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Thermodynamic identities and thermodynamic consistency of Equations of State

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Abstract

We present a systematic approach to construct complete equations of state (EOSs), or to ensure thermodynamic consistency of complete and incomplete forms of EOSs using a minimal and sufficient set of relations. We apply the proposed approach to some common classical equations of state for pure materials. In fact, classical equations of state come generally in an incomplete form that hides essencial properties necessary for thermodynamic consistency. If not aware of such constraints one may generalize the EOS, or fit its thermodynamic parameters from emprirical data or from ab-initio models in an inconsistent way.

I. INTRODUCTION

When a system is at thermodynamic equilibrium under a given set of conditions, it is said to be in a definite thermodynamic state. The state of the system can be described by a number of state quantities, called state functions. In the present paper, we consider closed systems with no change in composition, and in this case only two of these state quantities are independent. Hence, the state functions can be linked either by functional relations (e.g. an equations of state) which specifies a closed formula relationships between these quantities, or by thermodynamical identities linking the infinitesimal variations (or derivatives) for each triplet of these state quantities. If we limit ourselves to the 5 fundamental state functions : $\rho = \frac{1}{v}$, p, T, s, and e, being respectively the specific density (the inverse of the specific volume), pressure, temperature, specific entropy and specific internal energy, then $C_5^3 = 10$ thermodynamical identities can be expressed for a closed system. Other state functions such as specific enthalpy, specific free energy and specific Gibbs energy are obtained as simple functions of these fundamental quantities (e.g. $h = e + \frac{p}{\rho}$, $A = e - Ts$, $g = e + \frac{p}{\rho} - Ts$). Some authors may refer to p, v and T, as state variables for being quantities directly accessible using measure instruments, here we will use the term state function or state variable interchangebly.

If we choose ρ and s as independant thermodynamic variables, the variations of the other three fundamental variables may be expressed throught the three identities :

$$dp \;=\; c^2\, d\rho + \rho k\, T\, ds. \tag{1}$$

$$de = Tds + \frac{p}{\rho^2} d\rho. \tag{2}$$

$$dT = \frac{T}{C_v} ds + \frac{kT}{\rho} d\rho. \tag{3}$$

where we introduced the thermodynamic coefficients : c^2 the square of the speed of sound, k the Gruneisen parameter and C_v the thermal capacity at constant volume.

Remark 1 *We assume here that the choice of (ρ, s) as independant variables is possible. In general when adopting a given EOS for a material not all couple of variables are independants. For example, for perfect gazes, on can not choose e and T as independent variables.*

An equation of state (EOS) given in form $e = e(\rho, s)$ is said to be a complete EOS, because all the other state functions can be computed from it. $T(\rho, s) = \frac{\partial e}{\partial s}$, $p(\rho, s) = \frac{\partial e}{\partial s}$. An EOS of type $p = p(\rho, T)$ is not complete. See remark 2.

The quantities c^2, k and C_v are first order quantities in the sens that they are defined as derivatives (or coefficients) of the fundamental state functions (e.g. $c^2 = \frac{\partial p}{\partial \rho})_s$), and are also functions of the state, so of the chosen independant variables (ρ, s). Identities (1)-(3) implies that Shwartz-type relations should be verified, so we have from (1) :

$$\partial_s c^2)_\rho = \partial_\rho (\rho\, k\, T)_s \tag{4}$$

And from (2) we should have $\partial_\rho T)_s = \frac{1}{\rho^2} \partial_s p\Big)_\rho = \frac{kT}{\rho}$ (1st Maxwell relation) and this is already satisfied through (3) and (1). Finally from (3) we need to have :

$$\partial_\rho \left(\frac{T}{C_v} \right)_s = \partial_s \left(\frac{kT}{\rho} \right)_\rho \tag{5}$$

Equations (4) and (5) can be simplified to the form :

$$\partial_s \left(c^2 \right)_\rho = kT(k+1) + \rho T \partial_\rho \left(k \right)_s \tag{6}$$

$$\partial_\rho \left(C_v \right)_s = -\frac{{C_v}^2}{\rho} \partial_s \left(k \right)_\rho \tag{7}$$

Hence, we see that in $(\rho,\ s)$ variables and up to a reference state $(\rho_0,\ s_0,\ p_0,\ T_0,\ e_0)$, a complete equation of state may be given by any three thermodynamic parameters functions

$c^2(\rho, s)$, $k(\rho, s)$ and $C_v(\rho, s)$ as long as they are verifiying the constraints (6) and (7). We will refer to this choice as a $\{(\rho, s), c^2, C_v, k\}$ representation of the EOS.

II. THERMODYNAMIC IDENTITIES AND THERMODYNAMIC RELATIONS

From (1)-(3) one can derive the other 7 identities involving triplets of the 5 fundamental thermodynamic functions, to complete the set of the $C_5^3 = 10$ possible identities :

$$de = \frac{1}{\rho k} dp + \frac{1}{\rho^2}\left(p - \frac{\rho c^2}{k}\right) d\rho. \tag{8}$$

$$dT = \frac{1}{\rho k C_v} dp + \frac{1}{\rho}\left(kT - \frac{c^2}{k C_v}\right) d\rho. \tag{9}$$

$$dT = \frac{1}{C_v} de + \left(kT - \frac{p}{\rho C_v}\right)\frac{d\rho}{\rho}, \tag{10}$$

$$de = \frac{p}{\rho^2 c^2} dp + \left(T - \frac{pkT}{\rho c^2}\right) ds, \tag{11}$$

$$dT = \frac{kT}{\rho c^2} dp + \left(\frac{c^2 - k^2 T C_v}{C_v c^2}\right) T ds, \tag{12}$$

$$dT = \frac{\rho k T}{p} de + \left(\frac{p - \rho k C_v T}{p C_v}\right) T ds, \tag{13}$$

$$dT = \frac{\rho c^2 - \rho k^2 T C_v}{C_v(\rho c^2 - pk)} de + \frac{\rho k C_v T - p}{\rho C_v(\rho c^2 - pk)} dp, \tag{14}$$

