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Equations of state of detonation products: Influence of the repulsive intermolecular potential

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The aim of this study is to show the influence of the repulsive part of the intermolecular potential on the thermodynamical properties of hot gases at high pressures. For this purpose, a new model of equation of state, based on intermolecular potentials, has been built for gases at high temperature throughout a large range of pressure (1 bar to 0.5 Mbar). Two equations of state, based on this model, are compared in order to show the influence of the repulsive exponent of the potential on the thermodynamic properties of detonation products. Calculated results are compared to experimental data.

I. INTRODUCTION

According to the very useful detonation theory of Chapman and Jouguet (CJ) only one detonation regime is self-steady (a CJ state). In this framework, detonation studies have already provided much calculated and experimental data[1,2] related to the thermodynamic properties of detonation products. Although a good agreement generally exists between experimental detonation velocities and calculated ones in the Chapman-Jouguet state, a large discrepancy remains between experimental results and calculated CJ pressures and temperatures. Unexpectedly, experimental temperatures are generally higher than calculated CJ temperatures. Though the physical meaning of the measured temperature is neither well established nor quite understood, discrepancies between calculated results based on different equations of state (EOS) are difficult to explain because these EOS are generally based on quite different molecular and theoretical considerations and sometimes on empirical ones.

Our purpose is to give some contribution to the theoretical determination of detonation characteristics in showing the influence of the shape of the intermolecular potential on the temperature and pressure of detonation products at the CJ state. It may be emphasized that such a contribution leads to a better knowledge of the thermodynamics of gaseous mixtures at high temperature and pressure.

In this paper, we propose a new model whose main assumption lies in the dependence of the equation of state on the chosen intermolecular potential and especially on its repulsive part. Two equations of state, based on this model and adjusted with experimental data (detonation velocities of condensed explosives), are studied and compared. The strong dependence of the detonation temperature on the intermolecular potential is shown. Then, finally, we suggest how to choose the right potential according to available experimental data.

II. PRELIMINARY REMARKS

As in statistical mechanics, we use the volume V and the temperature T as independent variables. For mixtures, we add the molar fraction X_i of each component. So the suitable state function is the Helmholtz free energy $A=A(V,T,X_i)$.

Let us express the EOS as

$$\sigma(V,T,X_i)=\frac{PV}{nRT} . \tag{1}$$

For instance, the particular case of the ideal gas is represented by $\sigma(V,T,X_i)=1$.

The different state functions of gases may be determined using the following partial derivatives of σ:

$$\sigma_V=V\left[\frac{\partial\sigma}{\partial V}\right]_T , \tag{2}$$

$$\sigma_T=T\left[\frac{\partial\sigma}{\partial T}\right]_V , \tag{3}$$

$$\sigma_i=\left[\frac{\partial\sigma}{\partial X_i}\right]_{V,T,X_j\neq X_i} . \tag{4}$$

One can show that[3]

$$E=E^0+nRT\int_\infty^V\frac{\sigma_T}{V}dV , \tag{5}$$

$$S=S^0+nR\int_\infty^V\frac{(\sigma-1+\sigma_T)}{V}dV , \tag{6}$$

$$\mu_i=\mu_i^0-RT\int_\infty^V\frac{(\sigma-1+\sigma_i)}{V}dV , \tag{7}$$

where E, S, and μ_i denote, respectively, the internal energy, entropy, and chemical potential. Superscript 0 denotes the ideal-gas-state reference. Then, the Helmholtz free energy is given by

$$A=A^0-nRT\int_{\infty}^{V}\frac{\sigma-1}{V}dV\ . \qquad (8)$$

Therefore, we can infer several remarks:

(i) $\sigma_V=\sigma_T=\sigma_i=0$ for an ideal gas.

(ii) If $f(T)$ is such that

$$\sigma_T=f(T)\sigma_V\ , \qquad (9)$$

the internal energy becomes

$$E=E^0+nRTf(T)(\sigma-1) \qquad (10)$$

and does not require any numerical integration.

