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Analysis of the state equations of a real gas at high pressures with the virial coefficients obtained from controlled chaotic oscillations

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HIGHLIGHTS

- Thermal-mechanical device which can be used to investigate any state equation.
- Chaotic behavior obtained through harmonic variation of the first Lyapunov value.
- Estimation of an arbitrary number of virial coefficients from the chaotic data.
- Pressure errors of several state equations expanded in terms of virial coefficients.
- Validation of the model with another route to chaos and the fugacity coefficient.

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ABSTRACT

This paper investigates several cubic and non-cubic state equations of real gases at high pressures by using the virial coefficients estimated from chaotic oscillations with a mechanical-thermal device. The mechanical part is formed by a cylinder with a piston whose motion is limited by means of a nonlinear spring, a damper and a nonlinear control force to decouple the mechanical and thermal subsystems. To maintain the gas temperature approximately constant, a linear PI controller and a nonlinear control law which manipulates the flow rate of two heating coils inside the cylinder are added. The stability of the mechanical subsystem is analyzed through the first Lyapunov value, whose harmonic variation leads to chaotic behavior with great pressures and an almost constant temperature. The chaotic simulations for nonpolar gases are treated like experimental data to obtain an arbitrary number of virial coefficients which reproduce the state equation in a prescribed pressure range. The validity of the proposed device has been corroborated by using another alternative route to chaos and calculating the fugacity coefficient. The analytical calculations are in good agreement with the numerical simulations.

1. Introduction

In the analysis and design of chemical processes, the pressure of a real gas can be described as the sum of the pressure of an ideal one plus a series expansion in terms of densities or specific volumes. The coefficients of such expansion are known as virial coefficients, which only depend on the gas temperature and the potential interaction energy between the molecules (Prausnitz et al., 2000; Goodwin et al., 2010). For most fluids, only the first and second virial coefficients are experimentally known (Dymond and Smith, 1980; Dymond et al., 2002).

A state equation based on the virial expansion has been applied at relatively low pressures (Mason and Spurling, 1968; Annamalai and Puri, 2002), for which the two first coefficients provide the required precision for the applications. On the other hand, one of the advantages of the virial expansion is that it can be easily obtained for a gaseous mixture through simple combining rules from the virial coefficients of each of the gases present in the mixture (Prausnitz et al., 2000; Poling et al., 2001).

In this work we analyze the behavior and the precision of several cubic and non-cubic state equations when these equations are expanded in terms of virial coefficients. Reviews of such equations with and without translate volume can be found in Poling et al. (2001), Abbot (1979), Tsonopoulos and Heidman (1985), Wei and Sadus (2000) and Valderrama (2003) showing their advantages and disadvantages. The considered cubic equations in this paper are: i) Redlich-Wong (RK) (Redlich and Kwong, 1948), ii) Soave_Redlich-Kwong (SRK) (Soave, 1972), iii) Peng-Robinson (PR) (Peng and Robinson, 1976), iv) Peng-Robinson with

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translate volume (Tassios, 1993) and v) Van der Waals with translate volume (VDWt) (Tassios, 1993; Soave, 1984). The considered non-cubic equations are: vi) Beattie-Bridgeman (BB) state equation (Beattie and Bridgeman, 1927; Su and Chang, 1946; Hougen et al., 1954) and vii) Empirical state equation of high precision (HP) (Goodwin et al., 2010; Span, 2000; Gmehling et al., 2012). All the previous state equations are analyzed by using methane, nitrogen, oxygen and argon.

On the other hand, the device considered in this paper is a mechanical-thermal system formed by an adiabatic cylinder enclosing a real gas and a mobile piston moving along the cylinder axis. The piston is anchored to the cylinder through a nonlinear spring and a viscous damper. The thermal subsystem is formed by two heating coils inside the cylinder with the purpose of transferring heat to the gas. An external control force acts on the piston, thus balancing all the forces to maintain the piston motion within the cylinder limits as well for decoupling the mechanical and thermal subsystems. Two additional control devices are applied to the thermal subsystem: one is a linear PI controller and the other is a nonlinear control law for the heat supply by the helical coils by manipulating their flow rate. The purpose of these control devices is to maintain the gas temperature approximately constant (Albertos and Sala, 2004; Pérez-Molina et al., 2016).

The parameter values and the control laws have been chosen to obtain three equilibrium points. One of them is always a saddle and the other two are weak focuses, whose stability is analyzed by calculating the sign of the first Lyapunov value (Guckenheimer and Holmes, 1983; Wiggins, 2000; Pérez-Polo and Pérez-Molina, 2014). With the harmonic variation of the first Lyapunov value between negative values (stable weak focus) and positive values (unstable weak focus) the piston position jumps from one weak focus to the other one, thus providing a route to chaotic oscillations. Furthermore, the chaotic behavior is characterized by a great excursion in the pressure values, whereas the gas temperature remains approximately constant because of the control system.

