</sup>.

In order to measure the accuracy of the theoretical value of  $\Gamma$  obtained from each EOS, we compare the observed lapse

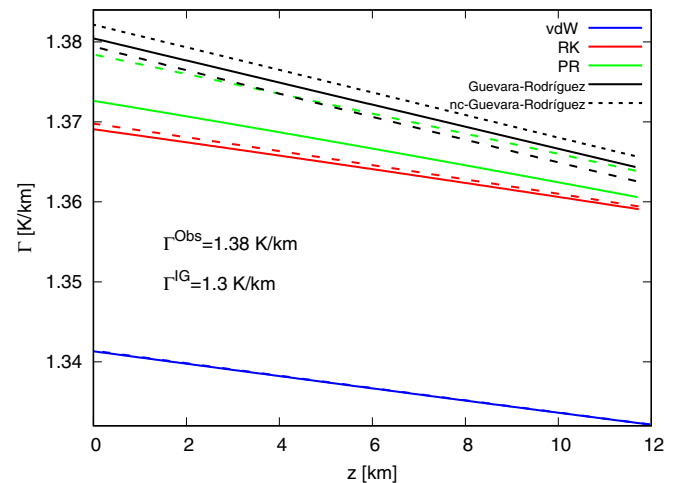


FIG. 1. DALR corresponding to different EOS (solid line) and their corresponding virial expansions up to third order (dashed line): van der Waals (blue line), Redlich-Kwong (red line), Peng-Robinson (green line), Guevara-Rodríguez (black line), and Guevara-Rodríguez noncubic (dotted line).

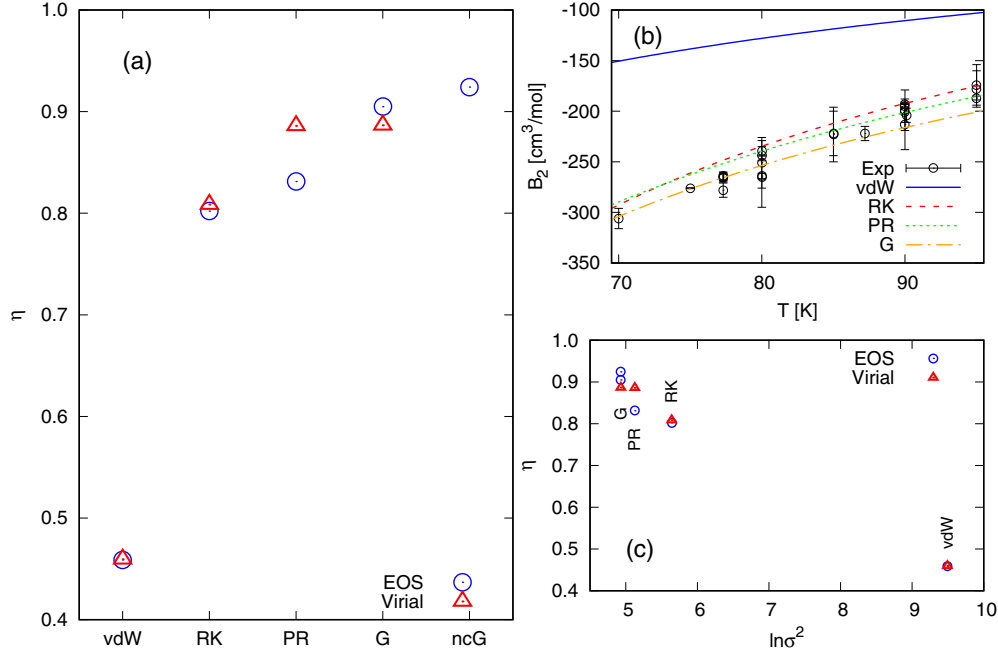


FIG. 2. (a) The values of  $\eta$  corresponding to different EOS (circles) and and their corresponding virial expansions up to third order (triangles). (b) Theoretical (lines) and experimental (circles)  $B_2$ . (c)  $\eta$  vs  $\sigma^2$  for complete EOS (circles) and virial expansions (triangles).

rate  $\Gamma^{\text{Obs}}$  to the average rate of change of  $T(z)$  obtained with  $\Gamma$ , which we call  $\bar{\Gamma}$ . We do this because  $\Gamma$  is not constant, whereas  $\Gamma^{\text{Obs}}$  is. Then, we define

$$\eta = \frac{\Gamma^{\text{IG}} - \bar{\Gamma}}{\Gamma^{\text{IG}} - \Gamma^{\text{Obs}}}, \quad (20)$$

which takes values around 0 when  $\bar{\Gamma}$  is close to  $\Gamma^{\text{IG}}$  and values close to 1 when  $\bar{\Gamma}$  is a good approximation to  $\Gamma^{\text{Obs}}$ . In Fig. 2(a) we show the values of  $\eta$  for the EOS under consideration. We also compare them to the values of  $\eta$  of their corresponding virial expansions.

