

The Operational Equations of State, 4: The Dulong-Petit Equation of State for Hydrocode

by Michael Grinfeld

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14. ABSTRACT The widely spread hydrocode approach is rooted in modeling liquid and gaseous substances. It also found many applications in modeling solids at high pressures, considerably exceeding the elasticity limit. The hydrocode approach uses the specific volume V and the specific internal energy E as independent thermodynamic variables. Because of that fact, the implementation of the hydrocode approach requires the complete equation of state in the form $S = S(V, E)$, where S is the specific entropy. We consider a model equation of state (EOS) based on the assumption of constant heat capacity C_v at fixed volume. We call this model EOS the Dulong-Petit (D-P) EOS. We focus on the problem of recovery of the full D-P EOS from appropriate experimental data.					
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1. Introduction and Definitions



“Why don’t you call it entropy...nobody knows what entropy really is, so in a debate you will always have the advantage.”

John von Neumann

From John von Neumann advice to Claude Shannon

From a purely thermodynamic point of view, the hydrocode approach means, by definition, that the specific volume V and the specific internal energy E are chosen as independent thermodynamic parameters of a two-parameter substance under study. Then, the specific entropy function $S = S(V, E)$ appears to be the corresponding canonically associated thermodynamic potential (1). The clause “canonically associated” means basically two things. First, having known $S = S(V, E)$, any other thermodynamic parameter can be expressed from it by means of differentiation and some algebraic operations only. In particular, no other experimental measurements or theoretical data are required. Second, there is full freedom in choosing the function $S = S(V, E)$: any particular choice does not violate the First and Second Laws of thermodynamics. In other words, full thermodynamic consistency is guaranteed when working with the canonically associated thermodynamic potential. Of course, this thermodynamic consistency does not automatically guarantee the *practical* applicability of the chosen canonically associated thermodynamic potential. In other words, the appropriated choice of $S = S(V, E)$ should be made based on comparison with relevant observations (2–4) (also see references 5–9 and hundreds of references therein).

As a synonym, the thermodynamic potential $S = S(V, E)$ will also be called the *complete* EOS for hydrocode.

Using the function $S = S(V, E)$, one can calculate automatically and uniquely the heat capacity $C_V = C_V(V, E)$ of the corresponding substance. The opposite is not true: having known the heat capacity $C_V = C_V(V, E)$, we cannot determine uniquely the thermodynamic potential $S = S(V, E)$. In this very sense, the heat capacity function $C_V = C_V(V, E)$ is one of the examples of the *incomplete* EOS for hydrocode. Other examples of the incomplete EOS for hydrocode are

probably more known to the readers. Those are, for instance, the pressure equation $P = P(V, E)$ or the classical Mie-Grüneisen EOS for hydrocode.

When using two or more incomplete EOS for hydrocode, we can face different situations. They can be thermodynamically consistent with each other but remain incomplete even acting in concert or they can be thermodynamically consistent with each other but contain redundant information. At last, and this is the most common situation, they can be thermodynamically incompatible. For instance, the incomplete Mie-Grüneisen EOS is incompatible with the incomplete EOS $C_v = C_v(V)$, or with the incomplete EOS $C_v = C_v(E)$, or with the incomplete EOS $C_v = C_v(T)$, where T is the absolute temperature.

Summarizing, a lot of information about the complete EOS $S = S(V, E)$ can be extracted from the function $C_v = C_v(V, E)$. Namely, with the help of the heat capacity $C_v = C_v(V, E)$, the function $S(V, E)$ of any relevant substance can be presented in the following form:

$$S(V, E) = A(V) + \int_{E^*}^E \frac{d\xi}{\int_{E^*}^{\xi} d\eta C_v^{-1}(\eta, E) + \Lambda(V)}, \quad (1)$$

where $A(V)$ and $\Lambda(V)$ are functions of specific volume V . Here, and in the following, the asterisk is used for thermodynamic parameters of a chosen reference state (V^*, E^*) and various thermodynamic functions in the reference state (in this sense, one should interpret the notation P^* or T^*).

The opposite is obviously true. With any mathematically legitimate choice of the functions $A(V)$ and $\Lambda(V)$ the formula (1) generates a thermodynamically consistent complete EOS for hydrocode. We will call (1) the heat-capacity-centered skeleton of the EOS for hydrocode.