Thermodynamic identities relating 'secondary' state functions h, A and g to any two primary variables among (ρ, p, e, s, T) can also be derived. For instance for $h(p, \rho)$:

$$dh = d(e + \frac{p}{\rho}) = \frac{1}{\rho k} dp + \frac{1}{\rho^2}\left(p - \frac{\rho c^2}{k}\right) d\rho + \frac{1}{\rho} dp - \frac{p}{\rho^2} d\rho$$

$$= \frac{1+k}{\rho k} dp - \frac{\rho\, c^2}{k} d\rho$$

We may retrieve from (8) the usual definition of k as Gruneisen parameter $k = \frac{1}{\rho}\frac{\partial p}{\partial e}\Big)_\rho$. Moreover, expressions for all the other thermodynamic coefficients may be derived from the identities above as functions of c^2, C_v and k (we recall that these three coefficients are linked by (6) and (7)):

- Isothermal bulk modulus K_T, Isothermal compressibility $\beta_T = \frac{1}{K_T}$, and isothermal speed of sound (for example from (9)):

$$K_T = \rho \frac{\partial p}{\partial \rho}\Big)_T = \rho \left(c^2 - k^2 C_v T\right)$$

$$\beta_T = \frac{1}{\rho c^2 - \rho k^2 C_v T}, \; c_T^2 = c^2 - k^2 C_v T.$$

Isentropic bulk and compressibility coefficients are given by $K_s = \rho c^2$ and $\beta_s = \frac{1}{K_s}$.

- Isobaric thermal expansion coefficient α_p and isochoric thermal expansion coefficient α_v :

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p = \frac{k C_v}{c^2 - k^2 T C_v}$$

.

$$\alpha_v = \frac{\partial P}{\partial T}\Big)_\rho = \rho k C_v$$

One can also define an isentropic thermal expansion coefficient :

$$\alpha_s = -\frac{1}{kT} = -\frac{1}{\rho}\frac{\partial \rho}{\partial T}\Big)_s$$

- Heat capacity coefficients : Isobaric heat capacity C_p, and heat ratio γ.

$$C_p = T\frac{\partial s}{\partial T}\Big)_p = \frac{C_v c^2}{c^2 - k^2 T C_v}, \; \gamma = \frac{c^2}{c^2 - k^2 T C_v}.$$

Also we note that, so far, the second principle of thermodynamics is not taken into account. We will briefly address this in section VI.

As noted an EOS of the form $e = e(\rho, s)$ (or $s = s(\rho, e)$, or $\rho = \rho(e, s)$) is complete as $p(\rho, s)$ and $T(\rho, s)$ can be computed from it. Alternatively the set of equations (6)-(7) provide a systematic way to check the thermodynamic consistency (in regard to definitions and the first principle) of an EOS in ρ, s variables. It provides also a systematic way to construct a complete EOS either from empirical relations or ab-initio considerations. The choice of the representation $\{(\rho, s), c^2, C_v, k\}$ is arbitrary and depending on the context, one can use other representations. We will present here few other choices that will be applied to several examples of equations of state.

III. DIFFERENT PRESENTATIONS FOR THERMODYNAMIC STATES DESCRIPTION

A. Representation : $\{(\rho, T), \alpha_v, c_T^2, C_v\}$

In this presentation we suppose (ρ, T) is a valid couple of independant variables for the thermodynamic evolution of the material. We express the different coeffcients as functions of $\{\alpha_v, c_T^2, C_v\}$:

$$dp = c_T^2 d\rho + \alpha_v dT \,, \tag{15}$$

$$de = \frac{p - \alpha_v T}{\rho}\frac{d\rho}{\rho} + C_v dT \,, \tag{16}$$

$$ds = \frac{C_v}{T} dT - \frac{\alpha_v}{\rho^2} d\rho \tag{17}$$

and the consistency relations are given by :

$$\partial_T (c_T^2)_\rho = \partial_\rho (\alpha_v)_T \tag{18}$$

$$\frac{1}{T}\partial_\rho (C_v)_T = -\frac{1}{\rho^2}\partial_T (\alpha_v)_\rho \tag{19}$$

The other thermodynamic parameters can be given in function of α_v, c_T^2 and C_v by :

$$\alpha_p = \frac{\alpha_v}{\rho c_T^2} \,,\ k = \frac{\alpha_v}{\rho C_v} \tag{20}$$

$$c^2 = c_T^2 + \frac{\alpha_v^2 T}{\rho C_v} \,,\ \gamma = 1 + \frac{\alpha_v^2 T}{\rho C_v c_T^2} \tag{21}$$

$$C_p = C_v + \frac{\alpha_v^2 T}{\rho c_T^2} \tag{22}$$

Remark 2 *A PVT relation of the form $p = f(\rho, T)$ sets α_v and c_T^2 (with relation* (18) *satisfied). The $C_v(\rho, T)$ parameter is then to be defined to form a complete EOS, with the constraint* (19)*; Hence, $C_v(\rho, T)$ should be defined only along an isochore : $T \to C_v(\rho_0, T)$.*

Remark 3 *The Helmotz free energy is defined by :*

$$A(\rho, T) = e(\rho, T) - Ts(\rho, T)$$

and if the form $A(\rho,T)$ is given all the thermodynamic quantities can be found from A by the following relations (in this order) : $s=-\frac{\partial A}{\partial T}\Big)_\rho$, $e=A+Ts$, $p=\rho^2\frac{\partial A}{\partial \rho}\Big)_T$, as we have $dA=\frac{p}{\rho^2}d\rho-sdT$.

From $s(\rho,T)$ we can compute C_v and α_v and from $p(\rho,T)$ we can compute c_T^2. Of course, this approach will automatically satisfy the relations of type (18) *and* (19).

