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Research paper

Development and Application of HEMSim: A Novel Thermochemical Code for Multiphase Combustion Analysis of Rocket and Gun Propellants

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Abstract: This study presents a comparison between HEMSim, a thermochemical code for energetic materials, and other thermochemical codes. The analysis focuses on the behavior of energetic materials under different regimes: isobaric combustion (rocket propellants) and isochoric combustion (gun propellants). HEMSim models complex multiphase systems, accounting for both condensed and gaseous products, with the gaseous phase described using a virial equation of state. In addition, the study examines the influence of the intermolecular potential model on the results, specifically comparing the widely used Lennard-Jones (L-J) potential with the more detailed Buckingham EXP-6 formulation. The goal is to assess whether the added complexity of the EXP-6 model leads to significant differences in the predicted thermodynamic properties. The results demonstrate the efficacy of HEMSim in capturing the thermodynamic behavior of propellants and provide valuable insights into the performance differences associated with varying potential models.

Keywords: combustion, energetic materials, virial equation of state, rocket propellant, gun propellant, HEMSim

1 Introduction

Combustion is defined as a process that transforms an energetic material, containing both an oxidizer and a fuel, into multiphase products in thermodynamic equilibrium with each other. It is a highly exothermic chemical reaction that plays a crucial role in a wide range of engineering applications, particularly in propulsion systems and energy conversion technologies. Combustion can occur under different thermodynamic conditions. When it takes place at constant pressure, it is referred to as isobaric combustion, while at constant volume, it is known as isochoric combustion.

Isobaric and isochoric combustion represent idealized cases that help analyze and understand real combustion processes, especially in the design and performance evaluation of engines and propulsion devices. Isochoric combustion is commonly used to model processes in closed systems, such as internal ballistic calculations for gun propellants. In contrast, isobaric combustion is more representative of open systems like rocket engines or gas turbines.

Thermochemical codes play a central role in the study and design of energetic materials, as they allow the prediction of combustion and detonation properties based on the chemical composition of a system. Among the most widely used thermochemical codes are the NASA CODE [1-3], CT [4], CHEETAH [5], EXPLO5 [6, 7] and the ICT-Thermodynamic Code [8-12]; all of these have been extensively validated, *e.g.* [13], and are used in both academic and industrial contexts. These tools rely on equilibrium chemistry, making use of large databases of thermodynamic properties.

The purpose of this study is to compare one of the HEMSim [14, 15] toolboxes, a MATLAB software designed to simulate both isobaric and isochoric combustion processes, against other commercial thermochemical codes. HEMSim provides a robust framework for modeling the behavior of energetic materials under various conditions and, through additional thermochemical and ballistic calculations, offers output data that are critical for assessing performance in applications such as rocket propulsion and gun systems. This makes it a valuable resource in the development and optimization of propellants and explosive formulations.

2 Virial Equation of State

HEMSim incorporates the virial equation of state [16], truncated at the third term, to describe the real thermodynamic behavior of the gaseous phase of the product mixture. The equation is defined as follows:

$$p = \frac{nRTZ}{v_g \alpha_g} \tag{1}$$

$$Z = 1 + \rho_{\mathrm{mol}} B(T) + {\rho_{\mathrm{mol}}}^2 \ C(T) \tag{2}$$

where p is the pressure, T is the temperature, R is the gas constant, $B(T)$ is the second virial coefficient of the gaseous mixture, $C(T)$ is the third virial coefficient of the gaseous mixture, n is the total number of moles in the gaseous phase per kilogram of explosive, v_g is the specific volume occupied by the gaseous mixture, α_g is the gaseous mass fraction and ρ_{mol} is the molar density of the gaseous mixture.

Within the framework of classical statistical mechanics, the second virial coefficient for non-polar, spherically symmetric molecules is fundamentally linked to the pairwise interaction potential $\varphi(r)$, and can be calculated using the following integral expression:

$$B(T) = \frac{2\,\pi\,N_A}{3\,k\,T} \int_0^\infty r^3 \frac{d\,\varphi(r)}{dr} \exp\left(-\varphi(r)/kT\right) dr \tag{3}$$

where N_A is the Avogadro constant, k is the Boltzmann constant, r is the separation distance between molecules and φ is the interaction energy.