For each appropriate substance, the functions $A(V)$ and $\Lambda(V)$ can and should be determined with the help of other theoretical means or by means of comparison with additional (to the measurements of $C_v(V, E)$) experimental data. In this series of reports, we deliberately concentrate on the methods of recovery of the complete EOS, based on using additional experimental data. To that end, we need experimental setups and appropriate measuring instruments. Sometimes, there are many available tools, sometimes only few. Sometimes, there are no devices available for direct measurements (for instance, for substances in the interiors of the Earth and other celestial bodies). In the last situation, the required information can be obtained from theoretical or indirect measurements (often demanding solution of inverse problems).

Obviously, for the recovery of two functions $A(V)$ and $\Lambda(V)$, we need two series of experimental data. The recovery formulas depend on the available experimental setups as well as on the measuring instruments available or deliberately chosen. Therefore, for one

substance, there is a wide variety of recovery formulas. Next, we present the recovery formulas for some choices of experiments and measurements. These formulas give the readers several potentially useful prototypes for direct usage or as patterns for the search the readers' own recovery formulas.

The recovery formulas are much easier when the heat capacity C_V is constant

$C_V(V, E) \equiv C = \text{const}$. In this case, both integrals in equation 1 can be calculated explicitly, so it reads

$$S(V, E) = A(V) + C \ln \frac{E - E_* + C\Lambda(V)}{C\Lambda(V)}. \quad (2)$$

It is convenient to introduce novel arbitrary functions $A(V)$ and $B(V)$ instead of the functions $A(V)$ and $\Lambda(V)$:

$$A(V) = A(V) - C \ln \frac{\Lambda(V)}{T^*}, \quad B(V) = E^* + CT^* - C\Lambda(V), \quad (3)$$

and to rewrite equation 2 in the form

$$S(V, E) = A(V) + C \ln \frac{E + CT^* - B(V)}{CT^*}. \quad (4)$$

Using standard thermodynamic identities, we arrive at the following formulas of the absolute temperature $T(V, E)$:

$$T(V, E) = \frac{E + CT^* - B(V)}{C}, \quad (5)$$

and pressure $P(V, E)$

$$P(V, E) = -B'(V) - A'(V) \frac{E + CT^* - B(V)}{C}. \quad (6)$$

The assumption of constant heat capacity C_V allows making many recovery formulas more explicit and transparent. It is both for deeper penetration into the corresponding physics and for developing benchmark solutions for more general and complicated models. However, it is not just a convenient case for theoretical analysis. Not being universal, the assumption of constant heat capacity C_V is often successfully used for gases and liquids. Moreover, experimenters Dulong and Petit noticed in the early the 19th century that this assumption can be successfully applied to solids at room and higher temperatures. That is why we use the term the Dulong-Petit (D-P) model of solid when dealing with the assumption of constant heat capacity.

2. Recovery of the D-P EOS From Experimental Data

2.1 Restoration of the D-P EOS From the Isentrope Measurements

Assume that we are capable of making isentropic loading-unloading experiments and consider a static adiabat $S = S^*$ passing through the ambient state. Assume that we have devices measuring the absolute temperature and pressure in the range of interest. Let $T_s^* = T_s^*(V)$ and $P_s^* = P_s^*(V)$ be the values of the temperature and pressure at $S = S^*$. In terms of these functions, the required operational equation of state can be presented in the following form:

$$\Sigma(V, E) = C \ln \frac{E - E^* + CT_s^*(V) + \int_{V^*}^V d\varpi P_s^*(\varpi)}{CT_s^*(V)} + S^*. \quad (7)$$

Using thermodynamic identities, we get the following formulas of the temperature and pressure functions:

$$T(V, E) = T_s^*(V) + \frac{E - E^*}{C} + \frac{1}{C} \int_{V^*}^V d\varpi P_s^*(\varpi), \quad (8)$$

and

$$P(V, E) = P_s^*(V) - \left[E - E^* + \int_{V^*}^V d\varpi P_s^*(\varpi) \right] \frac{d \ln T_s^*(V)}{dV}. \quad (9)$$