On other hand giving a PVT relation $p=p(\rho,T)$, one sets only $\frac{\partial A}{\partial \rho}\Big)_T$, so A is set up to a function $A_0=A(\rho_0,T)=\int_{T_0}^T s(\rho_0,T)dT+e_0-T_0s_0$ of T :

$$A(\rho,T)=\int_{\rho_0}^{\rho}\frac{p(r,T)}{r^2}dr+A_0(T)$$

B. Representation : $\{(\rho,p),c^2,\alpha_v=\rho kC_v,k\}$

We have :

$$dT=\frac{1}{\alpha_v}dp-\left(\frac{c^2}{\alpha_v}-\frac{kT}{\rho}\right)d\rho \tag{23}$$

$$de=\frac{1}{\rho k}dp+\frac{1}{\rho}(\frac{p}{\rho}-\frac{c^2}{k})d\rho \tag{24}$$

$$ds=\frac{1}{\rho kT}dp-\frac{c^2}{\rho kT}d\rho \tag{25}$$

With the Shwartz consistency relations :

$$\rho c^2\frac{\partial k}{\partial p}-\rho k\frac{\partial c^2}{\partial p}+\rho\frac{\partial k}{\partial \rho}+k^2+k=0 \tag{26}$$

$$\frac{C_v^2}{\rho}\frac{\partial k}{\partial p}+\frac{c^2}{\rho kT}\frac{\partial C_v}{\partial p}+\frac{1}{\rho kT}\frac{\partial C_v}{\partial \rho}=0 \tag{27}$$

We note that the last identity is the same as (7). The other thermodynamic coefficients can be expressed with relations presented previously in the (ρ,s,c^2,C_v,k) representation.

C. Representation : $\{(p,T),C_p,\kappa_T=\frac{1}{\rho^2c_T^2},\eta=\frac{\alpha_p}{\rho}\}$

We can write :

$$dv=d(1/\rho)=-\kappa_T dp+\eta dT. \tag{28}$$

$$de=(C_p-p\eta)\,dT-(\eta T-p\kappa_T)dp, \tag{29}$$

$$ds=\frac{C_p}{T}dT-\eta dp, \tag{30}$$

with the Shwartz relations :

$$\frac{\partial \kappa_T}{\partial T} + \frac{\partial \eta}{\partial p} = 0$$

$$\frac{\partial \eta}{\partial T} + \frac{1}{T}\frac{\partial C_p}{\partial p} = 0$$

The other thermodynamic coefficients can be expressed as :

$$k = \frac{\alpha_p c_T^2}{C_p - T\alpha_p^2 c_T^2}$$

$$\alpha_v = \rho c_T^2 \alpha_p$$

$$C_v = C_p - T\alpha_p^2 c_T^2 \,,\ \gamma = \frac{C_p}{C_p - T\alpha_p^2 c_T^2}$$

$$c^2 = \frac{C_p c_T^2}{C_p - T\alpha_p^2 c_T^2}$$

IV. LINK WITH CLASSICAL THERMODYNAMIC RELATIONS

Obviously, whatever is the chosen representation, the expressions for thermodynamic parameters verify all known thermodynamic relations:

$$\beta_T = \frac{1}{\rho c_T^2} = \frac{\gamma}{\rho c^2} = \gamma\beta_s \,,\ K_T = \rho c_T^2 = \frac{\rho c^2}{\gamma} = \frac{K_s}{\gamma} \quad \text{(Reech relation)}$$

$$\text{with } \gamma = \frac{C_p}{C_v} = \frac{K_s}{K_T} = \frac{c^2}{c_T^2} = \frac{c^2}{c^2 - k^2 T C_v},$$

$$c = \sqrt{\frac{K_s}{\rho}} = \sqrt{\frac{\gamma K_T}{\rho}} \quad \text{(Newton-Laplace)}$$

$$\alpha_p = \rho k C_v \beta_T = \rho k C_p \beta_s = \frac{k C_p}{c^2} \quad \text{(Gruneissen relation)}$$

$$C_p - C_v = T\frac{\alpha^2}{\rho\beta_T} \quad \text{(Mayer relation)},$$

and

$$\beta_T - \beta_s = \frac{\alpha^2 T}{\rho C_p} \quad \text{(Mayer relation)},$$

The advantage of the presented approach, where a representation is chosen to work with, is being systematic and avoiding wrangling with the above famous relations to express one coefficient as function of (two/three) others. It also does not ommit the consistency relations between these coeffiscents derivatives when they are defined by empiric relations, fitting experimental data or from ab-initio considerations.

We show in the next section how this systematic approach can be applied to introduce well know Equations of State along with their consistency conditions that are usually omitted in textbooks or presented as a complex results of thermodynamic relation wrangling.

V. A REVISIT OF SOME CLASSICAL EQUATIONS OF STATE

Equations of state are useful in describing the properties of fluids, mixtures of fluids, solids, and other forms of matter. Many examples of EOS are adopted to relate the different state functions of a given material, in diferent areas of physical sicences (fluids, mechanics, geology, astrophysics...etc).

A. Ideal and Perfect gaz EOS

The Ideal gas EOS is given by

$$p = \rho r T. \tag{31}$$

Hence and if we use the $\{(\rho, T), \alpha_v, c_T^2, C_v\}$ representation presented in section III A we get :

$$\alpha_v = r\,\rho \tag{32}$$

$$c_T^2 = rT \tag{33}$$

with relation (18) satisfied. Equation (19) implied then that C_v is function of T only. So, we conclude that a complete Ideal Gaz EOS is completely defined by a function $T \to C_v(T)$ and the PVT relation (31). All the thermodynamic coefficients can be calculated throught equations (20)-(22).

$$k(\rho, T) = \frac{r}{C_v(T)}\,,\ \alpha_p = \frac{1}{T},$$
$$c^2 = rT\left(1 + \frac{r}{C_v(T)}\right),$$
$$\gamma = \frac{c^2}{c_T^2} = 1 + \frac{r}{C_v(T)},$$
$$C_p = C_v(T) + r.$$

Usually the C_v dependence on T only is given in textbooks through proving the dependences of e or h on T only and this is obtained by wrangling the thermodynamic relations (Maxwell relations) and identities.