As can be seen, some models yield a better approximation to  $\Gamma^{\text{Obs}}$  than others. We conjecture that the accuracy of  $\Gamma$  is related to the precision with which an EOS reproduces the observed second virial coefficient. To substantiate this, we first determine how accurately a model reproduces  $B_2$  [see Fig. 2(b)], which is done by using the mean square distance  $\sigma^2$  between the theoretical  $B_2$  [see Eq. (8)] and the experimental data in Ref. [26] within the temperature range where the DALR was calculated. As depicted in Fig. 2(c),  $\eta$  improves as  $\sigma^2$  decreases, suggesting a possible criterion for the choice of an EOS that accurately reproduces the DALR of Titan.

## V. CONCLUSIONS

The formula for the DALR of atmospheres presented in this work represents an improvement to previous considerations in the literature, where intermolecular interactions are taken into account through a truncated virial expansion. In contrast, we have considered complete EOS that describe real gases, namely, a family of two-parameter cubic equations of state and the Guevara-Rodríguez noncubic equation. It is important to remark that the DALR depends on the adiabatic curves of the corresponding EOS, for which we have obtained a general

expression. In this step, we have considered moving molecules that rotate and vibrate. In those cases where we were not able to solve explicitly for the adiabatic volume, we have implemented numerical methods. We remark that an advantage of our approach is that Eq. (3) can be used with any EOS, regardless of what motivates its choice.

The expression we obtain for the lapse rate can be applied to any atmosphere if we have the required input. For example, it can be used to estimate the DALR for exoplanets (see Ref. [3]). We chose Titan's because its surface atmospheric conditions are close to those allowing for phase transitions, where contributions to the lapse rate from intermolecular interactions are known to be relevant. Notice that the role of molecular vibrations in Titan's atmosphere is not relevant. This is because the surface temperature of its atmosphere (94 K) is far from the vibrational temperature of  $N_2$  ( $\approx 3349$  K) [27]. In the particular case of the Guevara-Rodríguez cubic and noncubic equations, our result provides a better approximation to the observed data, when compared to the virial expansions up to the third order, which was the best prediction to our knowledge. This illustrates that the contribution of molecular interactions beyond the two- and three-particle ones can be relevant under certain circumstances.

This work can be extended in two different directions. One possibility is considering atmospheres that are composed of several gases. Taking into account all possible interactions within a mixture of gases is nontrivial, and the contribution of the latter to the DALR is unknown. The other possibility for future work consists of including intermolecular interactions and vibrations in other approaches to the atmospheric lapse rate, like the so-called “moist” lapse rate. The role of the latter in the relation between  $\eta$  and  $\sigma^2$  requires further analysis.