(iii) The equation of state (i.e., σ) is obtained by differentiation of A,

$$P=-\left[\frac{\partial A}{\partial V}\right]_T\ , \qquad (11)$$

$$\sigma=\frac{PV}{nRT}=-\frac{V}{nRT}\left[\frac{\partial A}{\partial V}\right]_T\ . \qquad (12)$$

In order to simplify notations, let us define ϕ by

$$\phi(V,T,X_i)=-\int_{\infty}^{V}\frac{\sigma-1}{V}dV\ . \qquad (13)$$

Then Eq. (8) becomes

$$A=A^0+nRT\phi(V,T,X_i)\ . \qquad (14)$$

That means that $\phi(V,T,X_i)=0$ for an ideal gas. Hence,

$$\sigma(V,T,X_i)=1-\left[\frac{\partial\phi}{\partial\ln V}\right]_{T,X_i}\ . \qquad (15)$$

From statistical mechanics, it is easy to establish a relation between the function ϕ and the partition function Z,

$$\phi=\ln(Z/Z_{\text{kin}})\ , \qquad (16)$$

where Z_{kin} represents the kinetic part of the partition function.

We now deal with simple molecular considerations. Assuming an intermolecular potential such as

$$\epsilon(r)=\frac{\lambda}{r^{\alpha}}\ , \qquad (17)$$

it can be shown (see, for example, Refs. 1, 4, and 5) that

$$\sigma_V/\sigma_T=\alpha/3\ . \qquad (18)$$

Therefore, a hard-sphere potential which corresponds to $\alpha=\infty$ leads (like the ideal gas EOS) to $\sigma_T=0$. Equation (5) shows that it leads to the lower value of the internal energy and to the upper value of the temperature at constant internal energy.

III. THE NEW MODEL

As empirical EOS are only suited to a short range of densities, our purpose is to obtain an EOS able to cover the largest one and represent as well the detonation products of gaseous mixtures at low initial pressure and those of condensed explosives. According to these former remarks and to previous results related to the EOS of detonation products,[6] we have chosen to build σ as a polynome which reduces at low density to the virial development of the Boltzmann EOS.[7] As this third-degree polyome is insufficient to describe gaseous mixtures at higl densities, we have adjusted coefficients of higher degrees by a least-squares method to fit the detonation velocity of high explosives. We considered only positive oxygen balance explosives[5] since their detonation products are supposed to be free of solid carbon and consist only of the gaseous phase. We have expressed ϕ as a function of the reduced variable x,

$$\phi=\phi(x)=x+0.625x^2/2+0.287x^3/3$$
$$-0.093x^4/4+0.014x^5/5\ , \qquad (19)$$

with

$$x=x(V,T,X_i)=\frac{\Omega}{VT^{3/\alpha}} \qquad (20)$$

and the ideal mixing law,

$$\Omega=\sum_i X_i\omega_i\ . \qquad (21)$$

It gives

$$\sigma=1+\frac{d\phi}{d\ln x}=1+x+0.625x^2+0.287x^3-0.093x^4$$
$$+0.014x^5\ . \qquad (22)$$

According to Refs. 1, 4, and 5, α corresponds to the exponent of the repulsive intermolecular potential of Eq. (17). ω_i are adjustable parameters which can be compared to covolumes. At high temperatures, the following relation may be established:

$$\frac{\omega_i}{T^{3/\alpha}}=b_i\quad(b_i=\text{covolumes})\ . \qquad (23)$$

(This law cannot be extended to low temperatures where the contribution of the attractive part of the potential is no longer negligible and the covolumes may become negative.)

Two equations of state, $H9$ and $H12$, were built according to this model, using, respectively, for the repulsive exponent $\alpha=9$ and 12. For each one, the parameters ω_i (Tables I and II) must be carefully chosen. The different covolumes proposed in the literature for the different components (see, e.g., Ref. 4) do not provide values for ω_i with the accuracy required to represent the detona-

TABLE I. Values of parameters ω_i (cc K$^{1/3}$/mole) for $H9$ EOS.

	ω_i
CO_2	781
CO	564
H_2O	431.5
N_2	548
H_2	54
O_2	624
NO	548

TABLE II. Values of parameters ω_i (cc $K^{1/4}$/mole) for $H12$ EOS.

	ω_i
CO_2	359
CO	278
H_2O	216
N_2	274
H_2	44
O_2	320
NO	272

tion products of high explosives. Therefore, we have carried out an adjustment by a least-squares method for each ω_i in order to fit detonation velocities of high explosives with positive oxygen balance.[5] Although such an adjustment seems to be more empirical than adjustments based on the properties of each component, it remains appropriate even if the ideal mixing law (21) is not a suitable assumption. This procedure does not really affect the values obtained from covolumes through Eq. (23).