Coming back to the EOS, and knowing a refrence state $(\rho_0, T_0, p_0, e_0, s_0)$ the expression of other state functions can be derived by integrating the thermodynamic identities II:

$$p(\rho, T) = r\rho T$$
$$e(T) = \int_{T_0}^{T} C_v(t)dt + e_0$$

$$s(\rho, T) = -r\, ln(\frac{\rho}{\rho_0}) + \int_{T_0}^{T} \frac{C_v(t)}{t} dt + s_0$$

The Helmotz free energy is given by :

$$A(\rho, T) = e - Ts = \int_{T_0}^{T} C_v(t)dt - T\int_{T_0}^{T} \frac{C_v(t)}{t} dt + r.T.ln(\frac{\rho}{\rho_0}) + e_0 - Ts_0$$

These formulae simplifies further if C_v is supposed constant, which is called by some authors the Perfect Gaz EOS.

$$p = r\rho T \quad , \quad e = C_v(T - T_0) + e_0 \quad , \quad s = -r\, ln(\frac{\rho}{\rho_0}) + C_v ln(\frac{T}{T_0}) + s_0$$

,

We note that in this case, one can not chose $T_0 = 0$ or $\rho_0 = 0$ as $\frac{1}{T}$ and $\frac{1}{\rho}$ needs to be integrable at T_0 and ρ_0. Hence the Perfect Gaz model cannot be valid around these conditions (absolute zero and infinite volume). Other ab-initio models for C_v with $C_v(T) \approx T^3$ (e.g. Debye model) or $C_v(T) \approx T$ near $T = 0$, are consistent with the Ideal Gaz EOS.

B. Other form for Perfect gaz EOS

Some authors introduce the perfect gaz EOS with the relation

$$p = \rho(\Gamma - 1)e \tag{34}$$

with a constant parameter Γ.

It is important to note that this form is indeed consistent with (31) only and only if the two conditions hold

$$\begin{cases} C_v \text{ is constant} \\ \text{There is a reference state such as } e_0 = C_v T_0 \end{cases}$$

If any one of the conditions does not hold then the form (34) is rather a special form of Mie-Gruneissen EOS, for witch the Gruneissen parameter is given by $k = \Gamma - 1$ and for which a varying C_v function is adminissible only if it depends on s only, as we will see in section V F. To stress it more one cannot adopt 34 along with a correlation $C_v = C_v(T)$.

C. Van de Waals EOS

The Van der Waals EOS is given by a pvt relation :

$$p = \frac{\rho r T}{1 - b\rho} - a\rho^2$$

We have from the PVT relation

$$c_T^2 = \frac{rT}{(1-b\rho)^2} - 2a\rho\,,\ \alpha_v = \frac{r\rho}{1-b\rho}$$

and the relation (19) implies :

$$\partial_\rho C_v)_T = 0$$

As for the perfect gaz, the VDW EOS is completely defined by a $T \to C_v(T)$ function. Having a model $C_v(T)$ we can compute the other thermodynamic properties as functions of ρ and T.

$$k(\rho, T) = \frac{r}{1-b\rho}.\frac{1}{C_v(T)}\,,\ \alpha_p = \frac{r(1-b\rho)}{rT - 2a\rho(1-b\rho)^2},$$

$$c^2 = \frac{rT}{(1-b\rho)^2}\left(1 + \frac{r}{C_v(T)}\right) - 2a\rho,$$

$$\gamma = \frac{c^2}{c_T^2} = 1 + \frac{r^2 T}{rT - 2a\rho(1-b\rho)^2}.\frac{1}{C_v(T)},$$

$$C_p = C_v(T) + \frac{r^2 T}{rT - 2a\rho(1-b\rho)^2}.$$

Also, given a reference state, we have the other state functions given by :

$$e = e_0 - a(\rho - \rho_0) + \int_{T_0}^{T} C_v(t)dt$$

$$s = s_0 - \int_{\rho_0}^{\rho} \frac{r}{x(1-bx)}dx + \int_{T_0}^{T} \frac{C_v(t)}{t}dt$$

$$= s_0 + r.ln(\frac{1/\rho - b}{1/\rho_0 - b}) + \int_{T_0}^{T} \frac{C_v(t)}{t}dt$$

and for the free energy :

$$A(\rho,T) = A_0 - a(\rho-\rho_0) - rTln(\frac{1/\rho - b}{1/\rho_0 - b}) + \int_{T_0}^{T} C_v(t)dt - T\int_{T_0}^{T}\frac{C_v(t)}{t}dt$$

We note that here that in contrast of the ideal gaz, a constant C_v model (which is compatible with VDW EOS) does not imply necessarly a contant γ or a constant C_p. A constant C_v with VDW EOS implies in fact a special case of Mie-Gruneisen model $k = k(\rho)$ presented in the section V F.