The chaotic behavior is exploited to obtain a dense set of simulation data which allow estimating the virial coefficients. In order to assure the presence of chaos, the sensitive dependence, all the Lyapunov exponents and the spectral power density have been calculated, thus corroborating also the accuracy of the simulation results (Guckenheimer and Holmes, 1983; Wiggins, 2000; Lichtenberg and Lieberman, 1992). By using polynomial least square adjustment, the pressures, temperatures and specific volumes of the gas, a desired number of virial coefficients are obtained for each state equation.

The pressure errors between the virial approximation and the exact equation have been compared, which has allowed estimating an admissible range of pressures for each state equation taking the one of high precision (HP) as a reference. It should be emphasized that the methodology presented in this work admits the use of other state equations, such as the one of reference (Valderrama, 1990). Finally, a discussion regarding the applicability of the proposed model is presented taking into account another route to chaos and the fugacity coefficient of the methane.

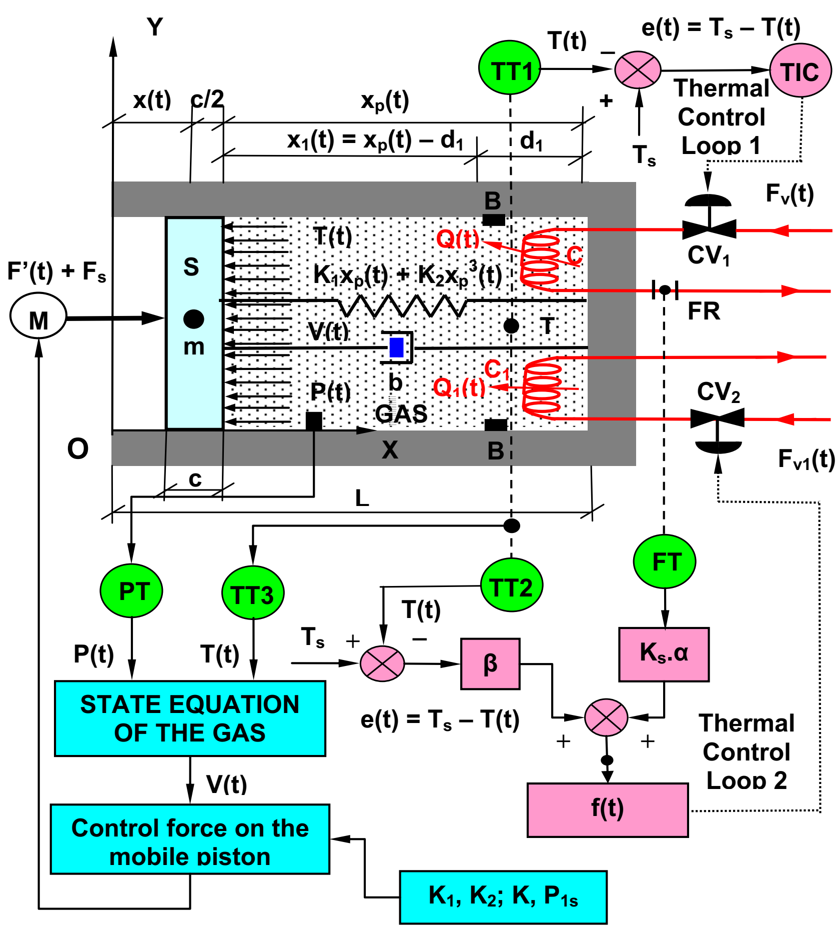

Fig. 1. Layout of the mobile piston inside a cylinder with nonlinear spring, damper, heating coils (C, C_1), loop 1 with a PI controller, nonlinear control loop 2 and control force F′(t). The parameter values are: L = 1 m, d_c = 0.1 m, S = 7.8540.10^{-3} m^2, d_1 = 0.1 m, c = 0.02 m, d = 0.98 m, V_{se} = 5.6341.10^{-3} m^3, K_s = 7.5020.10^8 J/m^3, α = 9.7262.10^{-11} m^3 mole K/J^2, β = 1.3333.10^{-10} mol m^3/J s, K_p = 1.8268.10^{-9} m^3/s K, f_c = 0.001, m = 1.1939 kg, K_1 = 311.64 N/m, K_2 = 449.84 N/m^3, K = 680.14 N/m^2, P_{1s} = 5287.7 N/m^2, b = 1 N m/s and Q_s = 6734.6 J/s. TT, FT and PT denote the temperature, flow and pressure transmitters respectively, whereas TIC is an indicator PI controller.