2.2 Restoration of the D-P EOS From the Isotherm Measurements

Consider an isotherm, $T = T^*$, passing through the ambient state. Let $S_T^* = S_T^*(V)$ and $P_T^* = P_T^*(V)$ be the values of the entropy and pressure on that isotherm. In terms of these functions

$$\Sigma(V, E) = C \ln \left[1 + \frac{E - E^*}{CT^*} - \frac{S_T^*(V) - S^*}{C} + \frac{1}{CT^*} \int_{V^*}^V d\varpi P_T^*(\varpi) \right] + S_T^*(V). \quad (10)$$

In order to make the last formula useful for the EOS recovery, we need a calorimeter, i.e., a device allowing to measure heat flux. Such a device should be used for measuring the heat supply $Q_T^*(V)$ along the isotherm $T = T^*$. That measurement would help to evaluate the entropy change $S_T^*(V) - S^* \equiv Q_T^*(V)/T^*$ and rewrite the EOS in the form of equation 11 as follows:

$$\Sigma(V, E) = C \ln \frac{E - E^* - Q_T^*(V) + CT^* + \int_{V^*}^V d\varpi P_T^*(\varpi)}{CT^*} + S_T^*(V). \quad (11)$$

Using the last formula and thermodynamic identities, we arrive at the following formulas of the temperature and pressure functions:

$$T(V, E) = T^* + \frac{E - E^*}{C} - T^* \frac{S_T^*(V) - S^*}{C} + \frac{1}{C} \int_{V^*}^V d\varpi P_T^*(\varpi), \quad (12)$$

and

$$P(V, E) = P_T^*(V) + \frac{1}{C} \frac{dS_T^*(V)}{dV} \left\{ E - E^* - T^* [S_T^*(V) - S^*] + \int_{V^*}^V d\varpi P_T^*(\varpi) \right\}. \quad (13)$$

2.3 Restoration of the D-P EOS From the Hugoniot Adiabata Measurements

The presence of the shock waves of extremely high intensity is a characteristic feature of numerous applications in ballistics of penetration. Therefore, an adequate reproduction of the corresponding shock waves is of a paramount importance for successful modeling efforts. To that end, modelers require knowledge of the EOS for the parameters that are close to the parameters observed in the shock-waves. It is therefore natural to use the shock-wave related measurements for the recovery of the EOS in the representative range of parameters. Next, we give the recovery formulas for some types of measurements relating to shock waves.

2.3.1 Hugoniot Adiabata: Internal Energy Density + Temperature Measurements

Assume that we have two sorts of measurements relating to the Hugoniot adiabat passing through the reference state (V^*, E^*) . We begin with the measurements of (i) the internal energy $E = E_H^*(V)$ on the Hugoniot adiabat and (ii) the absolute temperature $T = T_H^*(V)$ on the adiabat. The analysis of experimental measuring of the function $E = E_H^*(V)$ can be found in the reviews (5, 7). Direct measurement of the absolute temperature $T = T_H^*(V)$ for the shock waves of high intensity is a difficult engineering problem.

In terms of these two functions, $E = E_H^*(V)$ and $T = T_H^*(V)$, the complete EOS for the D-P model takes the following form:

$$\begin{aligned} \Sigma(V, E) - S^* = C \ln \frac{E - E_H^*(V) + CT_H^*(V)}{CT_H^*(V)} \\ - \int_{V^*}^V d\varpi \frac{1}{T_H^*(\varpi)} \left[2 \frac{E_H^*(\varpi) - E^*}{\varpi - V^*} + P^* - \frac{dE_H^*(\varpi)}{dV} \right]. \end{aligned} \quad (14)$$

A vigilance is required when the last formula is used for *numerical* recovery of the EOS. There is an apparent singularity at the ϖ approaching the lower limit $\varpi \rightarrow V^*$ in the integrand. Theoretically, the limit is finite and it is equal to P^*/T^* . It is somewhat more difficult to handle this issue when doing numerical experiments.