Different types of equations have been developed to describe the relationship between the interaction energy and the separation distance of a pair of molecules, each reflecting distinct molecular characteristics. Among these, the Buckingham potential, often referred to as the "EXP-6" potential [17], is particularly useful for modeling spherical non-polar molecules. This potential is defined by three key parameters: the stiffness α, the potential minimum distance from the molecule centre r_m, and the depth of the potential well ε:

$$\varphi(r) = \frac{\epsilon}{\alpha - 6}\left(6e^{\alpha(1 - r/r_m)} - \alpha(r_m/r)^6\right) \qquad r > r_c \tag{4}$$

$$\varphi(r) = \infty \qquad r \geq r_c \tag{5}$$

where r_c is the position of the potential maximum; a hard core is typically introduced for distances shorter than r_c to eliminate the unphysical singularity of the potential function as r → 0.

The Lennard-Jones (L-J) potential [18] is another widely used model. It is characterized by only two parameters: r_m and ε:

$$\varphi(r) = \frac{\epsilon}{6}\left(6\left(\frac{r_m}{r}\right)^{12} - 12\left(\frac{r_m}{r}\right)^{6}\right) \tag{6}$$

In the context of HEMSim, these models are employed to accurately represent the intermolecular interactions and describe the real thermodynamic behavior of gases. The second virial coefficient is calculated numerically using the following procedure, while the third is determined using the relation taken from [19] that links the third coefficient to the second. To compute the second virial coefficient, it is necessary to apply a correction to ε for polar molecules. In particular, the following correction is applied:

$$\epsilon_i = \epsilon_{0,i}\left(1 + \frac{\lambda_i}{T}\right) \tag{7}$$

where $\varepsilon_{0,i}$ corresponds to the potential well depth in the absence of any correction and λ_i represents a correction factor for the i-th chemical species, accounting for the polarity of the molecules. λ_i is equal to zero for nonpolar molecules.

To calculate the second virial coefficient of the mixture, an expression has been defined in Equation 3. However, in the actual implementation, the dimensionless second virial coefficient for each individual chemical species is first computed using Equation 8, and this quantity is then used to determine the overall mixture coefficient.

$$\widetilde{B}_\iota = \frac{3}{r_{m,i}^3}\int_p^\infty r^2\left(1 - e^{-\frac{\varphi(r)}{kT}}\right)dr \tag{8}$$

where represents the dimensionless second virial coefficient for each individual chemical species, p represents the starting point of integration: $p = 0$ if the L-J potential is used, or $p = r_c$ if the EXP-6 potential is applied.

Once the dimensionless coefficient, for each chemical species, is computed numerically using [20], it can be converted to its dimensional form, and mixing rules can then be applied to calculate the second virial coefficient of the mixture:

$$B_i = \frac{2\,\pi\,N_a\,r_{m,i}^3}{3}\widetilde{B}_\iota \tag{9}$$

$$B(T) = \sum \mathrm{X}_i B_i \tag{10}$$

where X_i represents the mole fraction of the i-th gas species.

3 Thermodynamic Model

The thermodynamic properties of combustion products, whether at constant volume or constant pressure, are determined under the assumption that the process is adiabatic and that the products reach chemical, mechanical, and thermal equilibrium. To describe the equilibrium state, different approaches are applied: Helmholtz free energy minimization is used for constant volume combustion, while Gibbs free energy minimization is employed for constant pressure combustion.

3.1 Isobaric combustion

The condensed combustion products are assumed to be incompressible because the pressures involved are not high enough to justify the application of equations of state that account for pressure effects. The heat of isobaric combustion Q_p is calculated using Hess's law. This law allows the heat of combustion to be expressed as the difference between the sum of the enthalpies of formation of the combustion products and the enthalpy of formation of the reactant:

$$Q_p = \sum n_i \cdot \Delta_f H^0_{i,prod} - \Delta_f H^0_{react} \tag{11}$$

where n_i is the molar composition of i-th combustion product per kilogram of explosive, $\Delta_f H^0_{i,prod}$ is the molar enthalpy of formation of i-th combustion products at 298 K and $\Delta_f H^0_{react}$ is the massive enthalpy of formation of the reactant at 298 K.