D. Redlich-Kwong EOS

The RK EOS is given by :

$$p = \frac{\rho r T}{1-b\rho} - \frac{a\rho^2}{T^\sigma(1+b\rho)}$$

where a, b, r and σ are constant parameters. From the PVT relation : we get

$$c_T^2 = \frac{rT}{(1-b\rho)^2} - a\rho\frac{2+\rho b}{(1+\rho b)^2}\ ,\ \alpha_v = \frac{r\rho}{1-b\rho} + \frac{a\rho^2\sigma}{T^{\sigma+1}(1+b\rho)}$$

and the relation (19) implies :

$$\partial_\rho C_v)_T = \frac{a\sigma(\sigma+1)}{(1+b\rho)}\frac{1}{T^{\sigma+1}}$$

Hence we have a special dependence of C_v on ρ :

$$C_v(\rho,T) = \frac{a\sigma(\sigma+1)ln(1+b\rho)}{bT^{\sigma+1}} + \phi(T)$$

The R-K EOS is completely defined by the function $\phi(T)$ function. A T only dependent C_v is NOT compatible with the K-S equation state unless $a=0$, $\sigma=0$ or $\sigma=-1$. Having a model $C_v(\rho,T)$ we can compute the other thermodynamic properties as functions of ρ and T.

$$k(\rho,T) = \frac{r}{(1-b\rho)C_v} + \frac{a\rho\sigma}{T^{\sigma+1}(1+b\rho)C_v},$$

$$\alpha_p = \frac{\frac{r}{1-b\rho} + \frac{a\rho\sigma}{T^{\sigma+1}(1+b\rho)}}{\frac{rT}{(1-b\rho)^2} - a\rho\frac{2+\rho b}{(1+\rho b)^2}}$$

$$c^2 = c_T^2 + \frac{\alpha_v^2 T}{\rho C_v}\ ,\ \gamma = \frac{c^2}{c_T^2}\ ,\ C_p = C_v + \frac{\alpha_v^2 T}{\rho c_T^2}.$$

Also, given a reference state, and from

$$de = -\frac{a(\sigma+1)}{T^\sigma(1+\rho b)}d\rho + \left[\frac{a\sigma(\sigma+1)ln(1+b\rho)}{bT^{\sigma+1}} + \phi(T)\right]dT$$

we have :

$$e = e_0 + \frac{a(\sigma+1)}{bT^\sigma}ln(\frac{b\rho_0+1}{b\rho+1}) - \frac{a(\sigma+1)ln(1+b\rho_0)}{b}\left[\frac{1}{T^\sigma} - \frac{1}{T_0^\sigma}\right] + \int_{T_0}^{T}\phi(t)dt$$

$$= e_0 - \frac{a(\sigma+1)}{b}\left[\frac{ln(1+b\rho)}{T^\sigma} - \frac{ln(1+b\rho_0)}{T_0^\sigma}\right] + \int_{T_0}^{T}\phi(t)dt$$

And for the entropy identity :

$$ds = \left[\frac{a\sigma(\sigma+1)ln(1+b\rho)}{bT^{\sigma+2}} + \frac{\phi(T)}{T}\right]dT - \left[\frac{r}{\rho(1-b\rho)} + \frac{a\sigma}{T^{\sigma+1}(1+b\rho)}\right]d\rho$$

$$s = s_0 - \int_{\rho_0}^{\rho}\frac{r}{x(1-bx)}dx + \int_{T_0}^{T}\frac{\phi(t)}{t}dt + \frac{a\sigma}{bT^{\sigma+1}}ln(\frac{1+b\rho_0}{1+b\rho}) - \frac{a\sigma ln(1+b\rho_0)}{b}\left[\frac{1}{T^{\sigma+1}} - \frac{1}{T_0^{\sigma+1}}\right]$$

$$= s_0 + r.ln(\frac{1/\rho - b}{1/\rho_0 - b}) + \int_{T_0}^{T}\frac{\phi(t)}{t}dt - \frac{a\sigma}{b}\left[\frac{ln(1+b\rho)}{T^{\sigma+1}} - \frac{ln(1+b\rho_0)}{T_0^{\sigma+1}}\right]$$

So for the free Helmotz energy :

$$\begin{aligned} A(\rho,T) = A_0 - rTln(\frac{1/\rho - b}{1/\rho_0 - b}) &- \frac{a(\sigma+1)}{b}\left[\frac{ln(1+b\rho)}{T^\sigma} - \frac{ln(1+b\rho_0)}{T_0^\sigma}\right] \\ &+ T\frac{a\sigma}{b}\left[\frac{ln(1+b\rho)}{T^{\sigma+1}} - \frac{ln(1+b\rho_0)}{T_0^{\sigma+1}}\right] \\ &+ \int_{T_0}^{T}\phi(t)dt - T\int_{T_0}^{T}\frac{\phi(t)}{t}dt \end{aligned} \quad (35)$$

$$\begin{aligned} A(\rho,T) = A_0 - rTln(\frac{1/\rho - b}{1/\rho_0 - b}) &- \frac{a}{b}\frac{ln(1+b\rho)}{T^\sigma} \\ &+ \frac{a(\sigma+1)}{b}\frac{ln(1+b\rho_0)}{T_0^\sigma} - T\frac{a\sigma}{b}\frac{ln(1+b\rho_0)}{T_0^{\sigma+1}} \\ &+ \int_{T_0}^{T}\phi(t)dt - T\int_{T_0}^{T}\frac{\phi(t)}{t}dt \end{aligned} \quad (36)$$

$$\begin{aligned} A(\rho,T) = A_0 - rTln(\frac{1/\rho - b}{1/\rho_0 - b}) &- \frac{a}{b}\frac{ln(1+b\rho)}{T^\sigma} \\ &+ \frac{a}{b}\left(\sigma + 1 - \frac{T}{T_0}\sigma\right)\frac{ln(1+b\rho_0)}{T_0^\sigma} \\ &+ \int_{T_0}^{T}\phi(t)dt - T\int_{T_0}^{T}\frac{\phi(t)}{t}dt \end{aligned} \quad (37)$$

The formulae we give here for $A(\rho, T)$, and for C_p for example, are more explicit than the one given in [5], with a direct link with the $C_v(\rho, T)$ correlation (that can be fitted experimentally).