2.3.2 Hugoniot Adiabata: Pressure + Temperature Measurements

Assume that the pressure measurements $P = P_H^*(V)$ on the Hugoniot adiabata are available in addition to the temperature measurements $T = T_H^*(V)$ and that the internal energy measurements $E = E_H^*(V)$ become redundant. In terms of the two functions, $P = P_H^*(V)$ and $T = T_H^*(V)$, the complete EOS for the D-P model takes the following form:

$$\begin{aligned} \Sigma(V, E) - S^* = C \ln & \frac{E - E^* + \frac{1}{2}(P_H^* + P^*)(V - V^*) + CT_H^*(V)}{CT_H^*(V)} \\ & + \frac{1}{2} \int_{V^*}^V d\varpi \frac{1}{T_H^*(\varpi)} \left[P_H^*(\varpi) - P^* - \frac{dP_H^*(\varpi)}{d\varpi} (\varpi - V^*) \right]. \end{aligned} \quad (15)$$

2.3.3 Hugoniot Adiabata + Isotherm

When only one series of measurements, $E = E_H^*(V)$ or $T = T_H^*(V)$, are available on the Hugoniot, then this series data should be combined with additional data obtained from some other experiments.

2.3.4 The Hugoniot Internal Energy $E_H(V)$ and Entropy $S_T(V)$ on Ambient Isotherm

Assume that we get data relating to the entropy values $S_T^*(V)$ on the ambient isotherm

$$T = T^*. \quad (16)$$

Then, the recovery formula reads

$$\begin{aligned} \frac{1}{C} \Sigma(V, E) = & \frac{1}{C} S_T^*(V) \\ & + \ln \frac{E - E_H^*(V) + \int_{V^*}^V d\varpi e^{\frac{S_T^*(\varpi) - S_T^*(V)}{C}} \left[\frac{dE_H(\varpi)}{d\varpi} - \frac{2E_H(\varpi) - 2E^* + P^*(\varpi - V^*)}{\varpi - V^*} \right] + CT^* e^{\frac{S_T^*(V) - S^*}{C}}}{CT^*}. \end{aligned} \quad (17)$$

2.3.5 The Hugoniot Pressure $P_H(V)$ and the Pressure Measurements $P_T(V)$ on Ambient Isotherm

This practical and important combination of data is presented in the third report of this series (4).

2.3.6 Hugoniot Adiabata + Isentrope

We consider the case when, in addition to one series of Hugoniot adiabat data, we take one more series of data relating to the isentrope.

2.3.7 The Hugoniot Internal Energy $E_H(V)$ and Temperature $T_S(V)$ on Ambient Isentrope Measurements

Assume that we get temperature measurements $T_S^*(V)$ on the ambient isentrope $S = S^*$. Then, the Dulong-Petit EOS for hydrocode can be presented in the following form:

$$\frac{\Sigma(V, E) - S^*}{C} = \ln \left\{ \frac{1}{C} \frac{E}{T_S^*(V)} + \frac{1}{C} \int_{V^*}^V d\varpi \frac{1}{T_S^*(\varpi)} \left[\frac{d \ln T_S^*(\varpi)}{d\varpi} E_H(\varpi) - \frac{2E_H(\varpi) - 2E^*}{\varpi - V^*} - P^* \right] \right\}, \quad (18)$$

where we assumed $E^* = CT^*$.

2.3.8 Given the Hugoniot Pressure $P_H(V)$ and Temperature $T_S(V)$ on Ambient Isentrope Measurements

For this combination of data, we arrive at the following recovery formula:

$$\frac{\Sigma(V, E) - S^*}{C} = \ln \left\{ 1 + \frac{E - E^* + \frac{1}{2}(P_H^*(V) + P^*)(V - V^*)}{CT_S^*(V)} + \frac{1}{2} \int_{V^*}^V d\varpi \frac{P_H^*(\varpi) - P^* - \frac{dP_H^*(\varpi)}{dV}(\varpi - V^*)}{CT_S^*(\varpi)} \right\}. \quad (19)$$

3. Conclusion

The problem of finding adequate EOS is one of the most important in many applications. It is also the central problem of classical thermodynamics. It cannot be solved by experiment or theory, taken separately; combination of both approaches is mandatory. Thermodynamics discusses how to make the combining non-contradictory, i.e., compatible with the laws of thermodynamics, and sufficient for avoiding any arbitrariness. We established the required explicit formulas for several sorts of available experimental data or data which might become available in future. We hope that some of these formulas will be able to trigger the imaginations of experimenters.

Needless to say, many more combinations of experimental set-ups are possible. They will require other recovery formulas. Hopefully, the presented formulas can play the role of the illuminating prototypes for the novel ones.

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