To determine the temperature reached by the detonation products, it is necessary to apply an energy balance. Assuming, by the first law of thermodynamics, that no work is performed during the process, the enthalpy of the system remains conserved. This condition can be expressed through the following relation:

$$Q_p = \Delta H \tag{12}$$

with:

$$\Delta H = \sum n_i (H^0_T - H^0_{298}) \tag{13}$$

where ΔH denotes the enthalpy difference of the reaction products evaluated between the reference state and the given temperature of 298.15 K.

3.2 Isochoric combustion

Isochoric combustion is generally associated with high-pressure conditions. For this reason, it becomes necessary to incorporate an additional equation of state to accurately account for the pressure effects on condensed-phase products. To address this, HEMSim employs the extended Murnaghan equation of state taken from [21] to describe graphite, standard, and excess properties. The heat of isochoric combustion Q_v is evaluated based on Hess's law. According to this principle, it can be determined as the difference between the internal energy of formation of the products and the reactant internal energy of formation:

$$Q_v = \sum n_i \cdot \Delta_f U^0_{i,prod} - \Delta_f U^0_{react}, \tag{14}$$

where $\Delta_f U^0_{i,prod}$ is the molar internal energy of formation of i-th combustion products at 298 K, $\Delta_f U^0_{react}$ is the massive internal energy of formation of the reactant at 298 K.

To determine the temperature reached by the detonation products, an energy balance must be applied. Assuming, by the First Law of Thermodynamics, that the process involves no work exchange, the internal energy of the system is conserved. This condition can be mathematically expressed as follows:

$$Q_v = \Delta U \tag{15}$$

with:

$$\Delta U = \sum n_i (U^0_T - U^0_{298}) \tag{16}$$

where ΔU is defined as the internal energy change of reaction products between a given and reference temperature.

4 Results

This section presents a comparison between the results obtained with HEMSim for the two selected potentials and those produced by the EXPLO5 and Fraunhofer Institute for Chemical Technology (ICT) codes, to verify the accuracy of the outcomes for both the isobaric and isochoric combustion numerical models. HEMSim takes into account nine gaseous species and two condensed phases, as described in detail in [14].

4.1 Results for isobaric combustion

Firstly, the thermodynamic results obtained with HEMSim are compared against EXPLO5 and the ICT code in Table 1. The first row reports HEMSim (HS) results using the L-J potential for virial coefficient calculations; the second row uses the EXP-6 potential. The last two rows show the results obtained with EXPLO5 and the ICT code, respectively. Results are given for temperature (T), density (ρ), enthalpy (H), entropy (S) and adiabatic gamma (γ).

Table 1. Isobaric combustion thermodynamics properties for a mixture of ammonium dinitramide (ADN) and hydroxyl-terminated polybutadiene (HTPB) (99/1 weight percent) at constant pressure (7 MPa) and density 1821 kg/m^3 under shifting equilibrium flow condition

Code	T [K]	ρ [kg/m^3]	H [kJ/kg]	S [kJ/kg K]	γ
HS$_{L\text{-}J}$	2324.2	8.907	–1077.3	9.740	1.228
HSEXP-6	2324.8	8.922	–1077.3	9.741	1.228
EXPLO5	2317.0	9.031	–1078.1	9.762	1.236
ICT	2250.8	9.225	–1196.6	9.686	1.235

In addition to the thermodynamic parameters, Table 2 shows the molar composition of the isobaric combustion products. To evaluate rocket propellant performance, HEMSim adopts the thermochemical model developed by Gordon and McBride [2]. This model enables the theoretical prediction of rocket engine performance by simulating the ideal isentropic expansion of combustion products through a nozzle. Relying on this framework, HEMSim provides key output parameters: the specific impulse I, the specific impulse at vacuum condition I_{vac}, the thrust coefficient C_F , the characteristic velocity c^* and the temperature at the exit T_e, offering valuable insight into the potential efficiency of the propellant formulations.