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$$p = \frac{R\,T}{V_m - b} - \frac{a\,\alpha(T)}{V_m^2 + 2bV_m - b^2} \tag{38}$$

$$a \approx 0.45724 \frac{R^2\,T_c^2}{p_c} \tag{39}$$

$$b \approx 0.07780 \frac{R\,T_c}{p_c} \tag{40}$$

$$\alpha = \left(1 + \kappa\left(1 - T_r^{\frac{1}{2}}\right)\right)^2 \tag{41}$$

$$\kappa \approx 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2 \tag{42}$$

$$T_r = \frac{T}{T_c} \tag{43}$$

We rewrite the P.R. EOS with the specific quantities as :

$$p = \frac{r\,T\rho}{1 - b\rho} - \frac{a(T)\rho^2}{1 + 2b\rho - b^2\rho^2}$$

We can compute directly ($v = \frac{1}{\rho}$):

$$c_T^2 = -\frac{rT}{(v-b)^2} + 2a(T)\frac{(v+b)}{[v^2 + 2bv - b^2]^2}\,,\ \alpha_v = \frac{r}{v-b} - \frac{a'(T)}{v^2 + 2bv - b^2}$$

and this EOS imposes that :

$$\partial_\rho C_v = -T/\rho^2 \partial_T \left[\frac{r}{v-b} - \frac{a'(T)}{v^2 + 2bv - b^2}\right]$$

$$\partial_\rho C_v = \frac{T a''(T)}{1 + 2b\rho - b^2\rho^2}$$

Hence

$$C_v(\rho, T) = \frac{T a''(T)}{2\sqrt{2}b} ln\left(\frac{\sqrt{2} - 1 + b\rho}{\sqrt{2} + 1 - b\rho}\right) + \phi(T)$$

And for the other thermodynamic coefficient we have :

$$k = \frac{\alpha_v}{\rho C_v} = \frac{rv}{(v-b)C_v} - \frac{a'(T)v}{(v^2 + 2bv - b^2)C_v}$$

$$c^2 = c_T^2 + \frac{T}{C^v}\left(\frac{rv}{(v-b)} - \frac{a'(T)v}{(v^2+2bv-b^2)}\right)^2$$

$$\gamma = 1 + \frac{T}{C^v}\frac{\left(\frac{rv}{(v-b)} - \frac{a'(T)v}{(v^2+2bv-b^2)}\right)^2}{-\frac{rT}{(v-b)^2} + 2a(T)\frac{(v+b)}{[v^2+2bv-b^2]^2}}$$

$$C_p = C_v + T\frac{\left(\frac{rv}{(v-b)} - \frac{a'(T)v}{(v^2+2bv-b^2)}\right)^2}{-\frac{rT}{(v-b)^2} + 2a(T)\frac{(v+b)}{[v^2+2bv-b^2]^2}}.$$

$$C_p = \frac{Ta''(T)}{2\sqrt{2}b}ln\left(\frac{\sqrt{2}-1+b\rho}{\sqrt{2}+1-b\rho}\right) + \phi(T) + T\frac{\left(\frac{rv}{(v-b)} - \frac{a'(T)v}{(v^2+2bv-b^2)}\right)^2}{-\frac{rT}{(v-b)^2} + 2a(T)\frac{(v+b)}{[v^2+2bv-b^2]^2}}.$$

Hence for e as function of T and ρ :

$$de = \frac{p-\alpha_v T}{\rho}\frac{d\rho}{\rho} + C_v dT\,, \tag{44}$$

$$ds = \frac{C_v}{T}dT - \frac{\alpha_v}{\rho^2}d\rho \tag{45}$$

$$de = \frac{Ta'(T)-a(T)}{1+2b\rho-b^2\rho^2}d\rho + \left[\frac{Ta''(T)}{2\sqrt{2}b}ln\left(\frac{\sqrt{2}-1+b\rho}{\sqrt{2}+1-b\rho}\right) + \phi(T)\right]dT$$

$$e(\rho,T) = e_0 + \frac{Ta'(T)-a(T)}{2\sqrt{2}b}ln\left(\frac{\sqrt{2}-1+b\rho}{\sqrt{2}+1-b\rho}\right) + \int_{T_0}^{T}\phi(t)dt$$

And for the entropy :

$$ds = \left[\frac{a''(T)}{2\sqrt{2}b}ln\left(\frac{\sqrt{2}-1+b\rho}{\sqrt{2}+1-b\rho}\right) + \frac{\phi(T)}{T}\right]dT - \left[\frac{r}{\rho(1-b\rho)} - \frac{a'(T)}{1+2b\rho-b^2\rho^2}\right]d\rho$$

$$s = s_0 + r.ln(\frac{1/\rho-b}{1/\rho_0-b}) + \int_{T_0}^{T}\frac{\phi(t)}{t}dt - \frac{1}{2\sqrt{2}b}\left[a'(T)ln\left(\frac{\sqrt{2}-1+b\rho}{\sqrt{2}+1-b\rho}\right) - a'(T_0)ln\left(\frac{\sqrt{2}-1+b\rho_0}{\sqrt{2}+1-b\rho_0}\right)\right]$$

So for the free Helmotz energy :

$$A(\rho,T) = A_0 + \frac{Ta'(T)-a(T)}{2\sqrt{2}b}ln\left(\frac{\sqrt{2}-1+b\rho}{\sqrt{2}+1-b\rho}\right) + \int_{T_0}^{T}\phi(t)dt - T\int_{T_0}^{T}\frac{\phi(t)}{t}dt -$$
$$rT.ln(\frac{1/\rho-b}{1/\rho_0-b}) + \frac{T}{2\sqrt{2}b}\left[a'(T)ln\left(\frac{\sqrt{2}-1+b\rho}{\sqrt{2}+1-b\rho}\right) - a'(T_0)ln\left(\frac{\sqrt{2}-1+b\rho_0}{\sqrt{2}+1-b\rho_0}\right)\right] \tag{46}$$

F. Mie-Gruneissen

All the EOS's presented before were in the form $P = f(\rho, T)$, hence we used a (ρ, T) representation. The general Mie-Gruneissen EOS presented in this section (and the Stiffened gaz EOS of the next section) are given in the form $e(p, \rho)$ or $p(\rho, e)$.