IV. RESULTS

A model of equation of state for gases at high temperature ($1000\ K < T < 5000\ K$) throughout a large range of pressure ($1\ \text{bar} < p < 0.5\ \text{Mbar}$) is particularly suited to study the detonation processes of both gaseous and condensed explosives. Experimental data are available only at the two extreme parts of this range of pressure: (i) Pressures between 1 and 2000 bar from detonation of gaseous explosive mixtures at initial pressures lower than 100 bar, and (ii) pressures between 50 and 500 kbar from detonation of condensed explosives.

The calculations were undertaken with the thermochemical QUATUOR code,[3,6] which allows one to use any equation of state. The composition of the detonation products is determined according to a new method presented elsewhere.[8] In some cases, solid carbon was taken into account in the calculations. That requires the use of an equation of state for solid carbon. We have chosen the model proposed by Tanaka.[2]

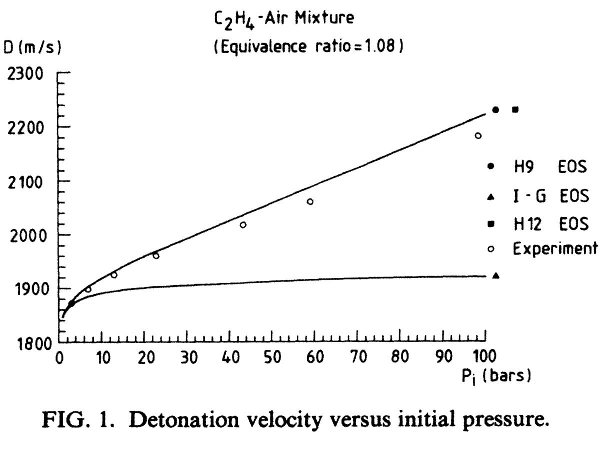

FIG. 1. Detonation velocity versus initial pressure.

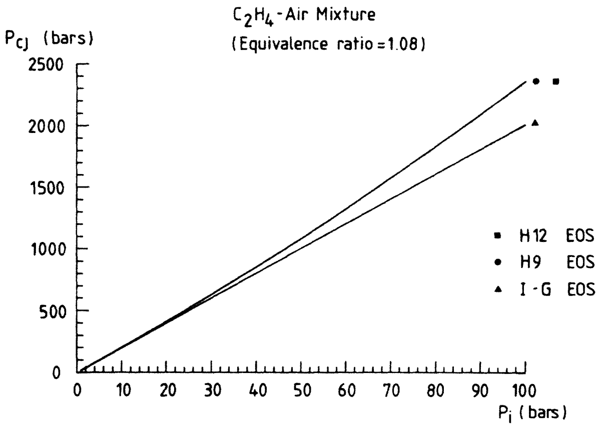

FIG. 2. CJ pressure versus initial pressure.

At low densities, the comparison between calculated and experimental values is based on experimental data provided by previous studies carried out by Presles and Bauer.[9] These data are related to an ethylene-air mixture at initial pressures up to 100 bar. The detonation velocity was measured with an accuracy better than 1%. Figure 1 shows that $H9$ and $H12$ EOS lead to calculated detonation velocities in good agreement with experimental ones in the whole range of initial pressure. On the basis of this parameter, no difference appears between the different intermolecular potentials. The ideal gas EOS provides good results for initial pressures less than 10 bar but gives results that are increasingly too low at higher initial pressures.

Calculated pressures and temperatures are presented in Figs. 2 and 3, respectively. No experimental data is presently available for these characteristics. First, these results show that intermolecular forces lead to higher pressures. But differences are negligible between the two considered intermolecular potentials. It appears that the CJ temperature increases if one takes into account a

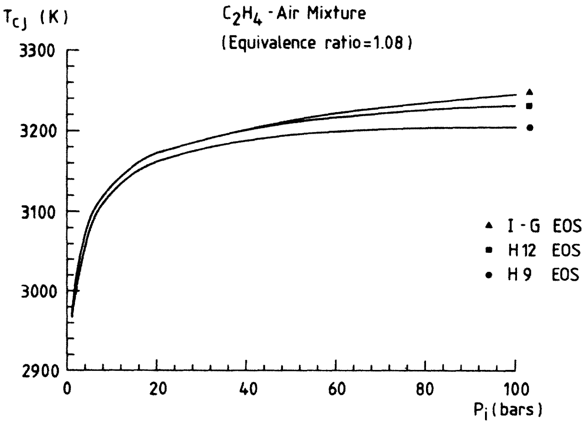

FIG. 3. CJ temperature versus initial pressure.