Table 2. Main species molar composition in [mol/kg] for ADN and HTPB mixture (99/1 weight percent) at constant pressure (7 MPa) and density 1821 kg/m^3

Product	HS$_{L\text{-}J}$	HSEXP-6	EXPLO5	ICT
H_2O	16.50	16.50	16.39	16.42
N_2	15.75	15.75	15.77	15.77
O_2	6.77	6.77	6.74	6.74
CO	0.0029	0.0029	0.0031	0.0018
CO_2	0.73	0.73	0.73	0.73
NO	0.41	0.41	0.37	0.38
$C_{(s)}$	0.0	0.0	0.0	0.0

The rocket performance results for the same mixture are compared in Table 3. Finally, for different mixtures, results are compared against EXPLO5 using various assumptions for flow expansion through the nozzle (Tables 4 and 5). The results show that the choice of interatomic potential does not lead to significant variations in the outcomes, both in terms of thermodynamic property calculations and rocket performance (Tables 1-3). HEMSim provides highly competitive results when compared to EXPLO5, despite using a smaller number of chemical species for the chemical equilibrium calculations. Minor differences can be observed when comparing the code with the results provided by ICT, which are attributable to slight discrepancies in the enthalpy of formation and chemical composition of the reactants. The results reported in Tables 4 and 5 were obtained by applying the EXP-6 intermolecular potential within the HEMSim simulation framework.

Table 3. Isobaric combustion rocket performance with assigned pressure ratio $p_c/p_e = 70$ under frozen flow condition, for a mixture of ADN and HTPB (99/1 weight percent) at chamber pressure $p_c = 7$ MPa and an energetic material density of 1821 kg/m^3

Code	T_e [K]	I [s]	I_{vac} [s]	c^* [m/s]	C_F
HS$_{\text{L-J}}$	975.7	215.8	231.5	1349.3	1.57
HSEXP-6	976.0	215.7	231.4	1348.9	1.57
EXPLO5	986.9	216.4	231.9	1350.6	1.57
ICT	935.0	211.8	227.2	1324.1	1.57

The analysis begins under the assumption of constant-pressure combustion, which allows for the evaluation of the thermodynamic conditions established within the combustion chamber. These conditions serve as the basis for a subsequent flow analysis, in which an idealized isentropic expansion is assumed to occur through a converging-diverging nozzle. Under this hypothesis, the evolution of the flow is tracked along the nozzle, enabling the calculation of key thermodynamic properties, such as temperature, density, and velocity, at both the throat and the exit sections. The comparison shows that the results obtained with HEMSim are in good agreement with those provided by EXPLO5. This holds both under the assumption of shifting equilibrium throughout the nozzle expansion and in the mixed condition, where chemical equilibrium is assumed up to the throat section and frozen flow from the throat to the nozzle exit. The most significant differences can be observed at the nozzle exit section and are primarily attributed to variations in the density of the combustion products. A possible explanation for this discrepancy lies in the difference in the number of chemical species considered in the calculations performed by HEMSim and EXPLO5.

Table 4. Isobaric combustion thermodynamics properties and rocket performance, with assigned pressure ratio p_c/p_e = 70 under equilibrium flow condition, for hydrazinium nitroformate (HNF) at constant pressure (7 MPa) and density 1875 kg/m^3

Variable	Unit	HEMSim			EXPLO5		
		Chamber	Throat	Exit	Chamber	Throat	Exit
T	[K]	3178.3	2874.8	1452.5	3084.0	2883.6	1643.7
ρ	[kg/m^3]	7.002	4.377	0.220	7.201	4.325	0.198
Flow velocity, u	[m/s]	–	1043.4	2430.9	–	1047.2	2490.3
Sound speed, c	[m/s]	1095.4	1043.4	751.9	1087.6	1047.2	783.0
Total number of moles, n_{tot}	[mol/kg]	37.5	37.2	37.5	37.9	37.6	36.9
S	[J/kg K]	9912	9912	9912	9938	9938	9938
Specific heat at constant pressure, c_p	[J/kg K]	1789.5	1753.3	1576.1	1768.9	1754.1	1592.4
Specific heat at constant volume, c_v	[J/kg K]	1479.6	1445.4	1264.0	1453.7	1441.6	1285.8