The Mie-Gruneissen EOS is given by

$$p(\rho, e) = p_K(\rho) + \rho k(\rho)(e - e_K(\rho))$$

or in (ρ, p) formulation

$$e(p, \rho) = e_K(\rho) + \frac{1}{\rho k(\rho)}(p - p_K(\rho))$$

with two functions $e_K(\rho)$ and $p_K(\rho)$, satisfying the relation [1]

$$\frac{de_K(\rho)}{d\rho} = \frac{p_K(\rho)}{\rho^2}$$

so that e_K and p_k are defined along an isentrope $s = s_0$.

We suppose also that we know a reference state $(\rho_0, e_0, p_0, s_0, T_0)$, so that $p_K(\rho_0) = p_0 = p(e_0, \rho_0)$ and $e_K(\rho_0) = e_0 = e(\rho_0, p_0)$.

From the EOS and the identity $de = \frac{1}{\rho k}dp + \frac{1}{\rho^2}(p - \frac{\rho c^2}{k})d\rho$ we have then $k = k(\rho)$, and also

$$c^2(p, \rho) = \left(\frac{k'}{k} + \frac{k+1}{\rho}\right)(p - p_K(\rho)) + p'_K(\rho)$$

A first consistency relation is automatically satisfied given the relation $e(p, \rho)$. Using (27) or (5) we have :

$$\partial_\rho (C^v)_s = 0$$

Hence C^v depends only on s and then we have for the temperature

$$\frac{dT}{T} = \frac{1}{C^v(s)}ds + \frac{k(\rho)}{\rho}d\rho$$

Hence to completely define the EOS in a (ρ, s) presentation we are free to choose the two functions $k(\rho)$ et $C^v(s)$. We can then compute all the quantities in the representation ρ, s:

$$ln(T) = \int_{s_0}^{s} \frac{dS}{C^v(S)} + \int_{\rho_0}^{\rho} \frac{k(r)dr}{r} + ln(T_0)$$

$$T(\rho, s) = T_0 e^{\int_{s_0}^{s} \frac{dS}{C^v(S)}} . e^{\int_{\rho_0}^{\rho} \frac{k(r)dr}{r}} = f(s).\Theta(\rho)$$

with $\Theta(\rho) = T_0 e^{\int_{\rho_0}^{\rho} \frac{k(r)dr}{r}}$ is the Debye temperature defined by $\frac{dln(\Theta)}{d\rho} = \frac{k}{\rho}$, and $f(s) = e^{\int_{s_0}^{s} \frac{dS}{C^v(S)}}$.

Hence for the speed of sound we have :

$$\partial_s (c^2)_\rho = \left[k(\rho)(k(\rho)+1) + \rho k'(\rho)\right].\Theta(\rho).f(s)$$

so

$$\begin{aligned} c^2(\rho,s) &= \left[k(\rho)(k(\rho)+1) + \rho k'(\rho)\right].\Theta(\rho) \int_{s_0}^{s} f(\sigma)d\sigma + c_0^2(\rho) \\ &= \left[k(\rho)(k(\rho)+1) + \rho k'(\rho)\right]\Theta(\rho)F_{s_0}(s) + c_0^2(\rho) \\ &= \left[k(\rho)(k(\rho)+1) + \rho k'(\rho)\right]\Theta(\rho)F_{s_0}(s) + p_K'(\rho) \end{aligned}$$

For the pressure and from $dp = c^2 d\rho + \rho k T ds = c^2 d\rho + \rho k(\rho) f(s)\Theta(\rho) ds$ we get :

$$\begin{aligned} p(\rho,s) &= \rho k(\rho)\Theta(\rho) \int_{s_0}^{s} f(\sigma)d\sigma + p_K(\rho) \\ &= \rho k(\rho)\Theta(\rho)F_{s_0}(s) + p_K(\rho) \end{aligned}$$

and we can check that :

$$\begin{aligned} c^2(\rho,s) &= \left[k(\rho) + \rho k'(\rho) + k^2(\rho)\right].\Theta(\rho).F(s) + p_K'(\rho) \\ &= \left[\frac{k'(\rho)}{k} + \frac{k(\rho)+1}{\rho}\right](p - p_K(\rho)) + p_K'(\rho) \end{aligned}$$

Also :

$$c_T^2(\rho,s) = c^2 - k^2 T C^v =$$

$$\left[k^2(\rho) + k(\rho) + \rho k'(\rho)\right].\Theta(\rho)F(s) - k^2(\rho).\Theta(\rho).f(s).C^v(s) + p_K'(\rho)$$

$$= \Theta(\rho)\left(\left[k^2(\rho) + k(\rho) + \rho k'(\rho)\right]F(s) - k^2(\rho).f(s).C^v(s)\right) + p_K'(\rho)$$

and the heat ratio is given by :

$$\gamma(\rho,s) = \frac{c^2}{c_T^2} = \frac{\left[k(\rho)(k(\rho)+1) + \rho k'(\rho)\right]F(s) + p_K'(\rho)/\Theta(\rho)}{\left[k(\rho)(k(\rho)+1) + \rho k'(\rho)\right].F(s) - k^2(\rho).f(s).C^v(s) + p_K'(\rho)/\Theta(\rho)}$$

and

$$C_p(\rho,s) = \gamma(\rho,s)\, C_v(s).$$

Finnaly, the complete form $e(\rho,s)$ is given by :

$$e(\rho,s) = \Theta(\rho)F(s) + \int_{\rho_0}^{\rho} \frac{p_K(r)}{r^2} dr.$$

$$e(\rho, s) = \Theta(\rho)F(s) + e_K(\rho)$$

To summarize, the Mie-Grunenssein EOS is completely defined by the functions $k(\rho)$, $C^v(s)$ and $p_K(\rho)$ (or $e_K(\rho) = e_0 + \int_{\rho_0}^{\rho} \frac{p_K(x)}{x^2} dx$) and a reference state (ρ_0, T_0, s_0, p_0, e_0).