TABLE III. Experimental and calculated characteristics of detonation products of usual condensed explosives: TNM (tetranitromethane), HNB (hexanitrobenzene), HN (hydrazine nitrate), NG (nitroglycerine) NM (nitromethane), RDX (hexogene), HMX (octogene), PETN (pentaerytritol tetranitrate), TNT (trinitroluene), tetryl.

			Expt.	$H9$	$H12$
TNM	$\rho_0=1.64$	D	6360[a]	6348	6314
		P	159[a]	147	140
		T	2800[a]	1544	2061
HNB	$\rho_0=1.973$	D	9300[a]	8144	8151
		P		320	309
		T		4833	5517
HN	$\rho_0=1.626$	D	8691[a]	8673	8650
		P		267	254
		T		1519	2129
NG	$\rho_0=1.59$	D	7580[a]	7548	7540
		P		224	217
		T		3900	4408
NM	$\rho_0=1.128$	D	6290[a]	6488	6520
		P	141[a]	119	118
		T	3380[a]	3412	3653
	$\rho_0=1.128$	T	3400[b]		
RDX	$\rho_0=1.8$	D	8754[a]	8753	8890
		P	347[a]	317	313
		T		3484	4089
	$\rho_0=1.66$	T	4300[b]	3675	4229
HMX	$\rho_0=1.9$	D	9100[a]	9097	9232
		P	393[a]	355	350
		T		3265	3928
	$\rho_0=1.63$	T	4300[b]	3680	4219
PETN	$\rho_0=1.763$	D	8300[a]	8230	8234
		P	335[a]	284	275
		T	3400-4200[a]	3715	4284
	$\rho_0=1.62$	T	4400[b]	3848	4391
TNT	$\rho_0=1.64$	D	6950[a]	7035	7017
		P	190[a]	180	175
		T		3669	4017
	$\rho_0=1.51$	T	3600[b]	3664	3991
Tetryl	$\rho_0=1.7$	D	7560[a]	7483	7511
		P		220	216
		T		4010	4435
	$\rho_0=1.61$	T	4250[b]	4006	4443

[a] Reference 1.
[b] Reference 10.

greater exponent for the repulsive potential. This result is not surprising if one considers Eqs. (18) and (5) together with (9) and (10).

At high densities, we use the experimental data (Table III) collected by Mader,[1] and temperature measurements obtained more recently by Kato *et al.*[10] The same tendency appears with greater differences between calculated pressures and temperatures but detonation velocities are always very close. Though these EOS have been adjusted to detonation velocities of some condensed explosives, large discrepancies may remain with experimental detonation velocities, especially for hexanitrobenzene. This case may be explained as a failure of the CJ theory.

V. CONCLUSION

A new model of equation of state, based on molecular interactions, has been built to give some contribution to the determination of the repulsive intermolecular potential. It appears that various EOS leading to the same detonation velocities may provide strongly different CJ temperatures and pressures depending on the intermolecular potential that is chosen. This clearly shows that the detonation velocity should not be solely used to adjust the EOS. The accuracy of experimental pressures (generally between 5 and 10 %) does not allow one to determine which is the right repulsive exponent, but though $\alpha=9$ leads to a good agreement between calculated and measured temperatures at low initial densities, $\alpha=12$ seems to be in better agreement with the recent results provided by Kato, mainly within a higher range of densities.

On the basis of the detonation velocity, the EOS $H9$ and $H12$ provide a good agreement with experimental results in the two ranges $1<P<2000$ bar and $50<P<500$ kbar. Hence, their ability to describe the intermediate range $1<P<50$ kbar is a reasonable assumption.

An improvement of the present model requires further information on detonation products. New experiments with different loading densities and accurate temperature measurements would be valuable.

Then, a more realistic potential such as an exponential repulsive potential leading to $\sigma_V/\sigma_T=(\alpha+\beta T)/3$ rather than Eq. (18) and taking into account the attractive part of the potential should improve the present model.

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