Table 5. Isobaric combustion thermodynamics properties and rocket performance, with assigned pressure ratio p_c/p_e = 70 under equilibrium flow condition from combustion chamber to the throat section, and frozen flow between the throat and the nozzle exit; for nitroguanidine at constant pressure (6 MPa) and density 1770 kg/m^3

Variable	Unit	HEMSim			EXPLO5		
		Chamber	Throat	Exit	Chamber	Throat	Exit
T	[K]	1820.6	1599.0	665.4	1822.1	1598.9	856.2
ρ	[kg/m^3]	8.159	5.147	0.322	8.245	5.143	0.263
u	[m/s]	–	904.8	1998.6	–	906.9	2025.9
c	[m/s]	961.9	904.8	598.9	965.2	906.9	647.3
n_{tot}	[mol/kg]	48.0	48.0	48.0	48.0	48.0	45.7
S	[J/kg K]	10408	10408	10408	10409	10409	10409
c_p	[J/kg K]	1845.3	1804.7	1540.5	1824.4	1788.0	1638.3
c_v	[J/kg K]	1450.2	1408.1	1141.2	1425.4	1388.7	1258.3

4.2 Results for isochoric combustion

In Table 6, the thermodynamic results and gun propellant performance evaluations obtained with HEMSim are compared against EXPLO5 and the ICT code. Subsequently, in Table 7, the molar compositions provided by the three different codes are reported. Finally, results in terms of chemical composition are compared with EXPLO5 for a mixture characterized by significant solid carbon formation, in the form of graphite (GR), in Table 8. As stated previously, there are no significant differences between the L-J and EXP-6 potentials, except for slight variations in the calculation of the gas phase covolume. HEMSim reproduces the same results as EXPLO5 with a small margin of error, while more significant differences can be observed when compared to the ICT code. The results for the same energetic material, in terms of chemical composition show that the HEMSim results align with those provided by EXPLO5, while slight differences can be observed when comparing with the ICT code, primarily due to differences in the atomic composition of the simulated energetic material. Finally, results are presented for a case involving the formation of condensed carbon in the form of graphite in Table 8. In this context, the term n_{gr} denotes the number of moles of graphite produced and n_{CH4} the produced moles of methane: HEMSim is capable of performing simulations even in the presence of large amounts of condensed phase materials. The comparison shows that the resulting chemical composition is identical in both cases.

Table 6. Isochoric combustion thermodynamics and gun propellant properties for JA-2 with constant volume conditions at loading density of 100 kg/m^3

Code	T [K]	P [MPa]	F [kJ/kg]	θ [cm^3/g]	Z	γ
HS_{L-J}	3405.9	131.9	1143.8	1.332	1.154	1.197
HSEXP-6	3403.3	128.8	1143.0	1.125	1.127	1.200
EXPLO5	3408.8	126.7	1147.2	0.946	1.104	1.22
ICT	3598.3	130.1	1170.6	1.004	–	1.217

where F identifies the force or specific energy, θ is the covolume of the gaseous phase and Z is the compressibility factor

Table 7. Main species molar composition in [mol/kg] for JA-2 with constant volume conditions at loading density of 100 kg/m^3

Product	HS_{L-J}	HSEXP-6	EXPLO5	ICT
H_2O	10.95	10.91	10.94	10.97
N_2	5.03	5.03	5.03	5.18
H_2	3.96	4.00	3.87	2.81
CO	15.35	15.32	15.34	13.38
CO_2	5.07	5.10	5.07	6.05
NO	0.023	0.025	0.031	0.0790
$C_{(s)}$	0.0	0.0	0.0	0.0