The dependance of C^v on s only implies that the Mie-Grunenssen EOS is not compatible with all models for C^v. A model of C^v as fonction of T is not compatibile with it. However the Debye model $C^v = C^v(\frac{T}{\Theta(\rho)})$ is compatible as $\frac{T}{\Theta(\rho)} = f(s)$. The Einstein model, with a constant Enstein temperature Θ_E, and C^v of the form

$$C^v = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1\right)^2}$$

is not. Two models that are compatible are for example

$$C^v = 3R\left(\frac{\Theta}{T}\right)^2 \frac{e^{\frac{\Theta}{T}}}{\left(e^{\frac{\Theta}{T}} - 1\right)^2} \quad (Enstein - Debye)$$

and

$$C^v = 9R\left(\frac{\Theta}{T}\right)^3 \int_0^{\frac{\Theta}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (Debyemodel)$$

G. Gruneissen and Stiffened gaz EOS

We consider the special case of Mie-Gruneissen EOS where the Gruneisen parameter k is supposed constant and where C_v is supposed constant as well.

In this case

$$\Theta(\rho) = T_0\left(\frac{\rho}{\rho_0}\right)^k$$

$$c^2 = \frac{k+1}{\rho}(p - p_K(\rho)) + p'_K(\rho)$$

$$f(s) = e^{\frac{s-s_0}{C^v}}$$

.

$$F(s) = C^v\left(e^{\frac{s-s_0}{C^v}} - 1\right) = C^v(f(s) - 1)$$

.

$$c^2 = \Theta(\rho)k(k+1)C_v(f(s) - 1) + p'_K(\rho)$$

$$c_T^2 = \Theta(\rho)\left(k\, C_v\, f(s) - k(k+1)C_v\right) + p'_K(\rho)$$

and the heat ratio is given by :

$$\gamma(\rho, s) = \frac{c^2}{c_T^2} = \frac{k(k+1)C_v\, f(s) - k(k+1)C_v + p'_K(\rho)/\Theta(\rho)}{kC_v f(s) - k(k+1)C_v + p'_K(\rho)/\Theta(\rho)}$$

It is worth noting that even in this simple case the heat ration γ is not necessarly constant and equal to $k+1$ as usually assumed.

Only the special case $p'_K(\rho) = k(k+1)C_v\Theta(\rho)$ so

$$p_K(\rho) = p_0 - \rho_0 T_0 k C_v + \rho k C_v \Theta(\rho)$$

gives

$$\gamma(\rho, s) = \gamma = k + 1.$$

and also implies the simple PVT relation :

$$p = p_0 + \rho C_v T.$$

and

$$e = e_0 + C_v T - \frac{p_0 - \rho_0 T_0 k C_v}{\rho}.$$

This case is exactly the Stiffened Gaz EOS [2] [3], with the Helmotz potential :

$$A(\rho, T) = C_v T \left(1 - ln(\frac{T}{T_0}) + (\gamma - 1) ln(\frac{\rho}{\rho_0})\right) - s_0\, T + \frac{p_\infty}{\rho} + e^*$$

We stress out that a relation of type $p = \rho(\Gamma - 1)(e - e_*) - \Gamma p_\infty$, with constant Γ is not suffiscent to have this simple PVT relation and to have a constant heat ratio $\gamma = \Gamma$, even if one supposes a constant C_v.

VI. NOTE ON THE IMPLICATION OF THE SECOND LAW OF THERMODYNAMICS AND STABILITY

In the previous section we did only explicit the implications of the first law of thermodynamics and of the function state defintions, on the consistency of equations of state.

The second law of thermodynamics and its implication on mechanical and termal stability of the described matter, can also be used to express more constraints on the ''degrees of freedom" in an EOS relation.

First we consider a $e(v = \frac{1}{\rho}, s)$ representation and compute

$$x = \frac{\partial^2 e}{\partial v^2} = \frac{c^2}{v^2} = \rho^2 c^2$$

$$y = \frac{\partial^2 e}{\partial s^2} = \frac{T}{C_v}$$

$$z = \frac{\partial^2 e}{\partial s \partial v} = -\frac{kT}{v}$$

$$x\,y - z^2 = \frac{T}{C_v}\frac{c^2 - k^2 T C_v}{v^2} = \frac{T}{C_v}\frac{c_T^2}{v^2}$$

Mechanical statibility implies for instance (See [6] page 209) :

$$c_T^2 > 0,$$

while thermal stability implies

$$C_v > 0.$$

A more general condition for statbilty of equilibrium states, implied by the second law of thermodynamics is the convexity of $e(v, s)$ (see the introduction of [7]). Hence if the hessien matrix of $e(\rho, v)$ is definite positive, wich boild down to the same identities $C_v > 0$, $c^2 > 0$ and $c_T^2 > 0$.

This also implied $\gamma > 0$ and $Cp > 0$, and by Mayer relation $Cp - Cv = T\alpha^2 c_T^2 > 0$ we have $\gamma > 1$.

VII. CONCLUSION

We presented a way to construct a complete set of thermodynamic relations and reviewed the thermodynamic consistency of many classical Equaion of States. The approach presented is general and can be used when 'inventing' new equations of state in research work or when fitting an EOS and thermodynamic coeffiscients with laboratory data. The approch allows to explicit ''the degrees of freedom'' for each EOS to avoid violating the thermodynamic consistency. As example, we explained by an elementary approach why many classical

equations of state, such as stiffened gaz (with constant heat ratio γ) can not be generalized by making C_v dependent on the temperature T without violating thermodynamical consistency.

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