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- [1] D. C. Catling, Planetary atmospheres, in *Treatise on Geophysics*, 2nd ed., edited by G. Schubert (Elsevier, Oxford, 2015), pp. 429–472.
- [2] E. Alvarez Navarro, B. Díaz, M. A. García-Ariza, and J. E. Ramírez, Effects of the second virial coefficient on the adiabatic lapse rate of dry atmospheres, *Eur. Phys. J. Plus* **134**, 458 (2019).
- [3] B. Díaz and J. E. Ramírez, Adiabatic lapse rate of nonideal gases: The role of molecular interactions and vibrations, *Phys. Rev. E* **102**, 042107 (2020).
- [4] C. Kittel, H. Charles Kittel, K. Charles, H. Kroemer, and K. Herbert, *Thermal Physics* (Freeman, San Francisco, 1980).
- [5] D. Vallero, The physics of the atmosphere, in *Fundamentals of Air Pollution*, 5th ed., edited by D. Vallero (Academic, Boston, 2014), pp. 23–42.
- [6] D. O. Staley, The adiabatic lapse rate in the venus atmosphere, *J. Atmos. Sci.* **27**, 219 (1970).
- [7] J. S. Lopez-Echeverry, S. Reif-Acherman, and E. Araujo-Lopez, Peng-Robinson equation of state: 40 years through cubics, *Fluid Phase Equilib.* **447**, 39 (2017).
- [8] G. F. Lindal, G. E. Wood, H. B. Hotz, D. N. Sweetnam, V. R. Eshleman, and G. L. Tyler, The atmosphere of Titan: An analysis of the Voyager 1 radio occultation measurements, *Icarus* **53**, 348 (1983).
- [9] G. Schmidt and H. Wenzel, A modified van der Waals type equation of state, *Chem. Eng. Sci.* **35**, 1503 (1980).
- [10] F. de J. Guevara-Rodríguez, A methodology to define the cubic equation of state of a simple fluid, *Fluid Phase Equilib.* **307**, 190 (2011).
- [11] J. M. García, A. R. Martínez, and F. de J. Guevara-Rodríguez, Equation of state to predict the solid-liquid-vapor phase coexistences of pure substances, *Rev. Mex. Fis.* **66**, 656 (2020).
- [12] J. Mayer and M. Mayer, *Statistical Mechanics* (Wiley & Sons, New York, 1940).
- [13] D. McQuarrie and J. Simon, *Molecular Thermodynamics* (University Science Books, California, 1999).
- [14] M. V. Ushcats, S. Y. Ushcats, L. A. Bulavin, and V. M. Sysoev, Equation of state for all regimes of a fluid: From gas to liquid, *Phys. Rev. E* **98**, 032135 (2018).
- [15] M. Zemansky and R. Dittman, *Heat and Thermodynamics: An Intermediate Textbook*, International Series in Pure and Applied Physics (McGraw-Hill, New York, 1997).
- [16] A. Matsumoto, Thermodynamic quantities of Redlich-Kwong gases in isobaric processes of coexistence of two phases, *Z. Naturforsch. A: Phys. Sci.* **60**, 783 (2005).
- [17] In the calculation of  $\phi(T)$  there is an arbitrary function  $f(T)$  that comes from the derivation of the contribution of the molecular interactions to the canonical partition function. However, it is fixed to zero in order to reproduce the adiabatic curves for the virial expansion reported in Ref. [3].
- [18] D. McQuarrie, *Statistical Mechanics* (University Science Books, New York, 2000).
- [19] J. E. Mayer, Theory of real gases, in *Thermodynamik der Gase/Thermodynamics of Gases*, edited by S. Flügge (Springer, Berlin, 1958), pp. 73–204.
- [20] M. V. Ushcats, Equation of State Beyond the Radius of Convergence of the Virial Expansion, *Phys. Rev. Lett.* **109**, 040601 (2012).
- [21] P. C. Tjiang and S. H. Sutanto, The efficiency of the Carnot cycle with arbitrary gas equations of state, *Eur. J. Phys.* **27**, 719 (2006).
- [22] J. D. Dymond, K. N. Marsh, and R. C. Wilhoit, *Virial Coefficients of Pure Gases and Mixtures*, Vol. 21 (Springer, Berlin, 2003).
- [23] R. T. Jacobsen, R. B. Stewart, and M. Jahangiri, Thermodynamic properties of nitrogen from the freezing line to 2000 K at pressures to 1000 MPa, *J. Phys. Chem. Ref. Data* **15**, 735 (1986).
- [24] D.-Y. Peng and D. B. Robinson, A new two-constant equation of state, *Ind. Eng. Chem. Fundam.* **15**, 59 (1976).
- [25] D. V. Petrov, I. I. Matrosov, D. O. Sedinkin, and A. R. Zaripov, Raman spectra of nitrogen, carbon dioxide, and hydrogen in a methane environment, *Opt. Spectrosc.* **124**, 8 (2018).
- [26] J. D. Dymond, K. N. Marsh, and R. C. Wilhoit, *Virial Coefficients of Pure Gases and Mixtures, Subvolume A Virial Coefficients of Pure Gases*, Vol. 21 (Springer, Berlin, 2002).
- [27] For instance, the contributions of the vibrations to the heat capacity [third and fourth term in Eq. (17)] range across the troposphere from  $4.12 \times 10^{-13}$  to  $4.48 \times 10^{-17}$  J/K; these contributions are negligible when compared to the contributions of the translational and rotational degrees of freedom ( $\approx 20.775$  J/K).