Table 8. Isochoric combustion molar composition for a mixture diesel oil and gaseous oxygen (99/1 weight percent) with constant volume conditions at loading density of 200 kg/m^3

Code	n_{gr} [mol/kg]	n_{CH4} [mol/kg]
HS_{EXP-6}	39.77	31.85
EXPLO5	39.18	32.15

4.3 Results for Virial Equation of State

The choice of intermolecular potential does not lead to any significant differences in the thermodynamic results, either for constant-pressure combustion or constant-volume combustion. In order to better understand the reason for this behavior, it is necessary to examine in detail the results obtained for the second virial expansion coefficient, under the same thermodynamic conditions, for the two different intermolecular potentials considered. The second virial expansion coefficient depends on two variables, the molar composition of the gaseous phase and the temperature of the system. A sensitivity analysis is carried out first as a function of temperature and then as a function of chemical composition, to assess the differences between the two potentials and identify any parameters that may amplify or mitigate such differences. The first simulation is performed with a fixed chemical composition, varying the temperature system from 2000 to 4000 K.

Table 9. Main species molar composition in [mol/kg] for nitroguanidine at constant pressure (6 MPa) and density 1770 kg/m^3

H_2	N_2	O_2	CO	NO	H_2O	CO_2	NH_3	CH_4
11.1	19.2	5.0e-10	8.1	2.0e-6	8.1	1.5	5.7e-3	4.0e-4

Table 10. Second and third virial expansion coefficient computed at fixed molar composition (Table 9) as function of the temperature for the L-J and EXP-6 intermolecular potential

Virial expansion coefficient	Unit	*T* [K]				
		2000	2500	3000	3500	4000
$B_{L\text{-}J}$	[m^3/mol]	3.40e-5	3.29e-5	3.20e-5	3.12e-5	3.05e-5
$B_{EXP\text{-}6}$	[m^3/mol]	2.78e-5	2.65e-5	2.54e-5	2.45e-5	2.37e-5
$C_{L\text{-}J}$	[m^6/mol^2]	1.34e-9	1.23e-9	1.14e-9	1.07e-9	1.01e-9
$C_{EXP\text{-}6}$	[m^6/mol^2]	1.12e-9	1.01e-9	9.30e-10	8.63e-10	8.08e-10

As the system temperature varies while keeping the chemical composition fixed, it can be observed that the differences in the second virial coefficient are on the order of 20% and remain essentially constant. In contrast, for the third virial coefficient, this difference appears to increase with rising temperature. In both cases, the differences between the calculations performed using the two potentials are negligible, which justifies the lack of significant differences in the computed thermodynamic properties of the mixture, since the order of magnitude of the results remains the same. The analysis now proceeds to examine what happens to the virial expansion coefficients at fixed temperature, by varying the chemical composition of the product mixture, specifically, by separately increasing the number of moles of polar and nonpolar species:

Table 11. Second and third virial expansion coefficient computed at fixed temperature (T = 3000 K) as function of water molar composition [mol/kg], for the L-J and EXP-6 intermolecular potential

Virial expansion coefficient	H_2O molar composition [mol/kg]			
	4	6	10	12
$B_{L\text{-}J}$ [m^3/mol]	3.29e-5	3.24e-5	3.16e-5	3.12e-5
$B_{EXP\text{-}6}$ [m^3/mol]	2.61e-5	2.57e-5	2.51e-5	2.49e-5
$C_{L\text{-}J}$ [m^6/mol^2]	1.19e-9	1.17e-9	1.12e-9	1.09e-9
$C_{EXP\text{-}6}$ [m^6/mol^2]	9.73e-10	9.51e-10	9.12e-10	8.94e-10

The variation in the number of moles of a polar molecule such as water does not affect the differences between the two potentials in terms of the second virial coefficient, which remain around 20%. Similarly, the trend of the third virial expansion coefficient remains consistent with the previous case. Finally, by varying the number of moles of a nonpolar molecule such as molecular nitrogen, the following results are obtained and shown in Table 12:

Table 12. Second and third virial expansion coefficient computed at fixed temperature ($T = 3000$ K) as function of molecular nitrogen molar composition, for the L-J and EXP-6 intermolecular potential

Virial expansion coefficient	N_2 molar composition [mol/kg]			
	10	15	25	30
$B_{L\text{-}J}$ [m^3/mol]	3.01e-5	3.12e-5	3.29e-5	3.35e-5
$B_{EXP\text{-}6}$ [m^3/mol]	2.37e-5	2.47e-5	2.62e-5	2.68e-5
$C_{L\text{-}J}$ [m^6/mol^2]	1.03e-9	1.09e-9	1.19e-9	1.23e-9
$C_{EXP\text{-}6}$ [m^6/mol^2]	8.38e-10	8.93e-10	9.71e-10	1.00.e-9

As in the previous cases, the differences in the second virial expansion coefficient remain of the same order of magnitude as the chemical composition of molecular nitrogen varies. However, the differences in the third virial expansion coefficient exhibit an opposite trend compared to the previous case, with the relative deviation decreasing as the percentage of molecular nitrogen increases. Data for the virial parameters of the different chemical species were taken from CHEETAH database [22].

5 Conclusions

The aim of this paper is, after an initial validation of the HEMSim code for constant-pressure and constant-volume combustion regimes, to investigate the differences arising from the use of the L-J versus the EXP-6 intermolecular potential. The main findings are summarized as follows:

- The constant-pressure combustion model was validated through a comparison with two different simulation tools, EXPLO5 and the ICT code. The results show that the discrepancies between the codes are minimal. When compared to EXPLO5, HEMSim produces similar results both for the thermodynamic calculations of constant-pressure combustion and for the evaluation of rocket propellant performance.
- Similarly, the constant-volume combustion model was validated by comparing the results with EXPLO5 and the ICT code. The conclusions are consistent, and it can be stated that HEMSim performs similarly to EXPLO5 in predicting the thermodynamic properties of the combustion products under isochoric conditions, as well as in the evaluation of gun propellants. Moreover, EXPLO5 and HEMSim yield similar results in terms of condensed carbon formation for a pure diesel oil mixture at constant volume.
- The use of the EXP-6 intermolecular potential does not significantly

alter the thermodynamic results when compared to the L-J potential. This suggests that the increased complexity of the EXP-6 expression does not provide a corresponding improvement in the accuracy of thermodynamic predictions. Therefore, in the context of simplifying the calculation of the second virial coefficient, the L-J potential is the more appropriate choice. It offers a good compromise between computational simplicity, since it requires fewer parameters, and the accuracy of the results.

- Additionally, a detailed investigation was conducted on the differences in the second and third virial coefficients. Regarding the second virial coefficient, it can be stated that variations with temperature, as well as with the chemical composition of polar and nonpolar molecules, result in differences of approximately 20%. However, these differences do not affect the overall thermodynamic properties of the gas mixture, because such a difference does not translate into an equally significant variation in terms of the compressibility factor. Therefore, the mixture maintains the same real behavior regardless of the potential used. Notably, opposite trends were observed when increasing the fraction of polar versus nonpolar molecules: in the former case, the second virial coefficient decreases, while in the latter it increases. A possible explanation for this phenomenon lies in the fact that polar molecules tend to exhibit directional attractive interactions, which lead to a decrease in second virial expansion coefficient. In contrast, nonpolar molecules are dominated by isotropic repulsive interactions, resulting in an increase in second virial expansion coefficient [23].
- Similarly, for the third virial coefficient, the divergence between the trends obtained using the two different potentials increases with temperature. This is expected, as the third virial coefficient is explicitly related to both the system temperature and the second virial coefficient; therefore, small differences in the second virial coefficient tend to be amplified as temperature increases. The behavior of the third virial coefficient as a function of chemical composition (in two scenarios: increasing the percentage of water, a polar molecule, and increasing the percentage of molecular nitrogen, a nonpolar molecule) follows the same trend as the second virial coefficient, due to the explicit relationship between them.

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Stefano Berrone:	other contribution to the publication

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